

## 6.9 Synthetic Fibers

### 6.9.1 General<sup>1-3</sup>

There are 2 types of synthetic fiber products, the semisynthetics, or cellulosics (viscose rayon and cellulose acetate), and the true synthetics, or noncellulosics (polyester, nylon, acrylic and modacrylic, and polyolefin). These 6 fiber types compose over 99 percent of the total production of manmade fibers in the U. S.

### 6.9.2 Process Description<sup>2-6</sup>

Semisynthetics are formed from natural polymeric materials such as cellulose. True synthetics are products of the polymerization of smaller chemical units into long-chain molecular polymers. Fibers are formed by forcing a viscous fluid or solution of the polymer through the small orifices of a spinnerette (see Figure 6.9-1) and immediately solidifying or precipitating the resulting filaments. This prepared polymer may also be used in the manufacture of other nonfiber products such as the enormous number of extruded plastic and synthetic rubber products.

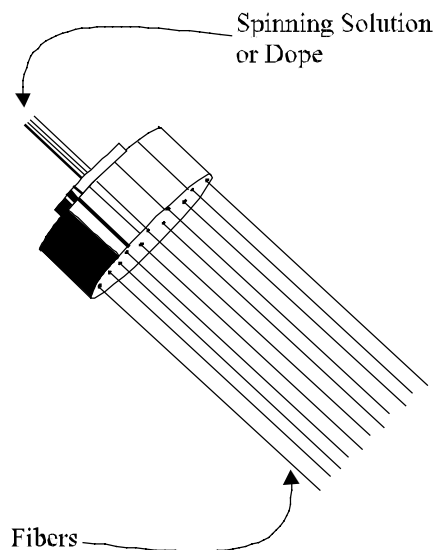


Figure 6.9-1. Spinnerette.

Synthetic fibers (both semisynthetic and true synthetic) are produced typically by 2 easily distinguishable methods, melt spinning and solvent spinning. Melt spinning processes use heat to melt the fiber polymer to a viscosity suitable for extrusion through the spinnerette. Solvent spinning processes use large amounts of organic solvents, which usually are recovered for economic reasons, to dissolve the fiber polymer into a fluid polymer solution suitable for extrusion through a spinnerette. The major solvent spinning operations are dry spinning and wet spinning. A third method, reaction spinning, is also used, but to a much lesser extent. Reaction spinning processes involve the formation of filaments from prepolymers and monomers that are further polymerized and cross-linked after the filament is formed.

Figure 6.9-2 is a general process diagram for synthetic fiber production using the major types of fiber spinning procedures. 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. (The polymerization of the fiber polymer is typically carried out at the same facility that produces the fiber.) Table 6.9-1 lists the different types of spinning methods with the fiber types produced by each method. After the fiber is spun, it may undergo one or more different processing treatments to meet the required physical or handling properties. Such processing treatments include drawing, lubrication, crimping, heat setting, cutting, and twisting. The finished fiber product may be classified as tow, staple, or continuous filament yarn.

Table 6.9-1. TYPES OF SPINNING METHODS AND FIBER TYPES PRODUCED

| Spinning Method      | Fiber Type                                                                              |
|----------------------|-----------------------------------------------------------------------------------------|
| Melt spinning        | Polyester<br>Nylon 6<br>Nylon 66<br>Polyolefin                                          |
| Solvent spinning     |                                                                                         |
| Dry solvent spinning | Cellulose acetate<br>Cellulose triacetate<br>Acrylic<br>Modacrylic<br>Vinyon<br>Spandex |
| Wet solvent spinning | Acrylic<br>Modacrylic                                                                   |
| Reaction spinning    | Spandex<br>Rayon (viscose process)                                                      |

#### 6.9.2.1 Melt Spinning -

Melt spinning uses heat to melt the polymer to a viscosity suitable for extrusion. This type of spinning is used for polymers that are not decomposed or degraded by the temperatures necessary for extrusion. Polymer chips may be melted by a number of methods. The trend is toward melting and immediate extrusion of the polymer chips in an electrically heated screw extruder. Alternatively, the molten polymer is processed in an inert gas atmosphere, usually nitrogen, and is metered through a precisely machined gear pump to a filter assembly consisting of a series of metal gauges interspersed in layers of graded sand. The molten polymer is extruded at high pressure and constant rate through a spinnerette into a relatively cooler air stream that solidifies the filaments. Lubricants and finishing oils are applied to the fibers in the spin cell. At the base of the spin cell, a thread guide converges the individual filaments to produce a continuous filament yarn, or a spun yarn, that typically is composed of between 15 and 100 filaments. Once formed, the filament yarn either is immediately wound onto bobbins or is further treated for certain desired characteristics or end use.

Since melt spinning does not require the use of solvents, VOC emissions are significantly lower than those from dry and wet solvent spinning processes. Lubricants and oils are sometimes added during the spinning of the fibers to provide certain properties necessary for subsequent operations such as lubrication and static suppression. These lubricants and oils vaporize, condense,

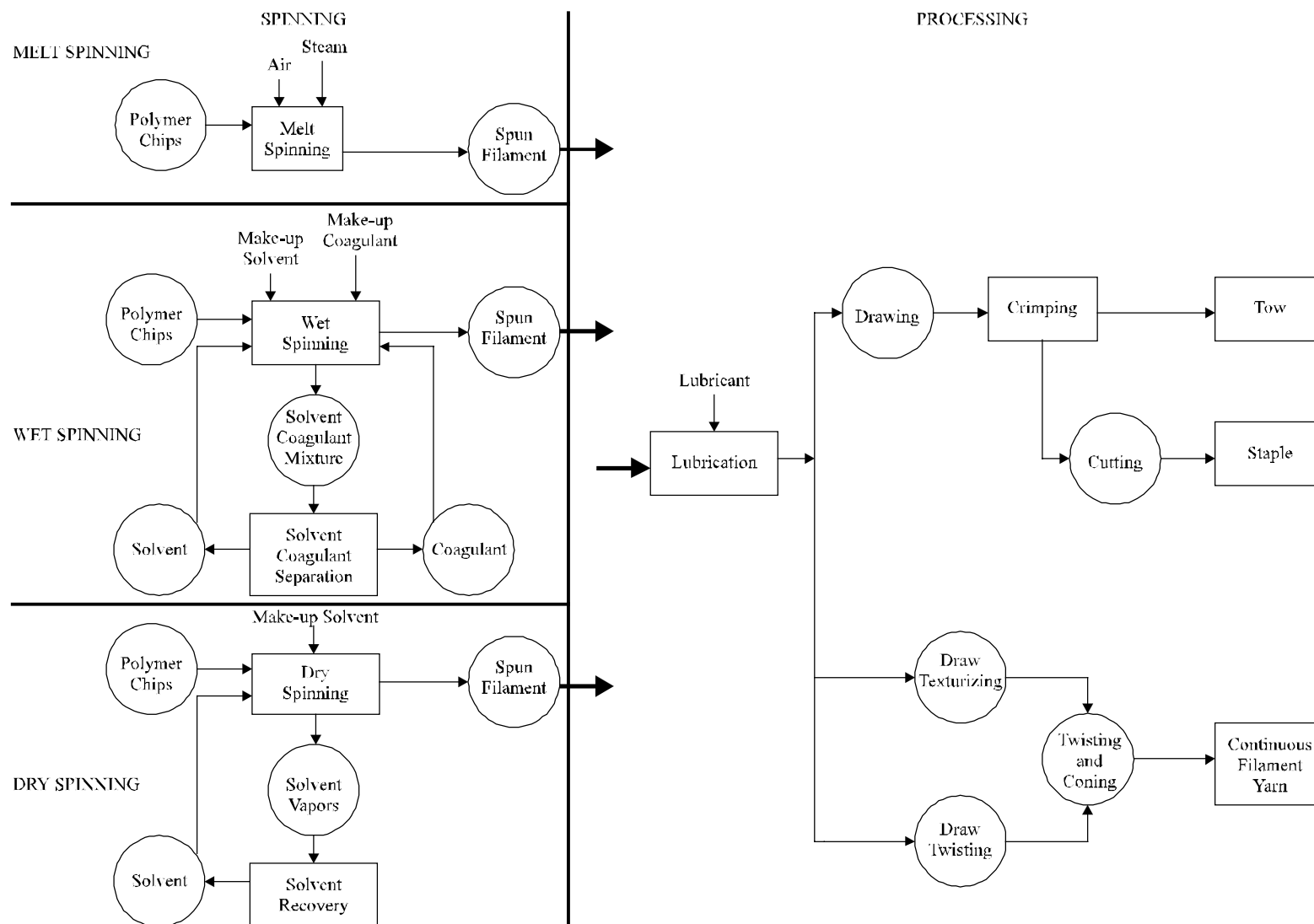


Figure 6.9-2. General process diagram for melt, wet, and dry spun synthetic fibers.

and then coalesce as aerosols primarily from the spinning operation, although certain post-spinning operations may also give rise to these aerosol emissions. Treatments include drawing, lubrication, crimping, heat setting, cutting, and twisting.

#### 6.9.2.2. Dry Solvent Spinning -

The dry spinning process begins by dissolving the polymer in an organic solvent. This solution is blended with additives and is filtered to produce a viscous polymer solution, referred to as "dope", for spinning. The polymer solution is then extruded through a spinnerette as filaments into a zone of heated gas or vapor. The solvent evaporates into the gas stream and leaves solidified filaments, which are further treated using one or more of the processes described in the general process description section. (See Figure 6.9-3.) This type of spinning is used for easily dissolved polymers such as cellulose acetate, acrylics, and modacrylics.

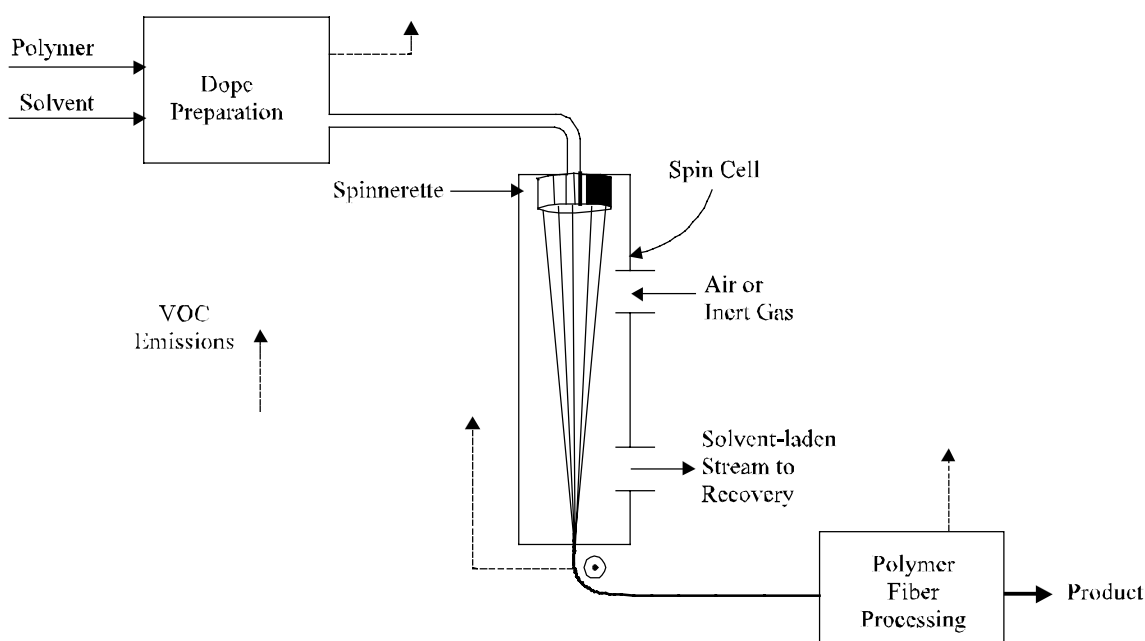


Figure 6.9-3. Dry spinning.

Dry spinning is the fiber formation process potentially emitting the largest amounts of VOCs per pound of fiber produced. Air pollutant emissions include volatilized residual monomer, organic solvents, additives, and other organic compounds used in fiber processing. Unrecovered solvent constitutes the major substance. The largest amounts of unrecovered solvent are emitted from the fiber spinning step and drying the fiber. Other emission sources include dope preparation (dissolving the polymer, blending the spinning solution, and filtering the dope), fiber processing (drawing, washing, and crimping), and solvent recovery.

#### 6.9.2.3 Wet Solvent Spinning -

Wet spinning also uses solvent to dissolve the polymer to prepare the spinning dope. The process begins by dissolving polymer chips in a suitable organic solvent, such as dimethylformamide (DMF), dimethylacetamide (DMAc), or acetone, as in dry spinning; or in a weak inorganic acid, such as zinc chloride or aqueous sodium thiocyanate. In wet spinning, the spinning solution is extruded through spinnerettes into a precipitation bath that contains a coagulant (or precipitant) such as aqueous

DMAc or water. Precipitation or coagulation occurs by diffusion of the solvent out of the thread and by diffusion of the coagulant into the thread. Wet spun filaments also undergo one or more of the additional treatment processes described earlier, as depicted in Figure 6.9-4.

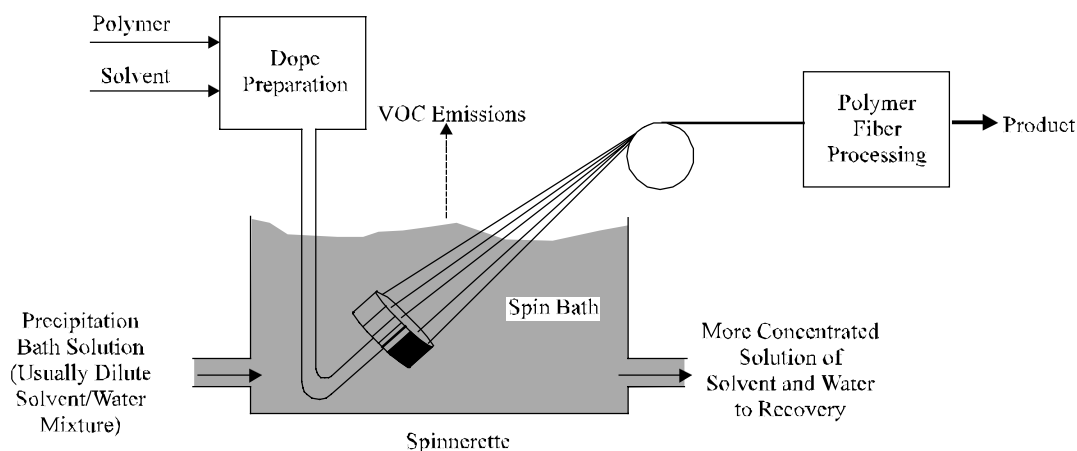


Figure 6.9-4. Wet spinning.

Air pollution emission points in the wet spinning organic solvent process are similar to those of dry spinning. Wet spinning processes that use solutions of acids or salts to dissolve the polymer chips emit no solvent VOC, only unreacted monomer, and are, therefore, relatively clean from an air pollution standpoint. For those that require solvent, emissions occur as solvent evaporates from the spinning bath and from the fiber in post-spinning operations.

#### 6.9.2.4 Reaction Spinning -

As in the wet and dry spinning processes, the reaction spinning process begins with the preparation of a viscous spinning solution, which is prepared by dissolving a low molecular weight polymer, such as polyester for the production of spandex fibers, in a suitable solvent and a reactant, such as di-isocyanate. The spinning solution is then forced through spinnerettes into a solution containing a diamine, similarly to wet spinning, or is combined with the third reactant and then dry spun. The primary distinguishable 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. Post-spinning steps typically include drying and lubrication. Emissions from the wet and dry reaction spinning processes are similar to those of solvent wet and dry spinning, respectively.

### 6.9.3 Emissions And Controls

For each pound of fiber produced with the organic solvent spinning processes, a pound of polymer is dissolved in about 3 pounds of solvent. Because of the economic value of the large amounts of solvent used, capture and recovery of these solvents are an integral portion of the solvent spinning processes. At present, 94 to 98 percent of the solvents used in these fiber formation processes is recovered. In both dry and wet spinning processes, capture systems with subsequent solvent recovery are applied most frequently to the fiber spinning operation alone, because the emission stream from the spinning operation contains the highest concentration of solvent and,

therefore, possesses the greatest potential for efficient and economic solvent recovery. Recovery systems used include gas adsorption, gas absorption, condensation, and distillation and are specific to a particular fiber type or spinning method. For example, distillation is typical in wet spinning processes to recover solvent from the spinning bath, drawing, and washing (see Figure 6.9-8), while condensers or scrubbers are typical in dry spinning processes for recovering solvent from the spin cell (see Figure 6.9-6 and Figure 6.9-9). The recovery systems themselves are also a source of emissions from the spinning processes.

The majority of VOC emissions from pre-spinning (dope preparation, for example) and post-spinning (washing, drawing, crimping, etc.) operations typically are not recovered for reuse. In many instances, emissions from these operations are captured by hoods or complete enclosures to prevent worker exposure to solvent vapors and unreacted monomer. Although already captured, the quantities of solvent released from these operations are typically much smaller than those released during the spinning operation. The relatively high air flow rates required in order to reduce solvent and monomer concentrations around the process line to acceptable health and safety limits make recovery economically unattractive. Solvent recovery, therefore, is usually not attempted.

Table 6.9-2 presents emission factors from production of the most widely known semisynthetic and true synthetic fibers. These emission factors address emissions only from the spinning and post-spinning operations and the associated recovery or control systems. Emissions from the polymerization of the fiber polymer and from the preparation of the fiber polymer for spinning are not included in these emission factors. While significant emissions occur in the polymerization and related processes, these emissions are discussed in Sections 6.6, "Plastics", and 6.10, "Synthetic Rubber".

Examination of VOC pollutant emissions from the synthetic fibers industry has recently concentrated on those fiber production processes that use an organic solvent to dissolve the polymer for extrusion or that use an organic solvent in some other way during the filament forming step. Such processes, while representing only about 20 percent of total industry production, do generate about 94 percent of total industry VOC emissions. Particulate emissions from fiber plants are relatively low, at least an order of magnitude lower than the solvent VOC emissions.

#### 6.9.4 Semisynthetics

##### 6.9.4.1 Rayon Fiber Process Description<sup>5,7-10</sup> -

In the United States, most rayon is made by the viscose process. Rayon fibers are made using cellulose (dissolved wood pulp), sodium hydroxide, carbon disulfide, and sulfuric acid. As shown in Figure 6.9-5, the series of chemical reactions in the viscose process used to make rayon consists of the following stages:

1. Wood cellulose and a concentrated solution of sodium hydroxide react to form soda cellulose.
2. The soda cellulose reacts with carbon disulfide to form sodium cellulose xanthate.
3. The sodium cellulose xanthate is dissolved in a dilute solution of sodium hydroxide to give a viscose solution.

Table 6.9-2 (English Units). EMISSION FACTORS FOR SYNTHETIC FIBER MANUFACTURING<sup>a</sup>

EMISSION FACTOR RATING: C

| Type Of Fiber                                   | Nonmethane Volatile Organics | Particulate         | References   |
|-------------------------------------------------|------------------------------|---------------------|--------------|
| Rayon, viscose process                          | 0                            | — <sup>c</sup>      | 7-8,10,35-36 |
| Cellulose acetate, filter tow                   | 112 <sup>d</sup>             | — <sup>c</sup>      | 11,37        |
| Cellulose acetate and triacetate, filament yarn | 199 <sup>d,e</sup>           | — <sup>c</sup>      | 11,38        |
| Polyester, melt spun                            |                              |                     | 41-42        |
| Staple                                          | 0.6 <sup>f,g</sup>           | 252 <sup>h,j</sup>  |              |
| Yarn <sup>k</sup>                               | 0.05 <sup>f,g</sup>          | 0.03 <sup>g,j</sup> |              |
| Acrylic, dry spun                               |                              |                     | 21,43-44     |
| Uncontrolled                                    | 40                           | — <sup>c</sup>      |              |
| Controlled                                      | 32 <sup>m</sup>              | — <sup>c</sup>      |              |
| Modacrylic, dry spun                            | 125 <sup>g,h</sup>           | — <sup>c</sup>      | 45           |
| Acrylic and modacrylic, wet spun                | 6.75 <sup>p</sup>            | — <sup>c</sup>      | 19,46        |
| Acrylic, inorganic wet spun                     |                              |                     | 47-48        |
| Homopolymer                                     | 20.7 <sup>g,q</sup>          | — <sup>c</sup>      |              |
| Copolymer                                       | 2.75 <sup>g,r</sup>          | — <sup>c</sup>      |              |
| Nylon 6, melt spun                              |                              |                     | 25,49        |
| Staple                                          | 3.93 <sup>g</sup>            | 0.01 <sup>g</sup>   |              |
| Yarn                                            | 0.45 <sup>s</sup>            | — <sup>c</sup>      |              |
| Nylon 66, melt spun                             |                              |                     | 26           |
| Uncontrolled                                    | 2.13 <sup>f,t</sup>          | 0.5 <sup>u</sup>    |              |
| Controlled                                      | 0.31 <sup>f,v</sup>          | 0.1 <sup>u</sup>    |              |
| Polyolefin, melt spun                           | 5 <sup>g</sup>               | 0.01 <sup>g</sup>   | 5,25,28,49   |
| Spandex, dry spun                               | 4.23 <sup>m</sup>            | — <sup>c</sup>      | 32           |
| Spandex, reaction spun                          | 138 <sup>x</sup>             | — <sup>c</sup>      | 50-51        |
| Vinyon, dry spun                                | 150 <sup>m</sup>             | — <sup>c</sup>      | 52           |

<sup>a</sup> Factors are pounds of emissions per 1000 pounds (lb) of fiber spun including waste fiber.<sup>b</sup> Uncontrolled carbon disulfide (CS<sub>2</sub>) emissions are 251 lb CS<sub>2</sub>/1000 lb fiber spun; uncontrolled hydrogen sulfide (H<sub>2</sub>S) emissions are 50.4 lb H<sub>2</sub>S/1000 lb fiber spun. If recovery of CS<sub>2</sub> from the "hot dip" stage takes place, CS<sub>2</sub> emissions are reduced by about 16%.<sup>c</sup> Particulate emissions from the spinning solution preparation area and later stages through the finished product are essentially nil.

Table 6.9-2 (cont.).

- d After recovery from the spin cells and dryers. Use of more extensive recovery systems can reduce emissions by 40% or more.
- e Use of methyl chloride and methanol as the solvent, rather than acetone, in production of triacetate can double emissions.
- f Emitted in aerosol form.
- g Uncontrolled.
- h After control on extrusion parts cleaning operations.
- j Mostly particulate, with some aerosols.
- k Factors for high intrinsic viscosity industrial and tire yarn production are 0.18 lb VOC and 3.85 lb particulate.
- m After recovery from spin cells.
- n About 18 lb is from dope preparation, and about 107 lb is from spinning/post-spinning operations.
- p After solvent recovery from the spinning, washing, and drawing stages. This factor includes acrylonitrile emissions. An emission factor of 87 lb/1000 lb fiber has been reported.
- q Average emission factor; range is from 13.9 to 27.7 lb.
- r Average emission factor; range is from 2.04 to 16.4 lb.
- s After recovery of emissions from the spin cells. Without recovery, emission factor would be 1.39 lb.
- t Average of plants producing yarn from batch and continuous polymerization processes. Range is from about 0.5 to 4.9 lb. Add 0.1 lb to the average factor for plants producing tow or staple. Continuous polymerization processes average emission rates approximately 170%. Batch polymerization processes average emission rates approximately 80%.
- u For plants with spinning equipment cleaning operations.
- v After control of spin cells in plants with batch and continuous polymerization processes producing yarn. Range is from 0.1 to 0.6 lb. Add 0.02 lb to the average controlled factor for producing tow or staple. Double the average controlled emission factor for plants using continuous polymerization only; subtract 0.01 lb for plants using batch polymerization only.
- w After control of spinning equipment cleaning operation.
- x After recovery by carbon adsorption from spin cells and post-spinning operations. Average collection efficiency 83%. Collection efficiency of carbon adsorber decreases over 18 months from 95% to 63%.

4. The solution is ripened or aged to complete the reaction.
5. The viscose solution is extruded through spinnerettes into dilute sulfuric acid, which regenerates the cellulose in the form of continuous filaments.

#### Emissions And Controls -

Air pollutant emissions from viscose rayon fiber production are mainly carbon disulfide (CS<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), and small amounts of particulate matter. Most CS<sub>2</sub> and H<sub>2</sub>S emissions occur during the spinning and post-spinning processing operations. Emission controls are not used extensively in the rayon fiber industry. A countercurrent scrubber (condenser) is used in at least one instance to recover CS<sub>2</sub> vapors from the sulfuric acid bath alone. The emissions from this operation are high enough in concentration and low enough in volume to make such recovery both technically and economically feasible. The scrubber recovers nearly all of the CS<sub>2</sub> and H<sub>2</sub>S that enters it, reducing overall CS<sub>2</sub> and H<sub>2</sub>S emissions from the process line by about 14 percent. While carbon adsorption systems are capable of CS<sub>2</sub> emission reductions of up to 95 percent, attempts to use carbon adsorbers have had serious problems.

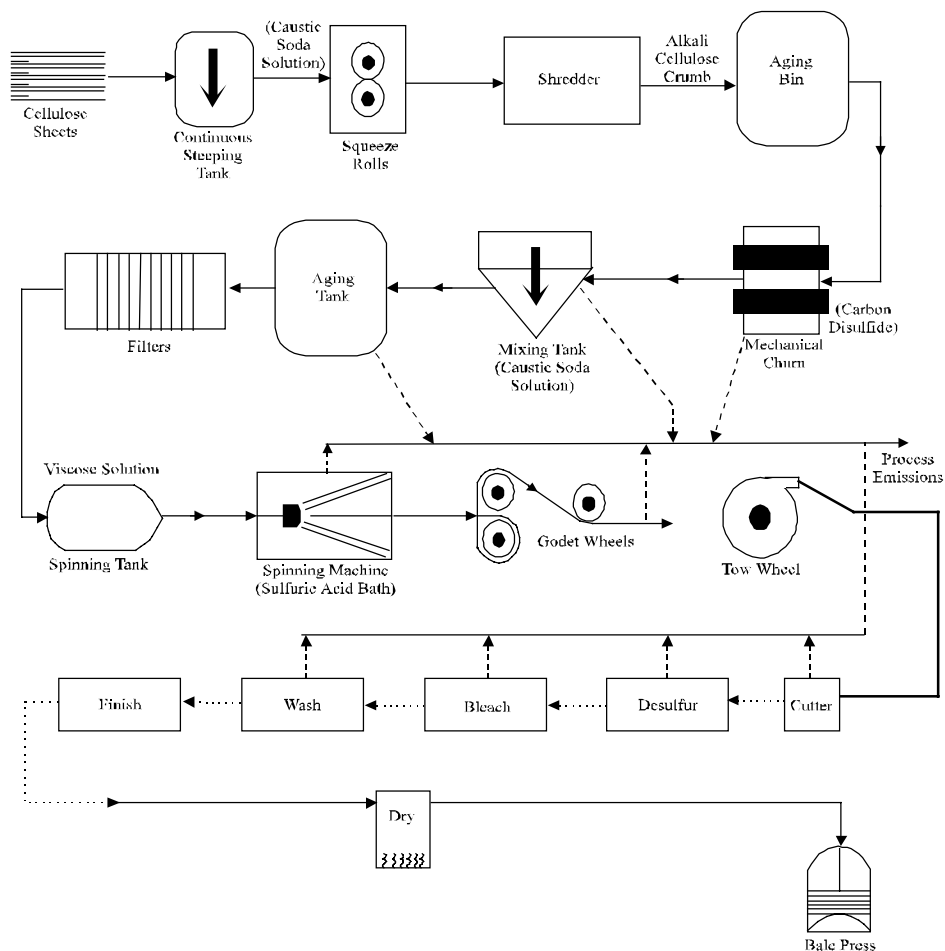


Figure 6.9-5. Rayon viscose process.

#### 6.9.4.2. Cellulose Acetate And Triacetate Fiber Process Description<sup>5,11-14</sup> -

All cellulose acetate and triacetate fibers are produced by dry spinning. These fibers are used for either cigarette filter tow or filament yarn. Figure 6.9-6 shows the typical process for the production of cigarette filter tow. Dried cellulose acetate polymer flakes are dissolved in a solvent, acetone and/or a chlorinated hydrocarbon in a closed mixer. The spinning solution (dope) is filtered, as it is with other fibers. The dope is forced through spinnerettes to form cellulose acetate filaments, from which the solvent rapidly evaporates as the filaments pass down a spin cell or column. After the filaments emerge from the spin cell, there is a residual solvent content that continues to evaporate more slowly until equilibrium is attained. The filaments then undergo several post-spinning operations before they are cut and baled.

In the production of filament yarn, the same basic process steps are carried out as for filter tow, up through and including the actual spinning of the fiber. Unlike filter tow filaments, however, filaments used for filament yarn do not undergo the series of post-spinning operations shown in Figure 6.9-6, but rather are wound immediately onto bobbins as they emerge from the spin cells. In some instances, a slight twist is given to the filaments to meet product specifications. In another area, the wound filament yarn is subsequently removed from the bobbins and wrapped on beams or cones (referred to as "beaming") for shipment.



Air pollutant emissions from cellulose acetate fiber production include solvents, additives, and other organic compounds used in fiber processing. Acetone, methyl ethyl ketone, and methanol are the only solvents currently used in commercial production of cellulose acetate and triacetate fibers.

VOC control techniques are primarily carbon adsorbers and scrubbers. They are used to control and recover solvent emissions from process gas streams from the spin cells in both the production of cigarette filter tow and filament yarn. Carbon adsorbers also are used to control and recover solvent emissions from the dryers used in the production of cigarette filter tow. The solvent recovery efficiencies of these recovery systems range from 92 to 95 percent. Fugitive emissions from other post-spinning operations, even though they are a major source, are generally not controlled. In at least one instance however, an air management system is being used in which the air from the dope preparation and beaming areas is combined at carefully controlled rates with the spinning room air that is used to provide the quench air for the spin cell. A fixed amount of spinning room air is then combined with the process gas stream from the spin cell and this mix is vented to the recovery system.

## 6.9.5 True Synthetic Fibers

### 6.9.5.1 Polyester Fiber Process Description<sup>5,11,15-17</sup> -

Polyethylene terephthalate (PET) polymer is produced from ethylene glycol and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). Polyester filament yarn and staple are manufactured either by direct melt spinning of molten PET from the polymerization equipment or by spinning reheated polymer chips. Polyester fiber spinning is done almost exclusively with extruders, which feed the molten polymer under pressure through the spinnerettes. Filament solidification is induced by blowing the filaments with cold air at the top of the spin cell. The filaments are then led down the spin cell through a fiber finishing application, from which they are gathered into tow, hauled off, and coiled into spinning cans. The post-spinning processes, steps 14 through 24 in Figure 6.9-7, usually take up more time and space and may be located far from the spinning machines. Depending on the desired product, post-spinning operations vary but may include lubrication, drawing, crimping, heat setting, and stapling.

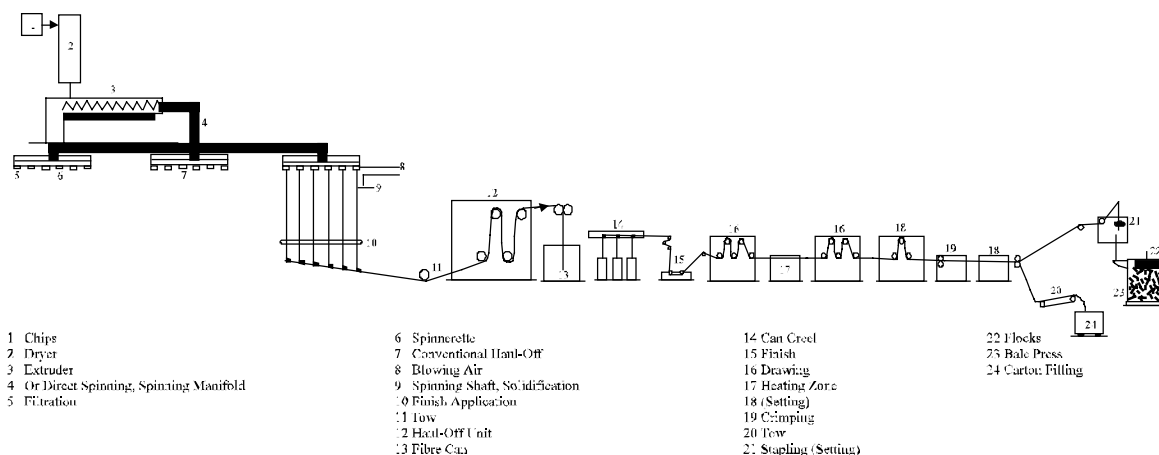


Figure 6.9-7. Polyester production.

### Emissions And Controls -

Air pollutant emissions from polyester fiber production include polymer dust from drying operations, volatilized residual monomer, fiber lubricants (in the form of fume or oil smoke), and the burned polymer and combustion products from cleaning the spinning equipment. Relative to the solvent spinning processes, the melt spinning of polyester fibers does not generate significant amounts of volatilized monomer or polymer, so emission control measures typically are not used in the spinning area. Finish oils that are applied in polyester fiber spinning operations are usually recovered and recirculated. When applied, finish oils are vaporized in the spin cell to some extent and, in some instances, are vented to either demisters, which remove some of the oils, or catalytic incinerators, which oxidize significant quantities of volatile hydrocarbons. Small amounts of finish oils are vaporized in the post-spinning process. Vapors from hot draw operations are typically controlled by devices such as electrostatic precipitators. Emissions from most other steps are not controlled.

### 6.9.5.2 Acrylic And Modacrylic Fiber Process Description<sup>5,18-24,53</sup> -

Acrylic and modacrylic fibers are based on acrylonitrile monomer, which is derived from propylene and ammonia. Acrylics are defined as those fibers that are composed of at least 85 percent acrylonitrile. Modacrylics are defined as those fibers that are composed of between 35 and 85 percent acrylonitrile. The remaining composition of the fiber typically includes at least one of the following: methyl methacrylate, methyl acrylate, vinyl acetate, vinyl chloride, or vinylidene chloride.

Polyacrylonitrile fiber polymers are produced by the industry using 2 methods, suspension polymerization and solution polymerization. Either batch or continuous reaction modes may be employed.

As shown in Figure 6.9-8 and Figure 6.9-9, the polymer is dissolved in a suitable solvent, such as dimethylformamide or dimethylacetamide. Additives and delusterants are added, and the solution is usually filtered in plate and frame presses. The solution is then pumped through a manifold to the spinnerettes (usually a bank of 30 to 50 per machine). At this point in the process, either wet or dry spinning may be used to form the acrylic fibers. The spinnerettes are in a spinning bath for wet spun fiber or at the top of an enclosed column for dry spinning. The wet spun filaments are pulled from the bath on takeup wheels, then washed to remove more solvent. After washing, the filaments are gathered into a tow band, stretched to improve strength, dried, crimped, heat set, and then cut into staple. The dry spun filaments are gathered into a tow band, stretched, dried, crimped, and cut into staple.

#### Emissions And Controls -

Air pollutant emissions from the production of acrylic and modacrylic fibers include emissions of acrylonitrile (volatilized residual monomer), solvents, additives, and other organics used in fiber processing. As shown in Figure 6.9-8 and Figure 6.9-9, both the wet and the dry spinning processes have many emission points. The major emission areas for the wet spin fiber process are the spinning and washing steps. The major emission areas from dry spinning of acrylic and modacrylic fibers are the spinning and post-spinning areas, up through and including drying. Solvent recovery in dry-spinning of modacrylic fibers is also a major emission point.

The most cost-effective method for reducing solvent VOC emissions from both wet and dry spinning processes is a solvent recovery system. In wet spinning processes, distillation is used to recover and recycle solvent from the solvent/water stream that circulates through the spinning, washing, and drawing operations. In dry spinning processes, control techniques include scrubbers, condensers, and carbon adsorption. Scrubbers and condensers are used to recover solvent emissions from the spinning cells and the dryers. Carbon adsorption is used to recover solvent emissions from storage tank vents and from mixing and filtering operations. Distillation columns are also used in dry spinning processes to recover solvent from the condenser, scrubber, and wash water (from the washing operation).

#### 6.9.5.3 Nylon Fiber 6 And 66 Process Description<sup>5,17,24-27</sup> -

Nylon 6 polymer is produced from caprolactam. Caprolactam is derived most commonly from cyclohexanone, which in turn comes from either phenol or cyclohexane. About 70 percent of all nylon 6 polymer is produced by continuous polymerization. Nylon 66 polymer is made from adipic acid and hexamethylene diamine, which react to form hexamethylene diammonium adipate (AH salt). The salt is then washed in a methyl alcohol bath. Polymerization then takes place under heat and pressure in a batch process. The fiber spinning and processing procedures are the same as described earlier in the description of melt spinning. The nylon production process is shown in Figure 6.9-10.

#### Emissions And Controls -

The major air pollutant emissions from production of nylon 6 fibers are volatilized monomer (caprolactam) and oil vapors or mists. Caprolactam emissions may occur at the spinning step because the polymerization reaction is reversible and exothermic, and the heat of extrusion causes the polymer to revert partially to the monomer form. A monomer recovery system is used on caprolactam volatilized at the spinnerette during nylon 6 fiber formation. Monomer recovery systems are not used in nylon 66 (polyhexamethylene adipamide) spinning operations because nylon 66 does not contain a significant amount of residual monomer. Emissions, though small, are in some instances controlled by catalytic incinerators. The finish oils, plasticizers, and lubricants applied to both nylon 6 and 66

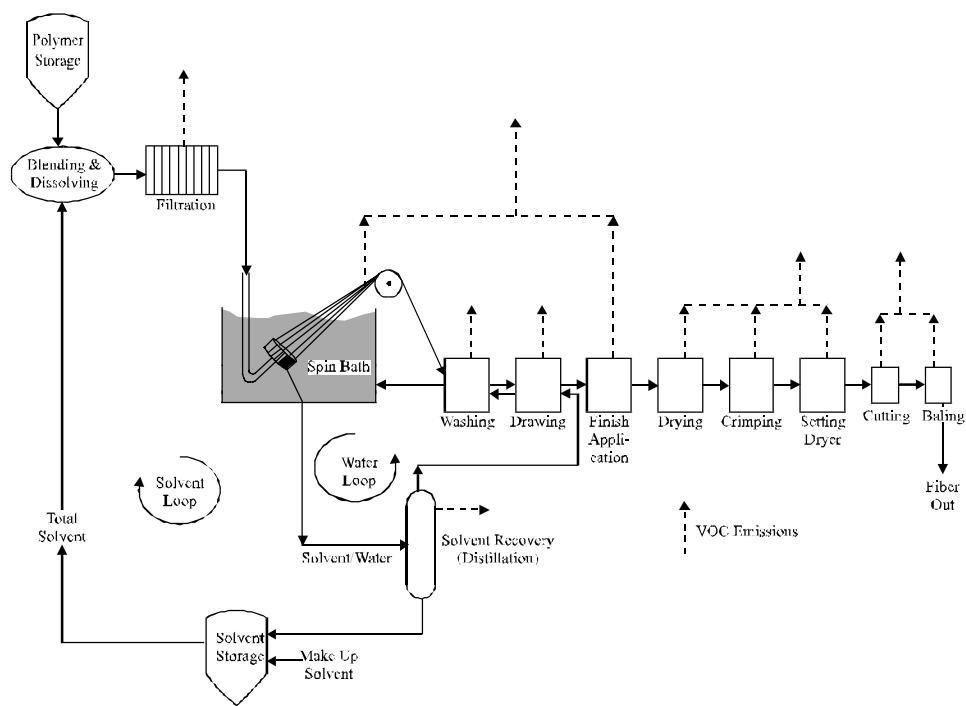


Figure 6.9-8. Acrylic fiber wet spinning.

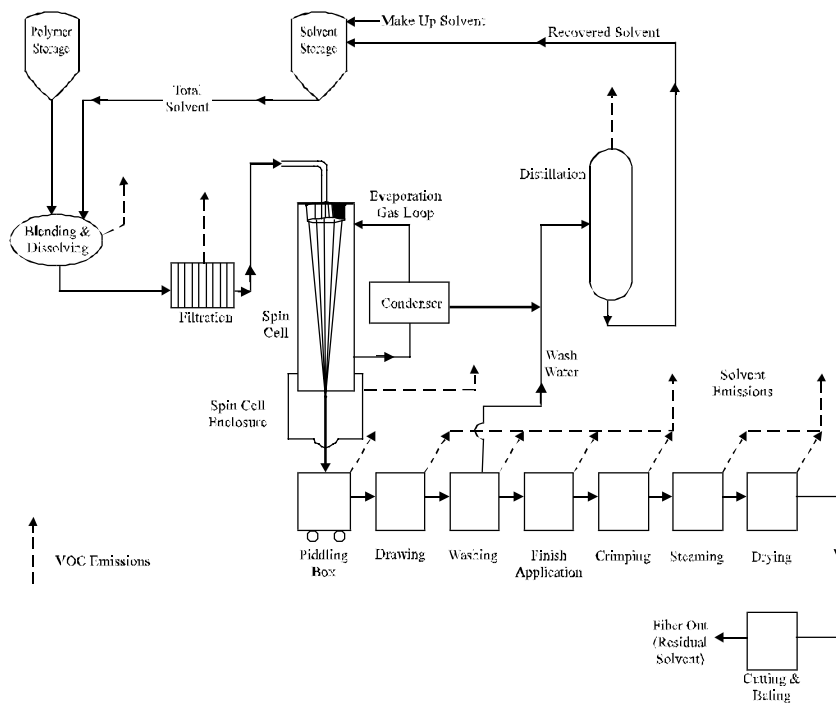


Figure 6.9-9. Acrylic fiber dry spinning.

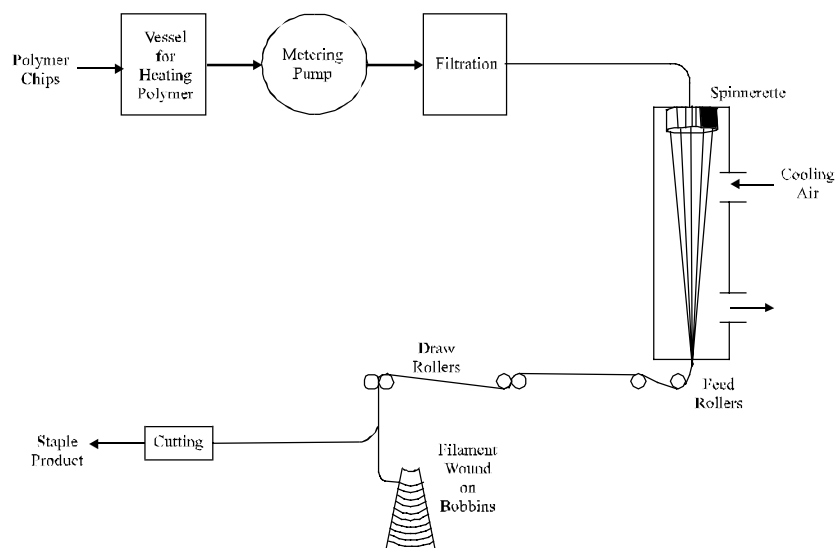


Figure 6.9-10. Nylon production.

fibers during the spinning process are vaporized during post-spinning processes and, in some instances such as the hot drawing of nylon 6, are vented to fabric filters, scrubbers and/or electrostatic precipitators.

#### 6.9.5.4 Polyolefin Fiber Process Description<sup>2,5,28-30</sup> -

Polyolefin fibers are molecularly oriented extrusions of highly crystalline olefinic polymers, predominantly polypropylene. Melt spinning of polypropylene is the method of choice because the high degree of polymerization makes wet spinning or dissolving of the polymer difficult. The fiber spinning and processing procedures are generally the same as described earlier for melt spinning. Polypropylene is also manufactured by the split film process in which it is extruded as a film and then stretched and split into flat filaments, or narrow tapes, that are twisted or wound into a fiber. Some fibers are manufactured as a combination of nylon and polyolefin polymers being melted together in a ratio of about 20 percent nylon 6 and 80 percent polyolefin such as polypropylene, and being spun from this melt. Polypropylene is processed more like nylon 6 than nylon 66 because of the lower melting point of 203°C (397°F) for nylon 6 versus 263°C (505°F) for nylon 66. The polyolefin fiber production process is shown in Figure 6.9-11.

#### Emissions And Controls -

Limited information is available on emissions from the actual spinning or processing of polyolefin fibers. The available data quantify and describe the emissions from the extruder/pelletizer stage, the last stage of polymer manufacture, and from just before the melting of the polymer for spinning. VOC content of the dried polymer after extruding and pelletizing was found to be as much as 0.5 weight percent. Assuming the content is as high as 0.5 percent and that all this VOC is lost in the extrusion and processing of the fiber (melting, spinning, drawing, winding, etc.), there would be 5 pounds of VOC emissions per 1,000 pounds of polyolefin fiber. The VOCs in the dried polymer are hexane, propane, and methanol, and the approximate proportions are 1.6 pounds of hexane, 1.6 pounds of propane, and 1.8 pounds of methanol.

During processing, lubricant and finish oils are added to the fiber, and some of these additives are driven off in the form of aerosols during processing. No specific information has been obtained to

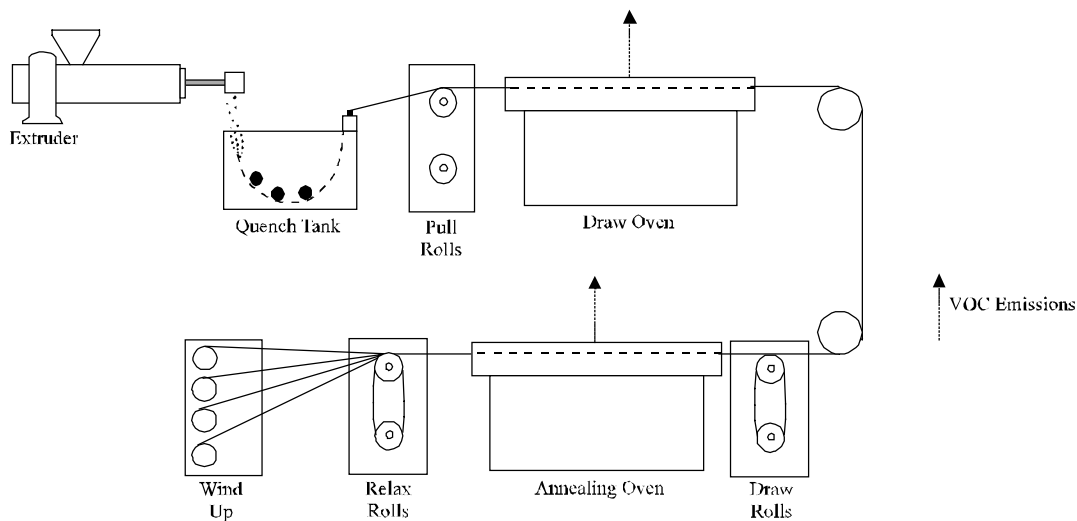


Figure 6.9-11. Polyolefin fiber production.

describe the oil aerosol emissions for polyolefin processing, but certain assumptions may be made to provide reasonably accurate values. Because polyolefins are melt spun similarly to other melt spun fibers (nylon 6, nylon 66, polyester, etc.), a fiber similar to the polyolefins would exhibit similar emissions. Processing temperatures are similar for polyolefins and nylon 6. Thus, aerosol emission values for nylon 6 can be assumed valid for polyolefins.

#### 6.9.5.5 Spandex Fiber Manufacturing Process Description<sup>5,31-33</sup> -

Spandex is a generic name for a polyurethane fiber in which the fiber-forming substance is a long chain of synthetic polymer comprised of at least 85 percent of a segmented polyurethane. In between the urethane groups, there are long chains that may be polyglycols, polyesters, or polyamides. Being spun from a polyurethane (a rubber-like material), spandex fibers are elastomeric, that is, they stretch. Spandex fibers are used in such stretch fabrics as belts, foundation garments, surgical stockings, and stocking tops.

Spandex is produced by 2 different processes in the United States. One process is similar in some respects to that used for acetate textile yarn, in that the fiber is dry spun, immediately wound onto takeup bobbins, and then twisted or processed in other ways. This process is referred to as dry spinning. The other process, which uses reaction spinning, is substantially different from any other fiber forming process used by domestic synthetic fiber producers.

#### 6.9.5.6 Spandex Dry Spun Process Description -

This manufacturing process, which is illustrated in Figure 6.9-12, is characterized by use of solution polymerization and dry spinning with an organic solvent. Tetrahydrofuran is the principal raw material. The compound's molecular ring structure is opened, and the resulting straight chain compound is polymerized to give a low molecular weight polymer. This polymer is then treated with an excess of a di-isocyanate. The reactant, with any unreacted di-isocyanate, is next reacted with some diamine, with monoamine added as a stabilizer. This final polymerization stage is carried out in dimethylformamide solution, and then the spandex is dry spun from this solution. Immediately after spinning, spandex yarn is wound onto a bobbin as continuous filament yarn. This yarn is later transferred to large spools for shipment or for further processing in another part of the plant.

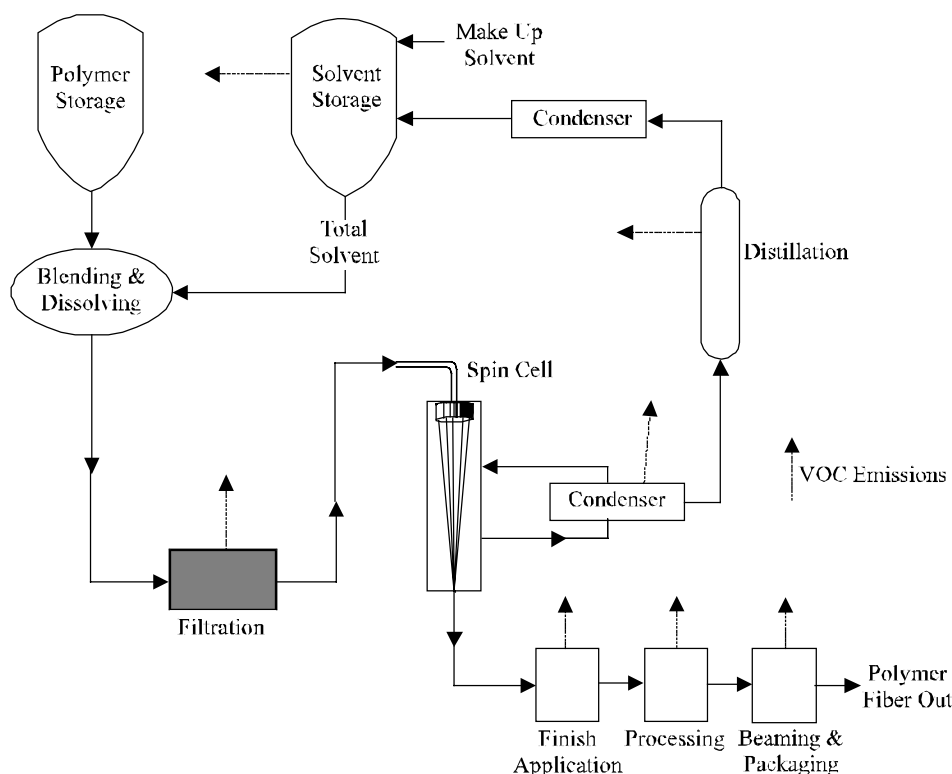


Figure 6.9-12. Spandex dry spinning.

#### Emissions And Controls -

The major emissions from the spandex dry spinning process are volatilized solvent losses, which occur at a number of points of production. Solvent emissions occur during filtering of the spin dope, spinning of the fiber, treatment of the fiber after spinning, and the solvent recovery process. The emission points from this process are also shown in Figure 6.9-12.

Total emissions from spandex fiber dry spinning are considerably lower than from other dry spinning processes. It appears that the single most influencing factor that accounts for the lower emissions is that, because of nature of the polymeric material and/or spinning conditions, the amount of residual solvent in the fiber as it leaves the spin cell is considerably lower than other dry spun fibers. This situation may be because of the lower solvent/polymer ratio that is used in spandex dry spinning. Less solvent is used for each unit of fiber produced relative to other fibers. A condensation system is used to recover solvent emissions from the spin cell exhaust gas. Recovery of solvent emissions from this process is as high as 99 percent. Since the residual solvent in the fiber leaving the spin cell is much lower than for other fiber types, the potential for economic capture and recovery is also much lower. Therefore, these post-spinning emissions, which are small, are not controlled.

#### 6.9.5.7 Spandex Reaction Spun Process Description -

In the reaction spun process, a polyol (typically polyester) is reacted with an excess of di-isocyanate to form the urethane prepolymer, which is pumped through spinnerettes at a constant rate into a bath of dilute solution of ethylenediamine in toluene. The ethylenediamine reacts with isocyanate end groups on the resin to form long-chain cross-linked polyurethane elastomeric fiber. The final cross-linking reaction takes place after the fiber has been spun. The fiber is transported from the bath to an oven, where solvent is evaporated. After drying, the fiber is lubricated and is wound on tubes for shipment.

## Emissions And Controls -

Essentially all air that enters the spinning room is drawn into the hooding that surrounds the process equipment and then leads to a carbon adsorption system (see Figure 6.9-13). The oven is also vented to the carbon adsorber. The gas streams from the spinning room and oven are combined and cooled in a heat exchanger before they enter the activated carbon bed.

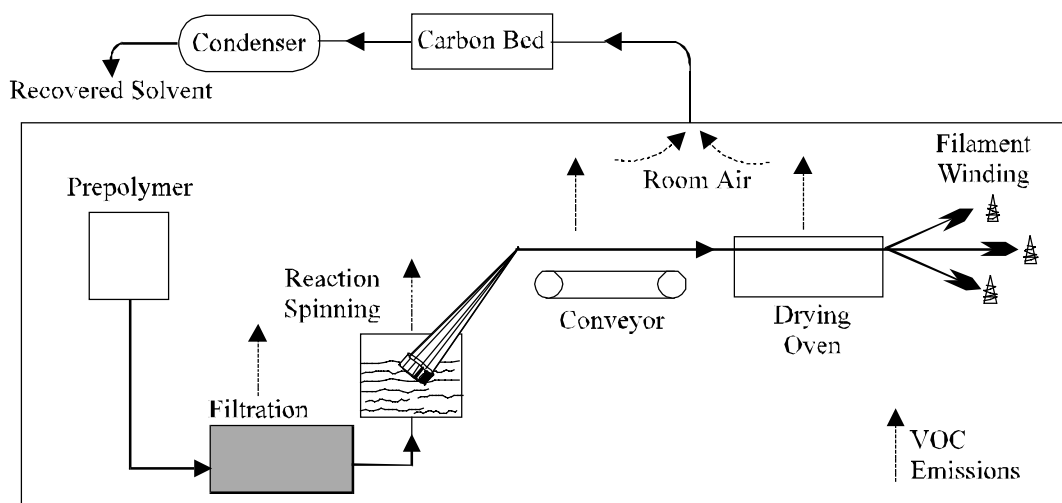


Figure 6.9-13. Spandex reaction spinning.

### 6.9.5.8 Vinyon Fiber Process Description<sup>5,34</sup> -

Vinyon is a copolymer of vinyl chloride (88 percent) and vinyl acetate (12 percent). The polymer is dissolved in a ketone (acetone or methyl ethyl ketone) to make a 23 weight percent spinning solution. After filtering, the solution is extruded as filaments into warm air to evaporate the solvent and to allow its recovery and reuse. The spinning process is similar to that of cellulose acetate. After spinning, the filaments are stretched to achieve molecular orientation to impart strength.

## Emissions And Controls -

Emissions occur at steps similar to those of cellulose acetate, at dope preparation and spinning, and as fugitive emissions from the spun fiber during processes such as winding and stretching. The major source of VOCs is the spinning step, where the warm air stream evaporates the solvent. This air/solvent stream is sent to either a scrubber or carbon adsorber for solvent recovery. Emissions may also occur at the exhausts from these control devices.

### 6.9.5.9 Other Fibers -

There are synthetic fibers manufactured on a small volume scale relative to the commodity fibers. Because of the wide variety of these fiber manufacturing processes, specific products and processes are not discussed. Table 6.9-3 lists some of these fibers and the respective producers.

Table 6.9-3. OTHER SYNTHETIC FIBERS AND THEIR MAKERS

| Fiber                   | Manufacturer |
|-------------------------|--------------|
| Nomex (aramid)          | DuPont       |
| Kevlar (aramid)         | DuPont       |
| PBI (polybenzimidazole) | Celanese     |
| Kynol (novoloid)        | Carborundum  |
| Teflon                  | DuPont       |

## GLOSSARY

|                           |                                                                                                                                                                                                                                                                                                                                         |
|---------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Crimping:                 | A process in which waves and angles are set into fibers, such as acrylic fiber filaments, to help simulate properties of natural fibers.                                                                                                                                                                                                |
| Coagulant:                | A substance, either a salt or an acid, used to precipitate polymer solids out of emulsions or latexes.                                                                                                                                                                                                                                  |
| Continuous filament yarn: | Very long fibers that have been converged to form a multifiber yarn, typically consisting of 15 to 100 filaments.                                                                                                                                                                                                                       |
| Cutting:                  | Refers to the conversion of tow to staple fiber.                                                                                                                                                                                                                                                                                        |
| Delusterant:              | Fiber finishing additives (typically clays or barium sulfate) used to dull the surfaces of the fibers.                                                                                                                                                                                                                                  |
| Dope:                     | The polymer, either in molten form or dissolved in solvent, that is spun into fiber.                                                                                                                                                                                                                                                    |
| Drawing:                  | The stretching of the filaments in order to increase the fiber's strength; also makes the fiber more supple and unshrinkable (that is, the stretch is irreversible). The degree of stretching varies with the yarn being spun.                                                                                                          |
| Filament:                 | The solidified polymer that has emerged from a single hole or orifice in a spinnerette.                                                                                                                                                                                                                                                 |
| Filament yarn:            | See continuous filament yarn.                                                                                                                                                                                                                                                                                                           |
| Heat setting:             | The dimensional stabilization of the fibers with heat so that the fibers are completely undisturbed by subsequent treatments such as washing or dry cleaning at a lower temperature. To illustrate, heat setting allows a pleat to be retained in the fabric while helping prevent undesirable creases later in the life of the fabric. |
| Lubrication:              | The application of oils or similar substances to the fibers in order, for example, to facilitate subsequent handling of the fibers and to provide static suppression.                                                                                                                                                                   |

|              |                                                                                                                                                                                                                                 |
|--------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Spinnerette: | A spinnerette is used in the production of all man-made fiber whereby liquid is forced through holes. Filaments emerging from the holes are hardened and solidified. The process of extrusion and hardening is called spinning. |
| Spun yarn:   | Yarn made from staple fibers that have been twisted or spun together into a continuous strand.                                                                                                                                  |
| Staple:      | Lengths of fiber made by cutting man-made fiber tow into short (1- to 6-inch) and usually uniform lengths, which are subsequently twisted into spun yarn.                                                                       |
| Tow:         | A collection of many (often thousands) parallel, continuous filaments, without twist, that are grouped together in a rope-like form having a diameter of about one-quarter inch.                                                |
| Twisting:    | Giving the filaments in a yarn a very slight twist that prevents the fibers from sliding over each other when pulled, thus increasing the strength of the yarn.                                                                 |

#### References For Section 6.9

1. *Man-made Fiber Producer's Base Book*, Textile Economics Bureau Incorporated, New York, NY, 1977.
2. "Fibers 540.000", *Chemical Economics Handbook*, Menlo Park, CA, March 1978.
3. *Industrial Process Profiles For Environmental Use - Chapter 11 - The Synthetic Fiber Industry*, EPA Contract No. 68-02-1310, Aeronautical Research Associates of Princeton, Princeton, NJ, November 1976.
4. R. N. Shreve, *Chemical Process Industries*, McGraw-Hill Book Company, New York, NY, 1967.
5. R. W. Moncrief, *Man-made Fibers*, Newnes-Butterworth, London, 1975.
6. *Guide To Man-made Fibers*, Man-made Fiber Producers Association, Inc. Washington, DC, 1977.
7. "Trip Report/Plant Visit To American Enka Company, Lowland, Tennessee", Pacific Environmental Services, Inc., Durham, NC, January 22, 1980.
8. "Report Of The Initial Plant Visit To Avtex Fibers, Inc., Rayon Fiber Division, Front Royal, VA", Pacific Environmental Services, Inc., Durham, NC, January 15, 1980.
9. "Fluidized Recovery System Nabs Carbon Disulfide", *Chemical Engineering*, 70(8):92-94, April 15, 1963.
10. Standards Of Performance For Synthetic Fibers NSPS, Docket No. A-80-7, II-B-83, "Viscose Rayon Fiber Production - Phase I Investigation", U. S. Environmental Protection Agency, Washington, DC, February 25, 1980.

11. "Report Of The Initial Plant Visit To Tennessee Eastman Company Synthetic Fibers Manufacturing", Kingsport, TN, Pacific Environmental Services, Inc., Durham, NC, December 13, 1979.
12. "Report Of The Phase II Plant Visit To Celanese's Celriver Acetate Plant In Rock Hill, SC", Pacific Environmental Services, Inc., Durham, NC, May 28, 1980.
13. "Report Of The Phase II Plant Visit To Celanese's Celco Acetate Fiber Plant In Narrows, VA", Pacific Environmental Services, Inc., Durham, NC, August 11, 1980.
14. Standards Of Performance For Synthetic Fibers NSPS, Docket No. A-80-7, II-I-43, U. S. Environmental Protection Agency, Washington, DC, December 1979.
15. E. Welfers, "Process And Machine Technology Of Man-made Fibre Production", *International Textile Bulletin*, World Spinning Edition, Schlieren/Zurich, Switzerland, February 1978.
16. Written communication from R. B. Hayden, E. I. duPont de Nemours and Co., Wilmington, DE, to E. L. Bechstein, Pullman, Inc., Houston, TX, November 8, 1978.
17. Written communication from E. L. Bechstein, Pullman, Inc., Houston, TX, to R. M. Clowers, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 17, 1978.
18. "Report Of The Plant Visit To Badische Corporation's Synthetic Fibers Plant In Williamsburg, VA", Pacific Environmental Services, Inc., Durham, NC, November 28, 1979.
19. "Report Of The Initial Plant Visit To Monsanto Company's Plant In Decatur, AL", Pacific Environmental Services, Inc., Durham, NC, April 1, 1980.
20. "Report Of The Initial Plant Visit To American Cyanamid Company", Pacific Environmental Services, Inc., Durham, NC, April 11, 1980.
21. Written communication from G. T. Esry, E. I. duPont de Nemours and Co., Wilmington, DE, to D. R. Goodwin, U. S. Environmental Protection Agency, Research Triangle Park, NC, July 7, 1978.
22. "Report Of The Initial Visit To duPont's Acrylic Fiber Plant In Waynesboro, VA", Pacific Environmental Services, Inc., Durham, NC, May 1, 1980.
23. "Report Of The Phase II Plant Visit To duPont's Acrylic Fiber May Plant In Camden, SC", Pacific Environmental Services, Inc., Durham, NC, August 8, 1980.
24. C. N. Click and D. K. Webber, *Polymer Industry Ranking By VOC Emission Reduction That Would Occur From New Source Performance Standards*, EPA Contract No. 68-02-2619, Pullman, Inc., Houston, TX, August 30, 1979.
25. Written communication from E. L. Bechstein, Pullman, Inc., Houston, TX, to R. M. Clowers, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 28, 1978.
26. Written communication from R. B. Hayden, E. I. duPont de Nemours and Co., Wilmington, DE, to W. Talbert, Pullman, Inc., Houston, TX, October 17, 1978.

27. "Report Of The Initial Plant Visit To Allied Chemical's Synthetic Fibers Division", Chesterfield, VA, Pacific Environmental Services, Inc., Durham, NC, November 27, 1979.
28. *Background Information Document — Polymers And Resins Industry*, EPA-450/3-83-019a, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1984.
29. H. P. Frank, *Polypropylene*, Gordon and Breach Science Publishers, New York, NY, 1968.
30. A. V. Galanti and C. L. Mantell, *Polypropylene — Fibers and Films*, Plenum Press, New York, NY, 1965.
31. D. W. Crumpler, "Trip Report — Plant Visit To Globe Manufacturing Company", D. Crumpler, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 16 and 17, 1981.
32. "Standards Of Performance For Synthetic Fibers NSPS, Docket No. A-80-7, II-I-115, Lycra Reamout Plan", U. S. Environmental Protection Agency, Washington, DC, May 10, 1979.
33. "Standards Of Performance For Synthetic Fibers NSPS, Docket No. A-80-7, II-I-95", U. S. Environmental Protection Agency, Washington, DC, March 2, 1982.
34. Written communication from W. K. Mohny, Avtex Fibers, Inc., Meadville, PA, to R. Manley, Pacific Environmental Services, Durham, NC, April 14, 1981.
35. Personal communication from J. H. Cosgrove, Avtex Fibers, Inc., Front Royal, VA, to R. Manley, Pacific Environmental Services, Inc., Durham, NC, November 29, 1982.
36. Written communication from T. C. Benning, Jr., American Enka Co., Lowland, TN, to R. A. Zerbonia, Pacific Environmental Services, Inc., Durham, NC, February 12, 1980.
37. Written communication from R. O. Goetz, Virginia State Air Pollution Control Board, Richmond, VA, to Director, Region II, Virginia State Air Pollution Control Board, Richmond, VA, November 22, 1974.
38. Written communication from H. S. Hall, Avtex Fibers, Inc., Valley Forge, PA, to J. R. Farmer, U. S. Environmental Protection Agency, Research Triangle Park, NC, December 12, 1980.
39. Written communication from J. C. Pullen, Celanese Fibers Co., Charlotte, NC, to R. A. Zerbonia, Pacific Environmental Services, Inc., Durham, NC, July 3, 1980.
40. Written communication from J. C. Pullen, Celanese Fibers Co., Charlotte, NC, to National Air Pollution Control Techniques Advisory Committee, U. S. Environmental Protection Agency, Research Triangle Park, NC, September 8, 1981.

41. "Report Of The Initial Plant Visit To Tennessee Eastman Company Synthetic Fibers Manufacturing, Kingsport, TN", Pacific Environmental Services, Inc., Durham, NC, December 13, 1979.
42. Written communication from J. C. Edwards, Tennessee Eastman Co., Kingsport, TN, to R. Zerbonia, Pacific Environmental Services, Inc., Durham, NC, April 28, 1980.
43. Written communication from C. R. Earnhart, E. I. duPont de Nemours and Co., Camden, SC, to D. W. Crumpler, U. S. Environmental Protection Agency, Research Triangle Park, NC, November 5, 1981.
44. C. N. Click and D. K. Weber, *Emission Process And Control Technology Study Of The ABS/SAN Acrylic Fiber and NBR Industries*, EPA Contract No. 68-02-2619, Pullman, Inc., Houston, TX, April 20, 1979.
45. Written communication from D. O. Moore, Jr., Pullman, Inc., Houston, TX, to D. C. Mascone, U. S. Environmental Protection Agency, Research Triangle Park, NC, April 18, 1979.
46. Written communication from W. M. Talbert, Pullman, Inc., Houston, TX, to R. J. Kucera, Monsanto Textiles Co., Decatur, AL, July 17, 1978.
47. Written communication from M. O. Johnson, Badische Corporation, Williamsburg, VA, to D. R. Patrick, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 1, 1979.
48. Written communication from J. S. Lick, Badische Corporation, Williamsburg, VA, to D. R. Goodwin, U. S. Environmental Protection Agency, Research Triangle Park, NC, May 14, 1980.
49. P. T. Wallace, "Nylon Fibers", *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA, December 1977.
50. Written communication from R. Legendre, Globe Manufacturing Co., Fall River, MA, to Central Docket Section, U. S. Environmental Protection Agency, Washington, DC, August 26, 1981.
51. Written communication from R. Legendre, Globe Manufacturing Co., Fall River, MA, to J. Farmer, U. S. Environmental Protection Agency, Research Triangle Park, NC, June 26, 1980.
52. Written communication from R. H. Hughes, Avtex Fibers Co., Valley Forge, PA, to R. Manley, Pacific Environmental Services, Inc., Durham, NC, February 28, 1983.
53. "Report Of The Phase II Plant Visit, DuPont's Acrylic Fiber May Plant In Camden, SC", Pacific Environmental Services, Inc., Durham, NC, April 29, 1980.