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SYNTHETIC FIBERS

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CHEMICAL PROCESS INDUSTRIES

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chapter 35
**SYNTHETIC FIBER AND
 FILM INDUSTRIES**

The ability of the chemist and the chemical engineer to create, from the test tube through the factory, products that are often superior to naturally occurring materials is one of the outstanding accomplishments of this age, and nowhere is it so graphically portrayed as by the modern synthetic fibers.¹ In the United States in 1972, \$167 million was spent for research in this field.

HISTORICAL. Although the word "fiber" originally referred only to naturally occurring materials (cotton, wool, etc.), it is now used extensively for synthetic products. The latter usage includes both celluloses and polyfibers. Cellulosics result when natural polymeric materials such as cellulose are brought into a dissolved or dispersed state and then spun into fine filaments. Viscose rayon, acrylics, and polyesters result from two methods of forming long-chain molecules: addition polymerization and condensation polymerization. The polymer is then taken from its melt, or solution, and processed into fiber form. Cellulose acetate really lies between these two classes, since in this case a natural polymer (cellulose) is converted into one of its derivatives (cellulose acetate), which is dissolved and spun into fiber form.

These synthetics, from their humble beginning in 1900, have grown to a total world production of more than 26,700 million lb in 1974 and, for the United States, to 8,100 million lb in 1974, including glass fibers. The United States started the manufacture of rayon in 1910 and produced in 1974 about 800 million lb of rayon and 380 million lb of acetate. Over 6,200 million lb of fibers was produced in 1974.² The list of synthetic fibers, which in 1900 included only nitrocellulose, today has many products, the *more important ones* being polyamides or nylons, fibers made from polyacrylonitrile (Orlon, Dacron, Fortrel), polyesters (Dacron, Fortrel), olefins (Marvess, Herculon), spandex fibers (Lycra, Glospan), glass (Fiberglas, Vitron), and cellulosic fibers (Viscose and acetate rayon). It is the purpose of this chapter to present a picture of the chemistry and engineering behind our modern "fashions out of test tubes." See Table 35.1.

Three of the more important general properties of fibers are length, crimp, and denier. Concerning length, there are essentially two types of fibers, continuous-filament and staple. *Continuous filaments* are individual fibers whose length is almost infinite. Silk, rayon, nylon, and most other true synthetics are manufactured in this manner. Cotton and wool are examples of natural fibers in the *staple* form, i.e., of short and more-or-less uniform length. Artificial staple fibers such as rayon, acetate, nylon, and polyester result from the cutting of long (untwisted continuous filaments) to uniform lengths, usually between 1½ and 6 in. *Crimp* is the curl, or waviness, placed in synthetic fibers by chemical or mechanical action, which is of great importance in the processibility of staple fibers.

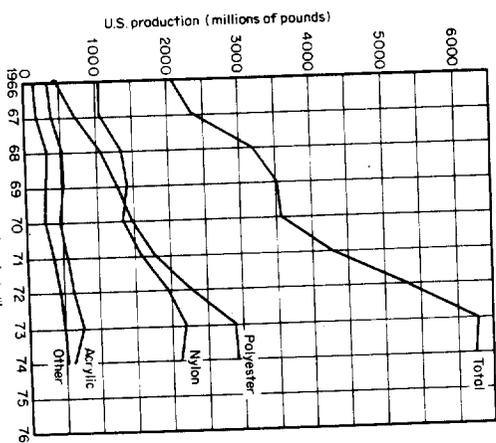
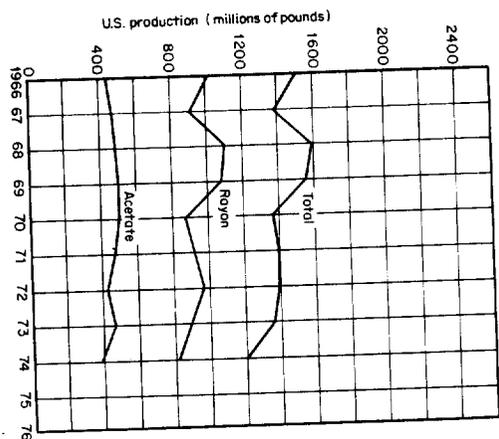


Fig. 35.1 Trends in the production of synthetic fibers.

¹Unger et al., *Fibers, Ind. Eng. Chem., Annual Review*, 53A(19), 653 (1961), Annual Suppl., 1962, p. 17, and following years.
²*Text. Organon*, June 1975, p. 71.

TABLE 35.1 Representative Synthetic Fibers and Films*

Classification	Polyfibers and film	Spinning†
Polyamides, or nylon, fibers	Nylon 66, nylon 6, Orlon	Melt
	Polyesters	
	Fibers: Rayon, Tenon, Kodal, Fortrel	Melt
	Films: Mylar, Conar, Kodar, Emar	Melt
	Acrylics and methacrylics	
	Other fibers	Dry
	Acetan fiber	Wet
	Creslan fiber	Wet
	Dynel fiber (vinyl-acrylic)	Dry
	Verd fiber	Dry
Frayls and Vinyldines	Saran fiber and film	Melt
	Vinyon N fiber‡	Dry
	Synolene	Dry
	Lycra	Dry
Nona	Wet	
	Wet	
Chlopan	Wet	
Olefin	Melt	
	Melt	
Polyethylene films	Melt	
Polypropylene fibers and films: Avonon, Herovlon	Melt	
Fiberglass	Class fibers	Melt
	Chalcote fibers and films	
Regenerated cellulose		
Fibers: Rayon (viscose), cuprammonium	Wet	
Films: Calophane	Wet	
Cellulose esters		
Acetate fibers and films: Acetel, Estrom	Dry	
Triacetate fiber: Arnel	Dry	

* Completely synthetic or semisynthetic (cellulosic). † Class as indicated in melt, dry, or wet. ‡ 40% vinyl and 40% acrylonitrile.

Cotton and wool possess natural crimp. Crimp is also introduced in some cases in continuous filament yarns to alter their appearance and feel, e.g., in nylon carpet yarn. *Denier* is a measure of weight per unit length. Each fiber has a *cross section*, and special characteristics are imparted by manufacturing polyfibers with different cross sections. A fiber has a cross section corresponding to 1 denier if 9,000 in of it weighs 1 g.

Films, as well as fibers, are changing. Nitrocellulose, once largely used especially for photographic film, has given way to acetate and polyester. Many other films are suited to the demand for their special properties, e.g., cellophane, Saran, Teflon, and polyethylene.

POLYFIBERS AND FILMS

The rapidly growing and versatile noncellulosic fibers are classified chemically and by the method of spinning in Table 35.1. The manufacture of all true synthetic fibers first begins with the preparation of a polymer consisting of extremely long, chainlike molecules. The polymer is spun in one of three ways (see below), resulting in most cases in a weak, practically useless fiber until it is *stretched further to orient the molecules and set up crystalline lattices*. Although the range of any one polymer is

TABLE 35.2 Comparison of Selected Synthetic Fibers

Fiber	Wool	Acrylic	Methacrylic	Polyesters	Nylon
Tensile strength, g/denier	1.0-1.7	4.0-5.0	3.0	4.4-6.6	4.7-5.6
Elongation, %	25-35	16-21	16	18-22	25-28
Draught recovery	0.99 at 2%	0.97 at 2%	0.80 at 2%	90-100 at 4%	100 at 8%
Strength, per	20,000-29,000	59,000-74,000	44,000-66,000	78,000-116,000	68,000-81,000
Stiffness, g/denier*	3.9	24	30	23-63	20
Alkali resistance†	90	21.9% at 90 RH	30	1.570	2,320
Water absorbency†	21.9% at 90 RH	2% at 95 RH	2%	0.5% at 95 RH	8% at 95 RH
Effect of heat	Becomes hard at 100°C, decomposes at 130°C	Sticking point 225°C	Sticking point 225°C	Sticking point 240°C	Melts 263°C
Effect of age	Little	Little	Little	Little	Slight
Effect of sun	Weakens	Very resistant	Slight	Little	Weakens
Effect of acids	Resistant	Resistant	Resistant	Resistant	Weakens
(concentrated, room temp.)					
Effect of alkalis	Superior	Partly resistant	Resistant	Resistant	Resistant
Effect of organic solvents	Resistant	Resistant	Resistant	Resistant	Resistant
Dyeability	Good	Good	Good	Difficult	Good
Resistance to moths	None	Wholly	Wholly	Wholly	Wholly
Resistance to mildew	Good	Wholly	Wholly	Wholly	Wholly

* Source: Wool vs. Synthetics, Chem. Week, 69(3), 11 (1951); Monroed, Man-Made Fibers, 6th ed., Wiley, 1975. † Wet-draw test, number of fibers. RH, Relative humidity. * Crease resistance.

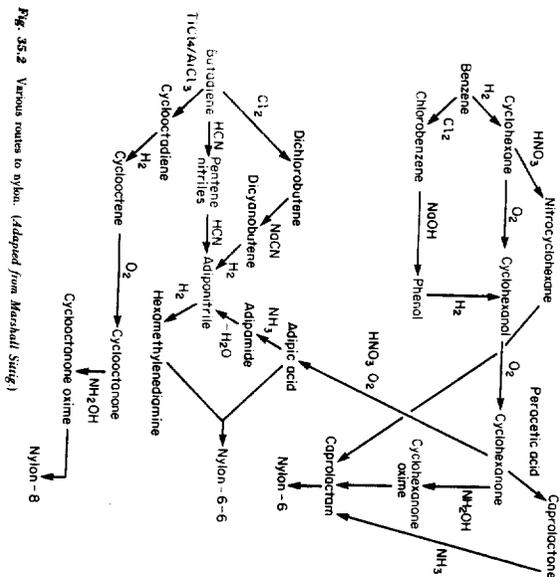
always limited by controlling the degree of orientation, crystallinity, and average chain length, a single polymer can be used to make a number of fibers with different mechanical properties; i.e., some can be weak and stretchy, others strong and stiff. The two elements important in determining the range of the polymer's mechanical properties are the attractive forces between the molecules and the flexibility and length of the molecular chains.

The three spinning procedures are *melt, dry,* and *wet*. Melt spinning, developed for nylon and also used for polyester, polyvinyl, polypropylene, and others, involves pumping molten polymer through spinneret jets. The polymer solidifies into filaments as it strikes the cool air. In dry spinning, as described for acetate, the polymer is dissolved in a suitable organic solvent. The solution is forced through spinnerets, and dry filaments result upon the evaporation of the solvent in warm air. Orlon and Vinyon are spun in this manner. Viscose rayon, Acetan, and Dynel staple are examples of wet-spun fibers. Here, as the solution emerges from the spinneret, it is coagulated in a chemical bath. Several polyfibers can be spun in several ways; Table 35.1 lists the method believed to be in widest commercial use. For a comparison of selected synthetic fibers, see Table 35.2.

POLYAMIDE, OR NYLON, FIBERS

NYLON (nylon 66) This fiber was the first truly all-synthetic fiber, resulting from the brilliant research of Carothers of the Du Pont Co.³ It opened up the entire field of true synthetic fibers, and in 1974 worldwide production was 5.7 billion lb. U.S. production was a little over 2 billion lb, and of this 70% was nylon 66 and 30% was nylon 6. In the rest of the world the split was 38% nylon 66 and 62% nylon 6. Nylon 66 is commonly produced by reacting hexamethylenediamine and adipic acid to form "nylon salt," or hexamethylene diammonium adipate. This compound by polymerization with the removal of a molecule of water, becomes polyhexamethylene adipamide, a linear polyamide. The two intermediates which form the nylon salt are currently produced from petrochemical raw materials (Fig. 35.2). The oxidation of cyclohexane is used to make adipic acid. Three processes for

³ Beldon, Development of Nylon, Ind. Eng. Chem., 34, 53 (1942).



the production of hexamethylenediamine are in current use: from butadiene, from propylene, and from adipic acid.⁴

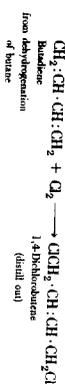
Formulations of the reactions involved are presented in the following discussion.

NYLON INTERMEDIATES

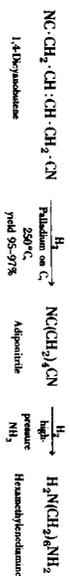
1. *Adipic acid* 1973 U.S. production was about 1.6 billion lb. of which 95% was used for nylon fibers and plastics.



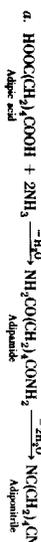
2. Hexamethylenediamine



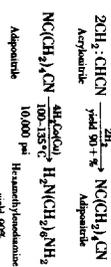
⁴Standish and Abrams, *Adipic Acid*, ECT 24 ed., vol. 1, pp. 405-421 (119 refs.); Haines, *Cyclohexane and Adipic Acid*, *Ind. Eng. Chem.*, 54(7), 23 (1962) (Review); Guvenen, Thermal Degradation for Cyclohexane, *Chem. Eng. (N.Y.)*, 70(15), 111 (1963); Strickland, Raw Materials for Mannamide Fibers, *Ind. Eng. Chem.*, 55(1), 37 (1963); Kren et al., High Purity Cyclohexane, *Chem. Eng. Prog.*, 60(9), 43 (1964); Scientific Design, *Chem. Eng. News*, June 6, 1964, p. 17; U.S. Pat. 3,245,199; 3,109,804; 3,240,820; 3,259,552; Amin, *Chem. Eng. (N.Y.)*, 81(2), 131 (1974); 81(11), 104 (1974).



Other routes to hexamethylenediamine:



b. Electrolytic hydrofluorination of acrylonitrile in solubilizing concentrated solutions of tetraethylammonium *p*-toluenesulfonate:⁵



3. Nylon salt and nylon



In the manufacture of the fiber,⁶ the aqueous nylon-salt solution starts on the top level and the materials move down by gravity through the various steps, which may be divided into the following coordinated sequence of unit operations (Op) and chemical conversions (Ch) as depicted in the flowchart in Fig. 35.3.

The hexamethylene diammonium adipate solution is pumped to the top level into evaporators and concentrated (Op). Acetic acid is added to the evaporator charge to stabilize the viscosity (Ch). After evaporation, the salt solution flows into jacketed autoclaves equipped with internal coils and heated by Dowtherm vapor (Fig. 35.4). Here the rest of the water is removed, the pigment dispersion agent (TiO₂) is added, and polymerization takes place (Op and Ch).

After polymerization is completed, the molten viscous polymer is forced out of the bottom onto a casing wheel by specially purified nitrogen at 40 to 50 psi. Each 2,000-lb batch is extruded as rapidly as possible to minimize differences due to thermal treatment of the polymer.

A ribbon of polymer about 12 in. wide and 1/4 in. thick flows on the 6-ft casing drum. Water sprays on the inside cool and harden the underside of the ribbon; the outer is cooled by air and water (Op). The ribbons are cut into small chips, or flakes, before being blended. Two or more batches are mixed to improve the uniformity of the feed to the spinning machine (Op).

The blenders empty into hoppers on a monorail which supply the spinning area (Op).

⁵New Trails to Nylon, *Chem. Week*, Oct. 12, 1963, p. 85; acrylonitrile costs half that of adipic acid; Monahan, New Routes to Adiponitrile from acrylonitrile, *Chem. Eng. (N.Y.)*, 72(20), 88 (1965); and 72(23), 230 (1965) (Chemical Engineering Award); excellent flowchart and photographs; New Adipic Processes, *Chem. Week*, May 12, 1971, p. 32. See Acrylonitrile, this chapter; Stieg, Polyamide Fiber Manufacture, *Notes*, 1972. ⁶See Nylon Production Technique, *Chem. Eng. (N.Y.)*, 53(3), 96 (1946) (reprinted flowchart, p. 148).

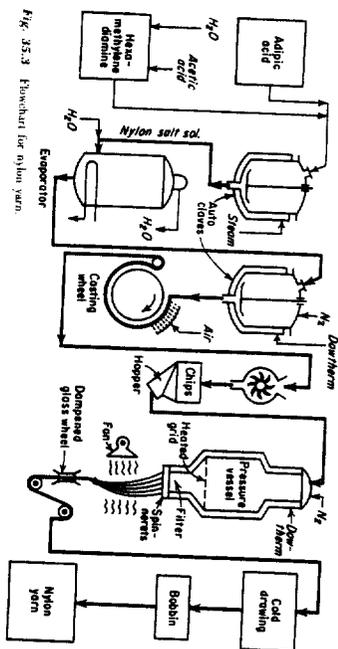


Fig. 35.3. Flowchart for nylon yarn.

A typical spinning unit is composed of a metal vessel surrounded by a Dowtherm vapor-heated jacket which keeps the temperature of the vessel above the melting point (263°C) of the nylon. Special precautions are again taken to keep the spinning oxygen-free. As the nylon flake enters the vessel it strikes a grid, where it melts and dribs through to the melt chamber below (Op). Screw molers are also used in place of grids.

The molten polymer passes through the porches in this chamber to the gear spinning pumps. They deliver it to a sand filter, which is followed by screens and spinnerets (Op).

The filaments are solidified by air in a cooling chimney and passed in a bundle through a steam-humidifying chamber, where the moisture content is brought to equilibrium in order to stabilize the length of the spun polymer (Op). This is not a problem after the stretching or drawing.

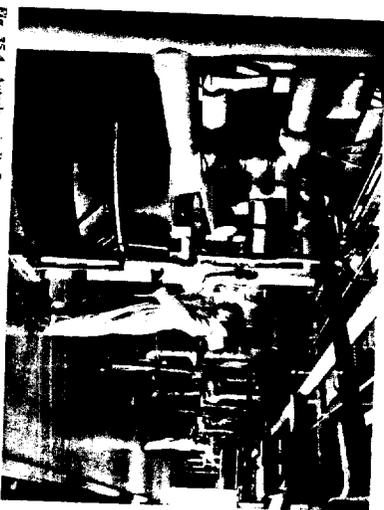


Fig. 35.4. Spinners in Du Pont nylon plants. In these complexes the chemical process known as polymerization takes place. In other words, small molecules are joined together to make large ones, and nylon polymer is created. Plants are located at Seaford, Del., at Martinsville and Richmond, Va., at Chattanooga, Tenn., and at Camden, S.C.

After lubrication in a finish roll, the yarn is stretched or drawn to the desired degree by passing it through a roller system. Here the strength and elasticity characteristics of nylon are developed, because the molecules are oriented from their previous comparatively haphazard arrangement (Op). Stretching may be from three- to sixfold, depending on the mechanical properties desired, being stronger when the orientation by stretching is greatest. The nylon filament is then shipped to various manufacturers for processing (Op).

In many plants continuous processing is more economical for larger production items. Here the pressure and temperature of the autoclave cycles are reproduced in a series of pipes and vessels. The continuous process favors uniformity of large-scale products, whereas the batch process favors flexibility among several products. Nylon is also a popular plastic molding powder and usable material. Like all other synthetic fibers that have become competitively popular, nylon in both the filament and staple form must have certain properties that are superior to natural fibers. It is stronger than any natural fiber and has a wet strength of 80 to 90% of its dry strength. Its good flexing qualities make it very desirable for women's hosiery, and it has good stretch recovery. Nylon's high tenacity has made it important in parachute fabrics and related nonapparel items. Nylon can be dyed by all acid and dispersed dyes (acetate). It has a low affinity for direct cotton, sulfur, and vat dyes.

NYLON 6' or nylon caprolactam, is based on a polymeric fiber from only one constituent, caprolactam (Fig. 35.2). $\text{HN}-(\text{CH}_2)_5\text{CO}-\text{NH}-$. Nylon 6 had a U.S. production of about 600 million lb in 1974, or about 43% of nylon 66. Nylon 6 is widely used in Europe and Japan. It possesses an expanding market for molding resins as well as for fibers. Most processes start only with lower-cost caprolactam⁹ (Fig. 35.2) from cyclohexanoneoxime from cyclohexane from benzene.

Other nylons have been prepared and have some interesting properties. Of these only nylon 610, prepared from hexamethylenediamine and sebacic acid, is produced commercially. Nylon 4 (from pyrrolidone) has received much publicity but has no commercial significance. Nylon 7 (7-aminopentanoic acid), nylon 8 (capryllactam), and nylon 9 (9-aminononanoic acid) are only laboratory products.

POLYESTERS

An important example of a polyester is polyethylene terephthalate,⁹ the condensation product of dimethyl terephthalate or terephthalic acid and ethylene glycol (Fig. 35.5). Terephthalic acid is made by oxidation from *p*-xylene in the presence of nitric acid or air. It is then esterified with methanol. About 0.6 lb of glycol and 1 lb of ester are added to the transesterification reactor for each pound of polyester. The polymerization is carried out at 260 to 300°C, using a vacuum. The reaction releases methanol and glycol, and a polymer chain containing approximately 80 benzene rings is formed. After filtering, the material is melt-spun in a manner similar to that described for nylon. The filaments are stretched, with the application of heat, to about three to six times their original length. Table 35.2 shows some of the interesting properties of this fiber: resilience, strength, and crease recovery. It is particularly well suited for woven fabrics such as men's summer suits, men's shirts, and women's dresses and blouses, and for knitwear for sweaters and shirts. Because of its strength, this polyester is important in the tire-cord and cordage fields; it is also used for sewing thread, fire hose, and V belts. In staple form it is employed as stuffing for pillows, sleeping bags, and comforters. Its production in 1974 approached 3 billion lb.

⁹Nylon, Nylon 6 and Related Polymers, *Ind. Eng. Chem.*, 58(10), 827 (1961); Caprolactam, *Chem. Rev.*, June 6, 1962, p. 74, and Mar. 14, 1964, p. 57 (outline of process).
 Nylon Processes Add Flavor and Caprolactam Press, *Chem. Eng. (N.Y.)*, 68(6), 92 (1961); Flowchart, *Chem. Eng. News*, Aug. 28, 1967, p. 82; Caprolactam, *Chem. Eng. (N.Y.)*, 81(6), 54 (1974).
 Sigmonander, *Polyester Fibers*, ECT, 1st ed., vol. 13, pp. 841-847, 1954 (41 ref.); Terephthalic Route, *Chem. Rev.*, Mar. 9, 1964, p. 57; Brown and Reinhart, *Polyester Fibers*, *Science* 173(3994), 287 (1971).

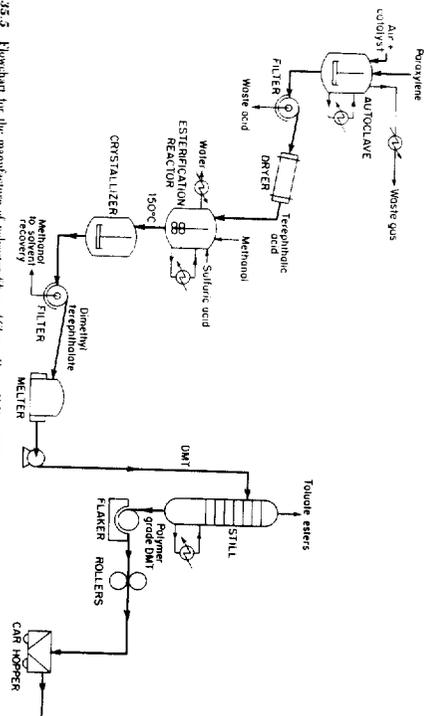
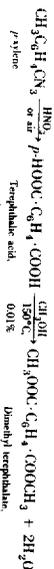


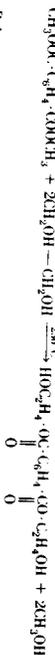
Fig. 35.5. Flowchart for the manufacture of polyester fibers. [Keram. Eng. (N.Y.), 70(5), 76 (1963).]

It is manufactured from ethylene glycol and terephthalic acid or dimethyl terephthalate¹⁰ and then polymerized.

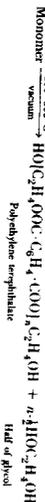
Dimethyl terephthalate:



The dimethyl terephthalate is purified by distillation and then subjected to alcoholysis with ethylene glycol to yield the monomer



Polymerization of the monomer:



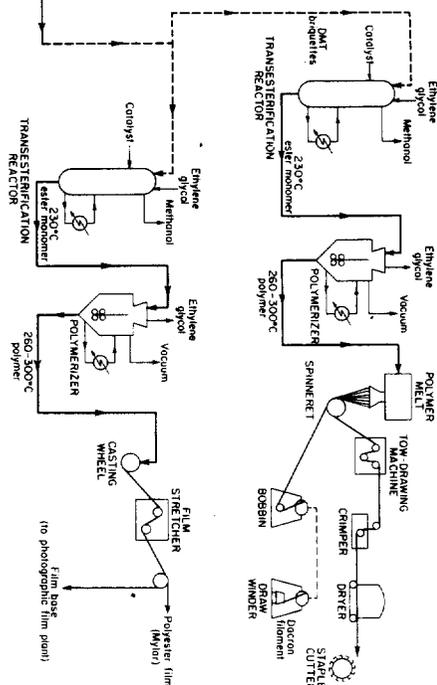
The polymer melt can be spun and stretched for polyester fiber, or cast on a wheel to form polyester film. Figure 35.5 is a flowchart of the entire process.¹¹

One of the big disadvantages of polyester fiber has been its great attraction for oily soil and its moisture repellency. A new process to graft acrylic acid chemically to the polyester surface and thus provide permanent wettability and soil release has been announced. An electrical discharge in argon gas is used to effect the grafting.¹²

¹⁰J. Polym. Chem. Eng. (N.Y.), 81(22), 114 (1974).

¹¹Quackenbush, Single Chemicals, Take. Hercules Report to DuPont, Chem. Eng. (N.Y.), 70(5), 76 (1963) (flowchart and description); Mitsubishi Pure Terephthalic Acid, Chem. Eng. (N.Y.), 72(9), 70 (1965) (toluene-benzene-terephthalate, flowchart); Japanese Firm Banks on Toluene Report to T. Chem. Eng. News, Aug. 10, 1965, p. 38.

¹²Schubert, Korte to a New Polyester, Text. Ind. (London), March, 1975, p. 91.



ACRYLICS AND MODACRYLICS

Polyacrylonitrile ($-\text{CH}_2\text{CHCN}-$)_n is the major component of several industrial textile fibers, but Du Pont's Orlon is the first to attain commercial-scale operation. Dyeable acrylics are generally copolymers with modifying constituents.

Orlon is made by polymerizing acrylonitrile, although it can be dissolved in many concentrated solutions of salts, like lithium bromide or sodium sulfolcarbate, or more successfully in other organic solvents, such as dimethylacetamide and tetramethylene cyclic sulfone. The solution is filtered and then dry-spun, utilizing the same spinning technique long used for acetate, namely, in solution through spinnerets, with the solvent evaporated to furnish the dry fiber. Unlike nylon which is drawn at room temperature, acrylics, like polyester, are drawn at elevated temperatures in a special machine. The fibers are stretched to three to eight times their original length to orient the molecules into long parallel chains for final strength. The staple fiber has esthetic properties like those of wool. The acrylics' resistance to chemical attack, and especially to weathering, makes them highly useful in several fields. Other acrylics, like Acrilan and Creslan, are spun wet into a coagulating bath. The end uses for acrylic fibers comprise sweaters, women's coats, men's winter suiting, carpets, and blankets. Blends with wool and other synthetics are common in some end uses. Acrylics are also suitable for pile fabrics and filter cloth.

MODACRYLIC FIBERS (Modified acrylics) This is a generic name for synthetic fibers in which the fiber-forming substance is any long-chain synthetic polymer composed of less than 85% but at least 35% by weight of acrylonitrile units (Federal Trade Commission).

Dynal is the name given by Carbide and Carbon to their staple copolymer modacrylic fiber made from a resin of 40% acrylonitrile and 60% vinyl chloride. The resin is converted into staple in a continuous wet-spinning process (cf. viscose rayon). The white resin powder is dissolved in acetone, filtered, and run through a spinneret, where the fibers are formed in an aqueous spinning bath. The fiber is dried, cut, and crimped. Dynal is similar to wool in many respects and has some

CELLULOSIC FIBERS AND FILMS

HISTORICAL. Cellulosics represent a mature industry in contrast to the rapidly developing poly-fibers but are still very large in size. They were the first to be developed. In 1664, Hooke prophesied that "silk equal to, if not better than, that produced by the silk worm will be produced by mechanical means." Swan exhibited in London in 1885 nitrocellulose fabrics woven from fibers prepared by mechanical squeezing solution through fine orifices. It remained for Chardonnet, "father of the rayon industry," to establish the first commercial unit for producing artificial silk, in 1891.

RAYON AND ACETATE

The basic process of producing cuprammonium rayon was patented in 1890, and the viscose process was discovered in 1892. The first patent for the production of cellulose acetate filaments was issued in 1894. In the United States commercial production of viscose rayon began in 1910, of nitrocellulose rayon in 1920, and of cellulose acetate in 1924. By 1926 the production of the various types of rayon and acetate exceeded the consumption of silk. Viscose, cuprammonium, and acetate yarns proved superior to denitrated nitrocellulose, which was discontinued in 1934.

USES, ECONOMICS, AND RAW MATERIALS. In 1974, the U.S. production and consumption of rayon and acetate were as shown in Fig. 35.1. The 1974 world production of rayon and acetate amounted to 7,700 million lb. Percentage-wise, according to process, this was viscose, 88; acetate and cuprammonium, 12. High-tensile viscose yarn is used mainly in cords for tires, hoses, and belting. The difference in strength between ordinary and high-tensile viscose depends on the amount of orientation imparted to the fiber molecules when they are made. The hydroxyl groups in the cellulose molecules allow water absorption to take place in the fiber and are the source of low wet strength. Hydroxyl groups serve as sites for hydrogen bonding and thus in the dry state serve to hold molecules together despite strong bending, resulting in fibers which tend to maintain their dry strength well even at high temperatures. The price of rayon and acetate varies according to the size of the filaments, process of manufacture, and type of finish. Textile rayon and acetate are used primarily in women's apparel, draperies, upholstery, and blends with wool in carpets and rugs.

Up to a few decades ago, the acetate process used only cotton linters as the source of cellulose. Now the viscose process is based on sulfite and a little sulfate pulp. If sheet cellulose, the form used in viscose manufacture, is desired, the sulfate pulp, after the bleaching treatment has been completed, is blended with several other batches, passed successively through a beater and a refiner (see Manufacture of Pulp for Paper in Chap. 33), and formed into sheets on a Fourdrinier. Viscose rayon is a major consumer of sulfuric acid, caustic soda, and carbon disulfide. Titanium dioxide is used in acid, sulfuric acid, and acetone. In addition to this important consumption of basic chemicals, the fiber industry needs significant quantities of dyes and other chemicals.

The viscose and the cuprammonium processes produce a filament of regenerated cellulose, and the acetate forms a thread that is a definite chemical compound of cellulose acetate. Although each of these processes is quite different as far as details of procedure are concerned, they all follow the same general outline: solution of the cellulose through a chemical reaction, aging or ripening of the solution (peculiar to viscose), filtration and removal of air, spinning of the fiber, combining the filaments into yarn, purifying the yarn (not necessary for acetate), and finishing (bleaching, washing, oiling, and drying).

¹Manufactures lined up in one direction by stretching during spinning and drawing. See Fig. 35.8. *ibid.*, vol. 17, p. 17, 1968.

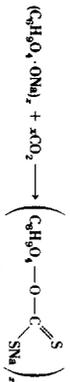
REACTIONS

Viscose, 20

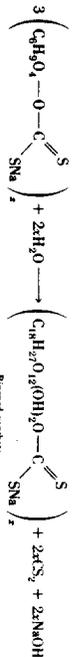


Cellulose

Alkali cellulose



Cellulose xanthate



Ripened xanthate



Viscose rayon

Cellulose acetate:



Cellulose

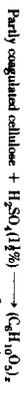
Cellulose acetate

Cuprammonium, 21



Cellulose

Schwannert's rayon



Cuprammonium rayon

VISCOSE MANUFACTURING PROCESS

The finished filament is pure cellulose, as shown by the equations but, because it consists of smaller molecules than the cellulose of the original wood pulp or cotton, it possesses different physical properties.

CHEMICAL CONVERSIONS AND UNIT OPERATIONS. The process, 22 as shown in Fig. 35.8, can be broken down into the following sequences:

The cellulose raw material (sheets made from sulfite or sulfate wood pulp) is charged to a steeping press containing vertical perforated steel plates and is steeped either batchwise or continuously in a caustic soda solution (17 to 20%) for about 1 h at 56 to 62°F (13) to dissolve α -cellulose:

²⁰The cellulose molecule is composed of a large undetermined number of glucose units, here represented as $(C_6H_9O_2OH)_x$. The value of x does not remain constant throughout these reactions. Each reaction causes a reduction in the molecular weight of the cellulose molecule, so that the viscose-rayon molecule is considerably smaller than the original cellulose. Some CS_2 breaks away from the cellulose xanthate during the ripening process.

²¹The cuprammonium process with a flow diagram was described in Ch 2, pp. 733f. *ibid.*, vol. 17, p. 704, 1968. Production of this filament is minor at the present time.

²²Burkholder and Suggan, Rayon's Latest Push into Fibers, *Chem. Eng.* (N.Y.), 71(14), 110 (1965); Cellulose and Viscose Rayon, *Chem. Metall. Eng.*, 46, 25 (1959); Continuous Rayon Spinning Process, *Chem. Eng.* (N.Y.), 54(11), 103 (1947); Mendenhall, *op. cit.*, Chap. 9.

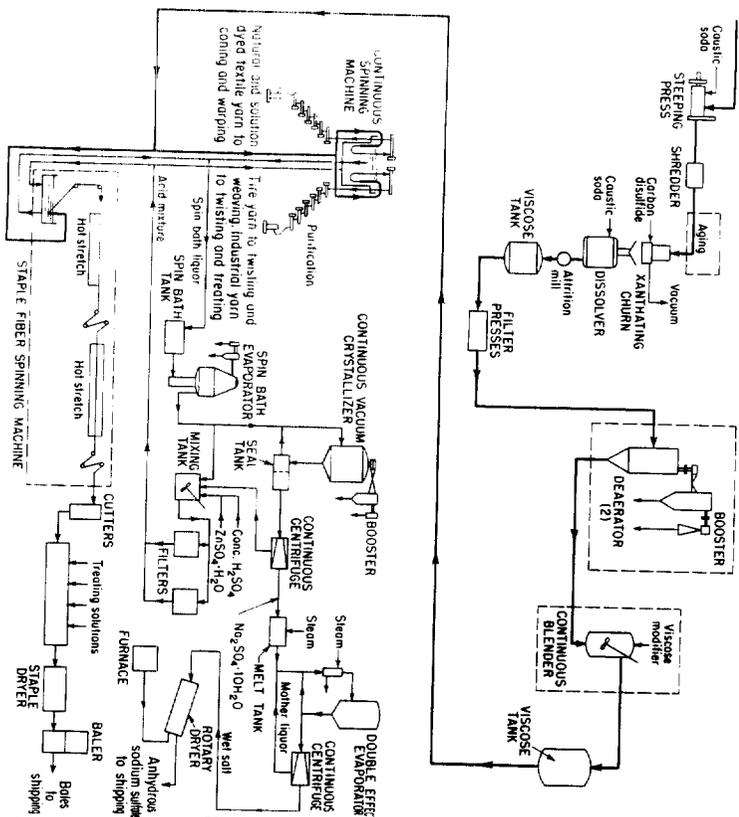


Fig. 35.8 Kautsch's latest push-line fibers. (Chem. Eng. (N.Y.), 71(14), 110 (1954).)

The excess liquor is drained off, thus removing impurities such as cellulose degradation products.²³ The soft sheets of alkali cellulose are reduced to small crumbs in a shredder (Op). This requires 2 to 3 h, and the temperature is maintained at 65 to 68°F.

The crumbs of alkali cellulose are aged either batchwise or continuously for 24 to 48 h at 75°F in large steel cans. Some oxidation and degradation²⁴ occur, although the actual chemical change is unknown (31). Physically, correct aging produces a solution after xanthation of correct viscosity for spinning.

The aged crumbs are dropped into large, cylindrical xanthating churns. Carbon disulfide weighing between 30 to 40% of the dry recoverable cellulose is slowly added under carefully controlled conditions.²⁵ See Lepert, *Industrial Wastes*, chap. 4, Atlas, 1951, for chemical waste recovery in the viscose rayon industry. The Washell²⁶ process is included.

²⁴ Lewis, Squares, and Broughton, *Industrial Chemistry of Cellulose and Amorphous Materials*, pp. 860ff., Macmillan, 1942.

temperature and reduced pressure over 2 h of churning, during which time the crumbs gradually turn yellow and finally deep orange, and coagulate into small balls (Ch):



Still in batch form, the cellulose xanthate balls are dropped into a jacketed dissolver (viscose) containing dilute sodium hydroxide. The xanthate particles dissolve in the caustic, and the final product, viscose solution, contains 6 to 8% cellulose xanthate and 6 to 7% sodium hydroxide (Ch).

This reaction takes 2 to 3 h. If desired, delustering agents such as titanium dioxide or organic pigments²⁷ are added to the viscose solution in the mixer. The result is a sticky, golden-brown, viscous liquid. From here on this description (Fig. 35.8) through ripening and spinning is continuous (Ch).

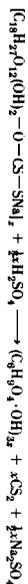
During the ripening chemical reaction



the proportion of combined sulfur decreases and the ease of coagulation increases (Ch). Thirty years ago, this conversion took 4 to 5 days; now improved technology has reduced it to about 24 h. In a series of tanks (only one is shown in Fig. 35.8), the reaction proceeds under deaeration and continuous blending with modifiers (viscose additives, mainly amines and ethylene oxide polymers) that control neutralization and regeneration rates (Ch).

Finally, in two continuous vacuum-flash boiling deaerators (at high vacuum and below room temperature), small air bubbles are removed that would either weaken the final yarn or cause breaks during spinning (Op).

Spinning is effected when thin streams of viscose from 750 to 2,000 holes in each thinlike spinneret are injected under gear-pump pressure into the spin bath; they coagulate, and the cellulose is regenerated (Ch) to form fiber:



Sulfuric acid in the spinning bath neutralizes free NaOH and decomposes xanthate as shown, and various viscous by-products containing sulfur, liberating S_2 , H_2S , CO_2 , and S . Salts such as $ZnSO_4$ and Na_2SO_4 coagulate the xanthate, forming relatively stable metal complexes. The sulfuric acid/salts ratio is a key control point, which, although coagulation and regeneration take place together, ensures that the xanthate gels before the acid can attack and decompose it. Four percent or more glucose prevents crystallization of salts in the filaments (Ch).

In Fig. 35.8 three separate continuous spinning and treating procedures are outlined for the coagulated filaments:

1. *Textile yarns* are twisted into continuous yarn as the filaments leave the spinneret. They are dyed (then or later) and sent to coning and warping (Op).
 2. *Tire yarns* are stretched to impart strength over a series of thread-advancing reels where wash and other treatments are applied (desulfurizing, desulfurizing (Na_2S), and bleaching (Op and Ch)).
 3. *Staple yarns* are spun on the machine in the lower part of Fig. 35.8 by combining filaments from many spinnerets without twisting and cutting them into uniform lengths. Each year more viscose filaments are made into staple fiber.
- The actual process of continuous spinning has reduced the time elapsed from hours to minutes. Three types of spinning are in general use: continuous, bucket, and bobbin. Three-quarters of United States production is from the long-used bucket type (Fig. 35.9).

²⁷ Finckel Recovery Nibs CS_2 , *Chem. Eng. (N.Y.)*, 70(6), 92 (1953).

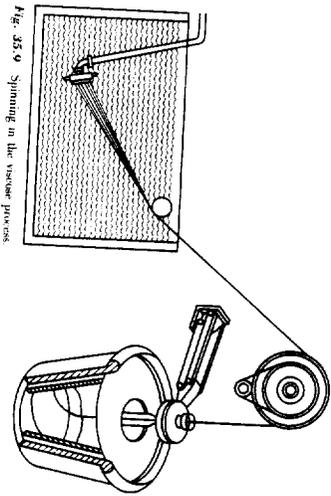


Fig. 35.9 Spinning in the viscose process.

The solution is extruded under pressure (gear pumps are used) through the spinneret into the spinning bath (Op), as described for the continuous process shown in Fig. 35.9. However, see Fig. 35.9 for general cogulation spinning.

The spinnerets are small cups of noble metal, containing minute holes through which the solution is extruded, as depicted in Fig. 35.9. Just ahead of the spinneret are the "randle filters" to remove, in a final filtration, any foreign matter that might clog the holes.

If a bucket machine is used, the spinneret head dips horizontally into the spinning solution, spinning at about 7,500 rpm (Op). This is illustrated by Figs. 35.9. The bucket imparts one twist per revolution and removes a greater portion of the occluded bath liquor through perforations in the periphery.

If a bobbin machine is used, the spinnerets point vertically upward into the spinning bath, and the filaments are wound on a revolving bobbin (Op). No twist is imparted to the thread. Yarn from either type is washed to remove the spinning liquor (Op) and disulfurized by treating with a 3 to 1% sodium sulfide solution (Ch).

Both types are washed (Op), bleached in hypochlorite solution (Ch), washed again, dried, and coated (Op).

PACKAGING FILMS Transparent viscose sheeting (cellophane) is manufactured from a solution similar to that used for rayon.²⁷ The spinning solution is extruded through a narrow slot into the cogulating bath and cast as a sheet onto a rotating drum, the lower side of which is submerged in the bath. The viscose film formed is transferred to succeeding tanks of warm water to remove the impurities. It is desulfurized in a basic solution of sodium sulfide and re-washed. The characteristic yellow tinge must then be removed in a hypochlorite bleach bath, after which the sheet is re-washed in order to impart softness and pliability, the film is passed through a glycerin bath, where it absorbs about 17% glycerin, after which it is dried. Much cellophane is subsequently made moistureproof by coating it on one side with a suitable nitrocellulose lacquer. (March of the Du Pont Co. was awarded the 1932 Schokopf Medal of the Buffalo Section of the American Chemical Society for this achievement.) Cellophane is widely used as a packaging and wrapping material. Viscose may be employed

²⁷Grade films are a thin roll of metal screen wrapped with fiber cloth.
²⁸Rankop and Van Horn, *Cellophane, Ind. Eng. Chem.*, 44, 2511 (1952) (many details, flowcharts, pictures, and references);
 Hydrex, *Manufacture and Properties of Regenerated Cellulose Films, Ind. Eng. Chem.*, 21, 1065 (1929).

to prepare a durable *cellulose sponge* by introducing a mixture of various sizes of Chaubert's salt crystals, hemp or fibrous material, and viscose into a box which is placed in a cogulating bath to regenerate the cellulose. The blocks are then leached with warm water to remove the crystals of salt, and cut into small-sized blocks for sale.

CELLULOSE ACETATE MANUFACTURING PROCESS

Cellulose acetate (and its homologs) are esters of cellulose and not regenerated cellulose. The spinning solution may be used to produce fibers, transparent film, or photographic film, or precipitated to form molding powder for plastics and the basic constituent of cellulose lacquers.²⁸

UNIT OPERATIONS AND CHEMICAL CONVERSIONS (Fig. 35.10) The raw material for the spinning solution is prepared by charging 100 lb of acetic anhydride, 100 lb of glacial acetic acid, and a small quantity of sulfuric acid as a catalyst to a jacketed, glass-lined, agitated, cast-iron acetylator (Op). The mixture is cooled to 45°F, and 35 lb of wood pulp is added slowly. The acetylation requires 5 to 8 h, and the temperature is maintained below 86°F (Ch).

The viscous fluid is diluted with equal parts of concentrated acetic acid and 10% sulfuric acid and allowed to age for 15 h at 100°F. Hydration of some of the acetate groups occurs (Ch). No method has been devised at present whereby cellulose can be converted directly to a product of the desired acetyl content. It is necessary to transform it first to the triacetate and then partly hydrolyze off the required proportion of acetate groups.²⁹

The hydration is stopped by running the mixture into a large volume of water and precipitating the secondary acetate (Op). The secondary acetate is centrifuged to separate it from the still strong acetic acid which is recovered, concentrated, and used over as shown in Fig. 35.11.

The flakes are washed several times by decantation (Op) and are then ready to be used in preparing the spinning solution by dissolving the dry flakes in acetone in a closed, agitated mixer. If desired, a debustering pigment is added (Op). Several batches are blended, filtered, and sent to the spinning machine (Op). The solution is forced through the spinnerets into a current of warm, moist air (Op). The acetone evaporates and is recovered, leaving a filament of cellulose acetate (Op).

These filaments are twisted and coned in the same manner as those of the previously described rayons (cf. Fig. 35.3) (Op). Some yarns are sold without a twist. Filament yarn is made by twisting

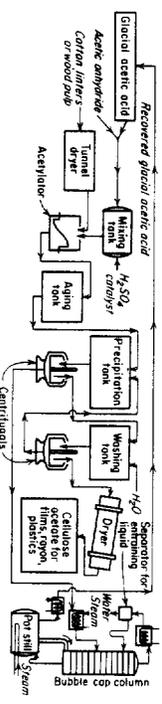


Fig. 35.10 Flowchart for cellulose acetate manufacture.

Pulp (wood pulp cotton linters)	0.70 lb
Acetic anhydride	1.00 lb
Acetic acid*	5.25 lb
Sulfuric acid	0.1 lb
Direct labor	0.04 man hrs
Acetone	0.2 lb

*Recovery is about 5 lb. per lb. of cellulose acetate.

²⁸Smith, *Cellulose Acetate Rayons, Ind. Eng. Chem.*, 32, 1555 (1940); for a pictured flowchart on cellulose acetate sponge yarn, see *Chem. Eng. (N.Y.)*, 52(1), 132 (1945).
²⁹How also the triacetate (Arnel) is dissolved and spun directly.

the threads before winding on the bobbin. Tow consists of threads gathered without twisting and is cut into short lengths for use as staple fibers.

The economical operation of the process depends on the recovery of as many of the chemicals as possible. For every pound of cellulose acetate about 4 lb of 30 to 35% aqueous acetic acid is obtained. Dilute acetic acid from various parts of the process is run through a Dorr Thickener to remove the last traces of acetate and then concentrated in a distilling unit and recovered to acetic anhydride. The acetone-laden air from the spinning machines, for example, may be passed through activated charcoal to absorb the solvent (which is subsequently recovered by steaming and rectification) or by cooling the air in water towers and simultaneously dissolving out the acetone, the water-acetone mixture subsequently being rectified. Liquid absorption and distillation are also employed.

The manufacture of transparent cellulose acetate sheeting comparable with cellophane (Viscose sheeting) is carried out by extruding an acetate "dope" of the required properties through a narrow slit onto a rotating drum, where, in the presence of warm air, the acetone solvent evaporates. The resulting sheet is pliable and moistureproof.

Cellulose triacetate fiber, Arnel, is spun and sold by Celanese Corp. It is reported to possess "resistance to glazing at high ironing temperatures, complete machine washability, low shrinkage in stretching, good crease and pleat retention, and an adaptability to a wide range of colors, designs and prints."³⁰ It is reported to be considerably superior to normal acetate in fiber properties and uniformity. The tricky part is to manufacture pure triacetate and then to dissolve it prior to spinning. The catalyst employed here is perchloric acid (versus sulfuric for ordinary acetate).

FINISHING AND DYEING OF TEXTILES

The textile industry, with sales of over \$30 billion in 1976 is second in size to the food industry, and many of its mill operations abound in chemical-engineering problems.³¹ Dyeing,³² bleaching, printing, special finishing, such as for crease recovery, dimensional stability, resistance to microbiological attack and to ultraviolet light, and flame resistance; scouring; water treatment; and waste disposal are outstanding examples of mill treatments where such unit operations as filtering, heating, cooling, evaporation, and mixing are involved. Some mill operations are discussed in a general manner elsewhere, e.g., under water treatment and waste disposal in Chap. 3, but here brief mention is given to the use of special finishing agents. Textile processors and finishers spend over \$1 billion for chemicals and dyes in each year.

The modification of fibers and fabrics by special treatments to change their properties and to improve their usefulness is increasing yearly. Three important finishes consist of *flameproofing*, or fire-retarding, *mildew*, or *rotproofing*, and *water repellency*. These are by no means the only lines of treatment. Temporary flameproofing of cellulose fibers is achieved by the application of ammonium salts or borax and boric acid. Ideal fabric flameproofing, which allows cleaning or laundering and yet maintains desirable fabric characteristics is yet to be achieved, although much research is directed toward this aim and some processes are finding commercial acceptance. Mildewproofing of cellulosic fabrics may be obtained by the use of many organic and inorganic compounds. Commonly used

³⁰Greene *et al.*, *Fibers*, *Ind. Eng. Chem.*, **47**, 1973 (1955); *Merrett*, *op. cit.*, Chap. 12.

³¹Chemical Engineering in the Textile Industry, *Chem. Eng. Prog.* (N.Y.), **55**(6), 122 (1959).

³²Boer, *Color Rules Synthetic Fibers*, *Chem. Abstr.*, **64**(1973), 19611, Manly, *Textile Press Treatments of Fibers*, Noves, 1976; *Silard, Bleaching Agents and Textiles*, *Chem. Abstr.*, **64**(1973), 19611, Manly, *Textile Press Treatments of Fibers*, Noves, 1976; *Silard, Bleaching Agents and Textiles*, *Chem. Abstr.*, **64**(1973), 19611, Manly, *Textile Press Treatments of Fibers*, Noves, 1976; *Silard, Bleaching Agents and Textiles*, *Chem. Abstr.*, **64**(1973), 19611, Manly, *Textile Press Treatments of Fibers*, Noves, 1976.

³³Smith, *Log of Textile Auxiliaries*, *Chem. Eng. News*, **29**, 548 (1951); *Chemical Processing*, *Chem. Eng. News*, **30**, 4153 (1952); *Jabson, Analytical Compositions for Textiles and J. Text. Inst.*, **1976**, *Carper, Nonwoven Textiles*, Noves, 1975.

³⁴Jullie, *Flameproofing Textile Fibers*, Reinhold, 1947; *Stimpson, Flame Retarding of Textiles*, *Ind. Eng. Chem.*, **42**, 414 (1950); *Plane Resistant Textiles*, *Chemist*, August 1970, p. 300; *Textile Makers' Special Finishing Research*, *Chem. Eng. News*, Mar. 30, 1970, p. 34.

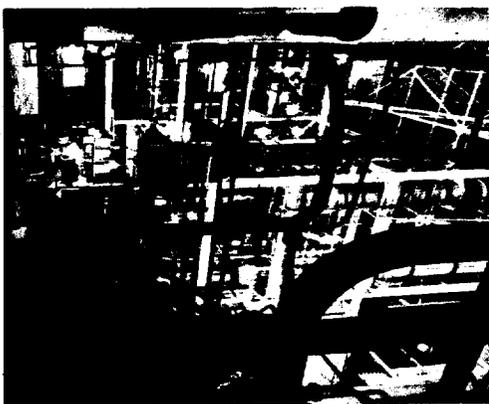


Fig. 35.11 The manufacture of acetic anhydride and the recovery of acetic acid; important stages in the manufacture of acetate rayon, take place in these towering columns and silos at the Weymouth, Va., plant of E. I. du Pont.

materials include acrylonitrile, chlorinated phenols, salicylanilide and organic mercurial compounds, copper ammonium fluoride, and copper ammonium carbonate. To produce water-repellent finishes durable to the usual cleaning processes, special quaternary ammonium compounds are heat-treated on the fiber. Shrinkproofing of wool employs various chlorinating processes, especially for socks, shirts, knitting yarns, and blankets. Another method for shrinkproofing woven fabrics is to coat them with a melamine formaldehyde product. Thermosetting resins are being widely used to impart crease or wrinkle resistance to cellulosic fibers. Commonly used products include urea-formaldehyde and melamine-formaldehyde resins. The fabric is treated with water-soluble precondensates, together with a condensation catalyst. The treated fabric is dried and heated at an elevated temperature to develop the resin within the fiber structure. Many other special treatments for fabrics include mothproofing; improving of resiliency; stiffening; softening; eliminating electrostatic charge during processing; staining; lubricating; and inhibiting atmospheric gas fading. In recent years chemical finishes have actually been used to react with the fiber material, e.g., cotton, and thereby to change its properties by esterification (carboxymethylation) or amination (2-aminoethylsulfuric acid).

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Chapter 36

RUBBER INDUSTRIES

Rubber has become a material of tremendous economic and strategic importance and is an excellent barometer of the industrialization of nations. In the United States, the per capita consumption of rubber is approximately 34 lb per person; in India it is scarcely 1 lb per person. Transportation, the chemical, electrical, and electronic industries, and the space effort are all major consumers of rubber. When supplies of natural rubber were shut off because of Japan's invasion of rubber-producing areas early in World War II, the United States built up a synthetic rubber industry which has continued to expand enormously, so that at the present time 70% of the rubber consumed in the United States is of synthetic origin. The rubber industry involves the production of monomers or raw materials for natural and synthetic rubbers, the various rubbers themselves, the importation of natural rubber, the production of rubber chemicals, and finally the fabrication of rubber products.

HISTORICAL. Columbus found the natives of the West Indies playing games with rubber balls. Rubber articles have been recovered from the sacred well of the Maya in Yucatan. Rubber, as we know it, is a product of the Americas but has achieved its greatest growth by transplantation to the Far East. The name "rubber" was apparently given by Priestley; the discoverer of oxygen, who first observed the ability of the material to "rub out" a pencil mark. The fact that rubberlike materials resulted from mere efforts to purify and keep such materials as styrene, butadiene, and the isoprene produced from the destructive distillation of natural rubber very early led to attempts to produce synthetic rubber. By the outbreak of World War I, inferior grades of rubber were being produced from dimethylbutadiene in Germany and in the U.S.S.R. Extensive research during the 1920-1930 period led to discovery of the emulsion copolymerization of butadiene and styrene, and of butadiene and acrylonitrile.

Goodyear is credited with the discovery of the cure, or vulcanization, of rubber with sulfur in 1839. This overcame the natural tackiness of rubber and commercialized it. Since then it has been found that many substances affect the rate of this reaction and that some subsidiary materials modify or improve the compound, making it possible to shape or fabricate an article which is then fixed into its final form by the curing reaction. The historical occurrence of most significance was the curtailment of natural rubber importation caused by Japanese invasions in 1941. This stimulated greatly both research and manufacture of various synthetic rubbers in the years following.

STATISTICS AND ECONOMICS

The cost of natural rubber has been subject to great fluctuations over the years. The price stability of the synthetics has undoubtedly contributed to their successful invasion of the market. Table 36.1 shows the consumption of various rubbers in the United States over a 22-year period, and it is clearly seen that natural rubber is being supplemented, but not supplanted, by synthetics, and that the world would be hard-pressed to exist with natural rubber as the only source of supply.