RAYON MANUFACTURE BY THE VISCOSE PROCESS[1]

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The first printed record referring to artificial silk or rayon is attributed to Dr. Robert Hooke, an eminent British scientist in "Micrographia" a copy of which is in the Rylands Library, Manchester, dated 1664. Many consider this the first conception of the artificial or mechanical production of silky filaments, similar to production of natural silk by silk worms. He is also credited with the prophetic statement: "I need not mention the use of such an invention nor the benefit that is likely to accrue to the finder."

Rene' A. F. Réaumur, a French naturalist and physicist, in his "L' Histoire des Insects," recorded in 1710 the possibility of making "artificial silk" as follows:

> Silk is only a liquid gum which has been dried; could we not make silk ourselves with gums and resins? This idea which would appear at first sight fancied, is more promising when examined more closely. It has already been proved that it is possible to make varnishes that possess the essential qualities of silk. China and similar varnishes are unaffected by solvents, water has no effect on them, the greatest degree of heat to which our fabrics are exposed could not change them. If we had threads of varnish we could make them into fabrics which by their brilliancy and strength, would imitate those of silk, and which would equal them in value, for good varnishes when properly dried have no smell. But how can we draw out these varnishes into threads? We cannot, perhaps, hope to draw out these threads as fine as those obtained from silk, but this degree of fineness is unnecessary, and it does not seem impossible either to spin them as fine as natural silk, when we consider to what extent art may be carried.

In spite of these predictions more than a century passed before reduction to practice through experimentation occurred. About 1840 Louis Schwabe of Manchester, England experimented with substances which could be drawn out through fine holes into filaments. With his suicide, efforts in this direction were temporarily discontinued. George Audemars, a chemist of Lusanne, Switzerland was one of the early experimenters with nitrocellulose and took out a patent in 1855 for transforming dissolved nitro-cellulose into fine threads, which he called "artificial silk." Ozonam is credited with the idea of forcing nitrocellulose solutions through fine orifices in 1862. This is the second mention of such a procedure but is more specific than the first. Sir Joseph W. Swan, a co-worker of Edison, made filaments by extruding collodion through fine orifices into a coagulating bath, denitrated them to remove inflammability, and exhibited some fabrics in London in 1885, which were designated as "artificial silk." He is considered the real inventor of the first man-made fibre. Count

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[1]Presented before the Chemistry Section of the Tennessee Academy of Science at the Johnson City meeting on December 8, 1950.

Chardonnet, a pupil of Pasteur, obtained his first French patent November 11, 1884. He is considered the "Father of the Rayon Industry." He exhibited the product at the great Paris Exhibition in 1889 after which plants were constructed in France, Belgium and in the United States at Hopewell, Virginia in 1920.

In the meantime the cuprammonium process was being developed. Schweitzer discovered that cellulose could be dissolved in alkaline copper reagent in 1857. The first alternative method, the cuprammonium process was announced by a French Chemist L. H. Despaissis in 1890. Germany then entered the field and made many technical contributions between 1891 and 1895. The first plant was constructed in Elberfeld, Germany in 1898 and a second in Oberbruch in 1899. This process was soon abandoned by the Germans. However, Dr. Elsaesser developed the cuprammonium-stretch-spinning process which made it possible, for the first time, to produce filaments finer than those of natural silk and by 1918 make the process commercially profitable. In 1925 the American Bemberg Corporation was organized and the Elizabethton plant constructed and has been producing ever since.

The third process to come into commercial operation and is today the largest in production of all the rayon processes is the viscose process. This process I shall describe to you somewhat more fully than the others. In 1891 Cross and Bevan discovered the underlying reaction which led to the development of the viscose process. The product of this reaction is alkali-cellulose-xanthate, or commonly called "xanthate." The patent covering the process was granted to these Englishmen the following year, 1892. In 1899 the Viscose Development Company was organized. The following are some examples of the applications: Carbonized viscose threads for incandescent lamp manufacture by Zurich Lamp Company; finish for linen fabrics in Ireland; finish for curtain fabrics, doorhandles, and valve wheels in England and cellulose films in France. It was also tried as a paper size and for artificial leather.

The first viscose textile yarn was exhibited in Paris in 1900 after the aging of the viscose solution was discovered accidentally. A partial solution to the spinning difficulties was effected by Topham in 1902 when centrifugal or "pot" spinning was discovered. This invention provides for the introduction of a spinning end of yarn into a hollow, revolving cylinder which introducted twist in the yarn and the centrifugal force lays the yarn against the side of the cylinder forming a "cake." Development was rapid from this point and soon this was the leading process. Courtoulds and Company, Ltd. took over the British rights and began operations in 1904, together with Vereinigte Glanzstoff Fabriken, A. G., and a group of French, Belgian and Swiss manufacturers. The greatest contributing factor to the rapid growth of the viscose process is the low cost of manufacturing, together with the fact that there is no expensive and troublesome recovery process involved.

In 1910 the American Viscose Company was established and the first American viscose plant constructed at Marcus Hook, Pennsylvania. This company is the biggest rayon producer in the world today. Other large American viscose yarn producers in diminishing order are: duPont, Industrial, Enka and North American. In all there are thirteen viscose rayon manufacturers in the United States.

A fourth process, the acetate process, was developed almost simultaneously with the viscose process, and there is some disagreement as to which came first. Cellulose-acetate as a chemical had been prepared in 1865 by Naudin and Schutzenberger. In 1894 it was discovered that zinc chloride or sulfuric acid catalyzed this reaction. In 1899 the first cellulose acetate filaments were produced by Bronnert at Mulhouse, Germany, but he made no use of it. The first successful cellulose-acetate rayon was produced in the United States. Eichengruen announced the first dry-spinning process for acetate rayon yarns in 1904. A cellulose acetate "dope" plant was built at Cumberland, Maryland, in 1918 and the product used by the government for coating of air-plane wings. In 1924 cellulose-acetate yarns were produced commercially under the trade name "Celanese." Today cellulose-acetate yarn production ranks second in volume of production in the United States.

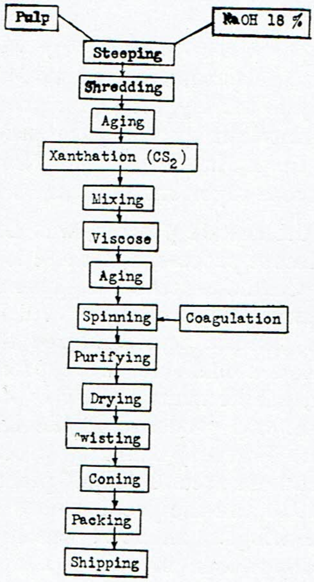
All four of these processes have one thing in common. They all use cellulose as a base and regenerated cellulose can be obtained as the final product. The three processes in use today are in operation in Northeast Tennessee; the acetate process at Kingsport, and the cuprammonium, and viscose processes in Elizabethton. In recent years a number of non-cellulosic materials have come into prominence as filament forming materials—notably nylon, orlon, vinyon and others.

The Viscose Process

Raw Materials. The principal raw materials in the viscose process for manufacturing rayon are: pulp (cotton or wood), sodium hydroxide, carbon disulfide, and sulfuric acid.

Pulp. Chemical pulps are derived from two principal sources: (1) cotton pulp from linters or hull fibers, (2) woodpulps, (a) soft woods as hemlock, spruce, fir and pine and (b) hardwoods as, beech, birch and maple. The pulps may be prepared by one of several methods commonly called the soda, sulfite and sulfate processes. The pulp is formed into sheets of appropriate size to be used in the steeping process. The sheets are placed in the steeping press and sodium hydroxide of approximately 18 percent admitted to the press at about 25° C. and the pulp allowed to steep for approximately one hour. The sodium hydroxide solution is drained off and the excess

Flow Sheet



liquor pressed out until the weight of the resulting alkali cellulose possesses a wet:dry press weight ratio of about 3:1 when the composition of the alkali cellulose is approximately 31 percent cellulose and 15 percent sodium hydroxide. The resulting product, now known as alkali-cellulose, is placed in a water cooled shredder maintained at approximately 30° C. while the swollen sheets are reduced to "crumbs." The crumbs are then aged in a closed vessel at about 30° C. for about 24 hours to effect the desired viscose viscosity. The aging temperature and time are important for viscosity control.

At the end of the aging period the alkali-cellulose "crumbs" are placed in a baratte or churn which can be rotated at a slow rate of speed, sealed, and carbon disulfide added to the extent of about 33 percent, based on the alpha cellulose content of the crumbs. The temperature is controlled by circulating water in the jacket of the baratte. About two hours are required for completion of this reaction $(C_6H_{10}O_5)_x + NaOH + CS_2 = \text{Cell-O-}\overset{\overset{S}{\|}}{C}\text{-SNa} + H_2O$ in which the main product is sodium-cellulose xanthate. As the reaction proceeds the color of the product changes progressively from white through various stages of yellow to orange. The ester, commonly called xanthate, is then charged into a mixer which contains an alkaline solution in which the xanthate dissolves forming a viscous solution of about the consistency of molasses and having a composition of about 7.5 percent cellulose and 6.5 percent sodium hydroxide. After filteration, deaeration, and aging the viscose solution is ready for spinning.

The viscose is then forced through small orifices 0.075 mm. (0.003") into a coagulating bath consisting of sulfuric acid, sodium sulfate, a product of the reaction between sodium hydroxide in the viscose and sulfuric acid of the coagulating bath, and other modifying agents as glucose, zinc and/or magnesium sulfate. The viscose is coagulated into filaments and is partially regenerated. Complete regeneration is effected by subsequent treatment, during which the excess sulfuric acid and salts are removed, carbon disulfide released and the cellulose regenerated in practically pure form. After the final purification step and before drying a lubricant is applied, usually an oil emulsion which may contain gelatin, to facilitate twisting or subsequent handling.

Continuous filament yarns are prepared for shipment in the form of cones, skeins, cakes, or beams, depending upon the ultimate use of the yarn.

Summary

Brief historical backgrounds have been presented for the four well known rayon processes using cellulose as the basic material, namely, the nitrate, cuprammonium, acetate, and viscose processes, with particular emphasis on the viscose process.[2]

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[2]Photographs were displayed of the various steps in the process, samples of raw materials used in the process were displayed, and a demonstration was given of the coagulation of a viscose film and a display of fabrics representing a variety of uses, including tire cord, was presented.

NEWS OF TENNESSEE SCIENCE

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The annual initiation and lecture, Vanderbilt Chapter, Society of the Sigma XI, was held on April 19. The lecturer for the occasion was Dr. George Gamow, Professor of Theoretical Physics in George Washington University, who spoke on "The origin and evolution of the Universe."

At the University of Tennessee, the seminar in the Department of Zoology and Entomology was addressed on March 27 by Mrs. Nyra C. Harrington, Oak Ridge National Laboratory, who spoke on "Quantitative cytochemical determinations by the photometric methods." On April 10, Dr. Louis A. Krumholz, Tennessee Valley Authority, Oak Ridge, spoke on "Studies in the dynamics of fresh-water fish populations."

Dr. Willis King, chief fish biologist for the Tennessee Fish and Game Commission, has resigned to become Chief of Fisheries Management for the U. S. Fish and Wildlife Service, in Washington, D. C. He will be in charge of fresh-water sport fishing development on federal lands and will serve as coordinator of this program with state developments.

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