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- Scope of Report: This report is a general survey of the manmade fiber phase of industrial chemistry from its beginning in the seventeenth century up to the present time. It includes a short summary of the history involved, and the major donations of its founders. The main portion of the report is taken up in the discussion of the general synthesis, structure, and properties of fiber forming molecules, and the review of the methods of production and other characteristics of some of the major man-made fibers found on the commercial market The economic, social, and future aspects of this today. relatively new industry are also covered in this paper. The technical aspects are not so involved that they cannot be comprehended by the person with a basic knowledge of elementary chemistry.
- Findings and Conclusions: The scientific research and ultimate end products contributed to this new industry by such men as Schoenbein, Chardonnet, and Carothers, will certainly go down in history among the greatest accomplishments of science during this era of civilization. The production of fibers from petroleum, milk, wood, seaweed, and other such raw materials illustrates man's ability to cope with his environment and to better his way of life. The ability of man to produce fiber forming molecules into which many special properties may be incorporated makes the future promises of this great industry almost unbelievable. The story of man-made fibers is only one of the many examples that could be used to illustrate the betterment of man through the miracles of science.

Maiseurtelle ADVISOR'S APPROVAL

MAN AND MAN-MADE FIBERS

Ву

JOHN SIDNEY HINES Bachelor of Science East Texas State College Commerce, Texas 1958

Submitted to the faculty of the Graduate School of the Oklahoma State University in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE May, 1961 MAN AND MAN-MADE FIBERS

Report Approved:

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CHAPTER I

INTRODUCTION

In order to provide our nation with better educated men and women, methods and materials for education in public and private schools, colleges, and universities in the United States are now in a definite state of change. Although all branches of the school system are being affected by this revolution, the main points of change involve subject matter with respect to its level and method of presentation. A very important step forward in this direction is the addition to the secondary school curriculum of advanced courses in science, mathematics, and other fields for presentation to the betterthan-average students.

Although these relatively new type courses appear in many different areas of subject matter and under many different names, they are all designed to delve deeper into the subject matter involved and to familiarize the student with current areas of interest and research in the field being studied. Presentation of such material by a compotent instructor can furnish inspiration as well as knowledge to the student seeking material of interest for further study.

In order to represent as thorough a coverage as possible of the subject matter and yet carry out the idea of presenting its current and practical viewpoint, a choice of certain basic

units of this nature is left to the discretion of the instructor. The following discussion of man-made fibers is designed to cover such a unit as it might be presented to a group of students in an advanced course in chemistry or natural science being taught at the secondary school level. The subject of man-made fibers with respect to its social, economic, and technical aspects is just one of the many informative views of different phases of industrial chemistry that might be presented. The technical approach, although not deep in detail, will very definitely afford knowledge to the student which will be useful in later academic studies, and the social and economic aspects will prove to be very enlightening from a practical point of view.

Although there is a large amount of literature on this subject available to the public, most of it is of a general nature, especially that found in periodicals. This report is a survey of a new and rather large area of industrial chemistry about which several books and many articles have been written and published. Since the intention here is toward chemistry, the basic chemical aspects of the field command more attention than areas which might be classified in terms of some other technical field.

The material utilized in the writing of this paper may be found in books, abstract journals, periodicals, encyclopedias, and industrial bulletins. Because of the generallity necessary for the purpose of this report, most of the material is presented in a revised form; however, certain parts

are exactly as they are found in the original reference. The presentation of the material surveyed would seem quite basic to an expert in the field of man-made fibers, however, it is presented in such a way that it may be committed to the intelligent high school student and be of value to him.

CHAPTER II

HISTORY

The past few decades have seen a definite rise of interest and activity in the chemical industry with respect to long chain, high molecular weight carbon compounds known as organic polymers. A new chemical industry has been built around the production and research needed to develop these molecules because their basic structure permits them to be made into yarn and ultimately woven into the new miracle fabrics utilized by all of us. During 1960, over five-hundred fibers not found in nature, fibers fashioned by man from simple, relatively common products such as natural gas, milk, wood, chicken feathers, corn, and glass were in varying stages of development or production throughout the world.¹ Nearly every one of these new fibers will serve man's needs better than its natural fiber competitor because of the incorporation of new, tailor-made qualities. These qualities include, among many things, the ability to hold in heat, resist chemical attack, retain a lifetime built-in crease, last longer than most natural fibers, and combine the strength of steel with the beauty of the finest natural fabrics known to man. These fibers are

¹O. A. Battista, "Synthetic Fibers Come of Age", <u>Science</u> <u>Digest</u>, Vol. 44, (October, 1958) p. 43.

also very useful because they can be made with specific services in mind, being outstanding in many properties or in one property as desired by the consumer and producer.

The first of these artificial fibers to be produced, rayon, was visualized several centuries ago, but was not produced in any sizable volume until the early twentieth century. Although the Chinese and Egyptians made attempts to produce an artificial fiber, the first notable suggestion came from Robert Hooke, appearing in his book, Micrographia, which was published in 1664. He stated that through microscopic research on the construction of natural fibers, he had come to the conclusion that a method could be devised for the product tion of an artificial glutinous composition, such as that of the silk worm, which might be used for making fiber.² However. Hooke's idea was simply that and nothing more. Chemical technology had not at that time advanced to such a stage as to be able to develop such a process. It was not until the nineteenth century that the production of such a viscous compound from which a fiber could be drawn came into the realm of chemical knowledge.

The discovery of guncotten, nitrocellulose, by Schoenbein in 1846, produced the key for the formation of a viscous solution predicted as being necessary for the making of artificial fiber. Schoenbein found that by dissolving nitrocellulose in a mixture of alcohol and ether, a thick, colloidal solution, which could be drawn into fibers, was produced. In the

²Joseph Leeming, <u>Rayon</u> (Brooklyn, 1950), pp. 2-4.

development of the new industry that became inevitable through the work of Schoenbien, two discoveries were made through research that proved to be very important in the resultant commercial production of artificial fiber. These two developments were the discovery of a mechanical process for producing wood pulp and the invention of the spinneret for spinning the filaments produced into fiber. The first material used for making spinnerets was glass, but because of breakage and other problems, this material was later changed to alloys of precious metals such as gold, platinum, and iridium.

The development of the mechanical process for producing wood pulp led to the first patent(British) for a process of producing rayon.³ In 1855, George Audernars applied for this patent which was for his process for producing an artificial fiber, rayon, from the bark of mulberry trees. Another very important contribution leading to the full scale production of rayon came from J. W. Swan. In his search for a good light bulb filament he became the first to develop the use of spinnerets for the commercial production of rayon filament.

The main effort in the development of an artificial fiber belongs to a Frenchman, Count Hilaire de Chardonnet.⁴ Although Chardonnet was an aristocratic hobbyist, as were most of the early scientists of France and England, he was scientifically

³R. W. Moncrief, <u>Man-Made</u> <u>Fibers</u> (3rd ed., New York, 1959), p. 113.

⁴Leeming, pp. 9-15.

educated and possessed the enthusiasm and energy necessary for long hours of research. Although he was put on the track of a method for producing artificial fiber quite by accident, he spent twenty-nine years in research and development before achieving the results he desired. The Count obtained a patent for his process on May 12, 1884, and began production soon thereafter. He exhibited fabrics made from his fiber at the Paris Exhibition of 1889, and by 1891, was able to go into full scale production. His small factory produced about onehundred pounds of nitrocellulose rayon each day. From this very modest beginning, products of rayon have become second only to cotton on the commercial market for textiles.

Three other processes for the improvement of rayon followed the nitrocellulose type produced by Chardonnet. These new processes resulted in the production of cupramonium rayon, viscose rayon, and acetate rayon. In each case the fiber produced showed new and better properties with respect to its predecessor.

The discovery and ultimate commercial production of rayon was the first and largest step toward the development of a new branch of chemistry and of chemical industry. Rayon was being produced commercially in 1891, yet it was not until the late 1930's that any new artificial fiber came into production. These new fibers had been in the research and developmental stage for many years, but chemical industry was satisfied to remain shy of them. The first new fiber that appeared on the production line after the advent of the improved rayons was

referred to as casein fiber, and was produced from regenerated protein. Regeneration refers to the fact that the original molecules are produced first in natural products, then reprocessed by industry to change or introduce certain properties which are necessary to manufacture a good fiber. Casein fibers were first produced from a natural product of milk. They appeared on the commercial market in 1937.

Up until 1939, all fibers produced by industry had been referred to as artificial fibers because their basic components could be found in nature in practically usable form; however, in 1939, the first truly synthetic fiber, nylon, appeared on the commercial market.⁵ This was the first fiber that was actually produced by the joining of short chain molecules through the process of polymerization. These new synthetic polymers combined both strength and versatility, and ultimately started the trend of tailor-made fibers that is so prevalent in industry today. Following the debut and resulting success of nylon, the textile markets have been flooded with new and better fibers made by man with promise of more to come.

⁵Moncrief, pp. 291-292.

CHAPTER III

GENERAL SYNTHESIS, STRUCTURE, AND PROPERTIES OF FIBER FORMING MOLECULES

It seems strange that the production of a true synthetic fiber should have been so long delayed. The reason for this delay was that before a substance can synthesized it must be analyzed; it was, for example, useless to attempt to try to synthesize penicillin until analysis had revealed its chemical constitution. In the case of polymers for fibers, the same delay with respect to their analysis characterized the efforts to synthesize them. Thirty years ago fibers were thought to be complex and irregular bodies of no simple design; they were not given any kind of treatment in chemistry, and a student could pass through an honors school of chemistry without hearing fibers mentioned.

The first real insight into the structure of fibers came with the application of x-ray diffraction analysis methods to the study of their structure.¹ The patterns produced by x-ray diffraction revealed both molecular dimensions and atom arrangement within the molecule. Thus it was found that the constituen

¹R. W. Moncrief, <u>Man-Made</u> Fibers (3rd ed., New York, 1959), p. 25.

molecules of natural and artificial fibers were long and narrow in structure, and from this and other information, chemists began to visualize the possibility of building long molecules from short molecules which were available.

The problem of producing these long molecules from the available components proved to be a very difficult task because of lack of information. The study of macromolecules had been sadly neglected in the evolution of chemical knowledge down through the centuries. Anytime a reaction produced and insoluble, infusible, non-crystalline, and unreactive substance, it was considered to have been a failure; and the resulting product was discarded and disregarded. W. H. Carotheri a research chemist for a major chemical company, realized the value of the properties of these wasted substances, and began. definite research on the formation of polymers through use of some of these failure reactions in hopes that fiber producing materials would result.² He discovered that molecules which had a functional group, such as the hydroxyl or amino group, at either end could combine together to produce a molecule twice as long which also had a functional group at either end. By repeating this process of combination, very long molecules may be produced. The resulting molecule of such a process is called a polymer, and the process itself is referred to as polymerization.

Polymerization is now recognized as the principle method

²J. J. Press, ed., <u>Man-Made</u> <u>Textiles</u> <u>Encyclopedia</u> (New York, 1959), p.111.

of production in the formation of long, synthetic molecules. There exists two major types of polymerization: condensation polymerization and addition polymerization.^{3,4} Each type results in the macromolecules necessary for fiber production, but each type is used to produce the long molecules from different types of compounds.

Condensation polymerization involves the splitting off of the elements of water or of some other simple compound, such as ammonia or hydrogen chloride, when the molecules combine to form a chain. This type of combination is used in the synthesis of long molecules from hydroxy acids and from amino acids, both of which are organic compounds. Fiber filaments produced by condensation polymerization are polyamides which go to make up nylon, and polyesters which go to make up Dacron.

Addition polymerization consists of the union of several molecules of a compound with a redistribution of valency bonds. No splitting off of elements occurs in this process. Many unsaturated compounds, compounds containing double or triple bonds, will polymerize under suitable conditions. A very well known example of this process is the production of polyethylene by addition of molecules of ethylene under conditions of high temperature and pressure. Other fibers produced by this method are Vinyon, Orlon, and Acrilan.

³R. Robson, <u>The Man-Made Fibers Industry</u> (New York, 1958), pp. 119-122.

⁴Moncrief, pp. 42-48.

All synthetic fibers, whether produced by condensation or addition polymerization, are characterized by the fact that they are very long with respect to their diameter. The average width of a synthetic fiber molecule is ten to fifteen microns, a micron being one-thousandth of a millimeter. The length is variable according to the use of the fiber. Other structural properties of fibers which govern the physical and chemical properties of the fiber are cross-section shape of the filaments produced, and the structure of the constituents of the long chain molecule.

Cross-section shape is dependent upon the method of production of the fiber, which will be discussed later, and upon the spacial construction of the molecules making up the filament. Most filaments are round, but this is not always true. Nylon and Dacron are fibers of round cross-section; however, Vinyon and Orlon have dog-bone cross-sections; viscose rayon filaments are highly serrated; and cellulose acetate fibers are lobed. One of the major requirements of a man-made fiber is that all of its filaments have the same uniform crosssection shape. Properties controlled by fiber cross-section shape are strength, elasticity, luster, and texture.

As can be noted from the preceding statements, fibers vary greatly from one kind to another; however, these differences at times are dependent upon chemical structure alone. Terylene, British-made Dacron, which contains many benzene rings in its chain formation, has properties very similar to those of Nylon 66 polymer; however, this nylon polymer is a

most perfect example of a straight chain molecule. Such evidence as this and the fact that the glucose ring is very prominent in polymers such as viscose rayon, gives proof that small ring structures are not detrimental to the properties of the fibers characterized by having these component chemical structures. One very important property which is dependent upon chemical structure and constitution is solubility. An interesting fact to note with respect to this is that most compounds containing hydroxyl groups are soluble in water. However, fibers of cellulose, which contain many hydroxyl groups per constituent ring of glucose, lose this property because of the high degree of polymerization and the interaction of the hydroxyl groups of neighboring molecules through hydrogen bonding.⁵

The presence of carboxyl groups, amino groups, and hydroxyl groups all affect the solubility of fibers in different solvents; the fiber's susceptibility to dyestuffs; the melting point; and many other minor properties which can be tailored for specific uses. The properties of each synthetic fiber can always be closely attributed to its chemical constitution which includes component molecules of the chain, molecular components, spacial arrangement, and bonding linkages.

Thus far this discussion has covered the synthesis, structure, and properties of the molecules involved in the production of man-made fibers. The conversion of polymers

⁵R. W. Moncrief, <u>Artificial Fibers</u> (New York, 1950), p. 67.

into fiber form will be briefly discussed in this paragraph. There are three major methods of producing fibers from polymerized molecules.⁶ They are as follows: melt extrusion method, in which the polymer is melted, forced through a spinneret, and the resultant fibers solidified by cooling in air; wet spinning, in which the polymer is melted, forced through a spinneret, and the resultant fibers passed into a liquid bath for coagulation; and dry spinning, in which the polymer is melted, forced through a spinneret, and the resultant fibers solidified by the evaporation of the solvent retained from the melt solution. As can be noted from the preceding descriptions, all of the prominent spinning processes have in common the extrusion of the fiber-forming polymer, in liquid form, through fine orfices. The processes differ only in the methods of polymer liquification and filament solidification. Each being dependent upon the other. Probably the main process used in industry today is that of wet spinning. Some fibers produced through wet spinning are viscose rayon, Acrilan, and Courtelle. Fibers produced by other methods are nylon and Perlon by melt extrusion, and acetate rayon by dry spinning.

⁶Rowland Hill, ed., <u>Fibers</u> From Synthetic Polymers (New York, 1953), pp. 363-412. 14

 $= \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} \sum_{j=1}^{n-1$

CHAPTER IV

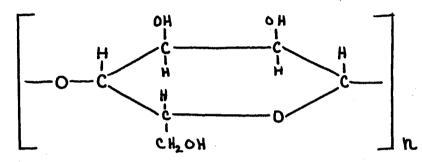
THE MAJOR MAN-MADE FIBERS BEING PRODUCED TODAY

Of all the artificial and synthetic fibers produced by industry throughout the world, many are alike in chemical structure and properties, but are sold under different trade names which do not relate the different characteristics exhibited by the fibers. This is very confusing when left unexplained in literature, because the uninformed reader is left with the impression that all fibers are different in chemical structure and constitution, properties, and performance.

In order to clarify this situation the following discussion will take up the chemical structure, natural sources of raw materials, major properties, and uses of some of the main types of fibers now in production. Each of the specific manmade fibers which will be discussed is produced by a major company in the United States, and will be referred to under its most familiar trade name. Each one of these fibers has one or more counterparts of practically the same structure and properties, which is produced in one or more foreign countries, and usually appears on the textile market under a different trade name from that most familiar to us.

The first fiber to be discussed is viscose rayon. There are several types of rayon, but viscose is the most popular

of all of these.^{1,2,3,4} Viscose rayon is an artificial fiber produced through regeneration of cellulosic material. The major source of the cellulose molecules utilized in the process is wood pulp of which cellulose is a major constituent. The original material is run through several chemical reactions, and a polymer of the following chemical structure is produced:



The subscript, n, refers to the fact that a very large number of similiarly constructed molecules are joined together to form the resulting long chain macromolecule. The basic ring structure exhibited by the preceding structural formula is that of the simple sugar, glucose. The polymer which constitutes the final filament of viscose rayon differs from the naturally formed cellulose molecule only in that the chains of glucose molecules are somewhat shorter and more uniform in length than those of the naturally formed molecules. This

¹Joseph Leeming, <u>Rayon</u> (Brooklyn, 1950), pp. 25-39.

²R. W. Moncrief, <u>Artificial Fibers</u> (New York, 1950), pp. 86-132.

³R. W. Moncrief, <u>Man-Made Fibers</u> (3rd ed., New York, 1959), pp. 118-183.

⁴Jane Cleeland, "What are Man-Made Fibers?", <u>Country</u> <u>Gentleman</u>, Vol. 124, (March, 1954) p. 120.

shortening through chemical processing is referred to as degradation, and unless it is properly controlled, can be very dangerous with respect to loss of strength and fibrous quality of the polymers.

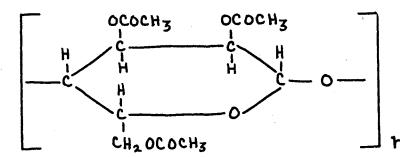
Viscose rayon fiber is produced by the dry spinning process, and the cross-section shape of the filament is highly serrated, that is, notched or saw-toothed. It has a specific gravity of 1.52, is very absorbent, has a very low elasticity rating, and is reasonably strong. The durability of viscose rayon is about medium with respect to other man-made fibers; it is easily attacked by moulds, mildew, and sunlight; and it has a very low resistance to heat. Some of its more attractive properties are that it is relatively easily dyed, and its fibers can be made to resemble those of wool or cotton in almost any fabric constitution. From some of the properties described here, one might assume that the production of the viscose rayon fiber is almost a waste of time; however, its versatility, produced mainly through blending, has placed it. second only to cotton on the textile markets of the world. The main use of fabrics containing viscose rayon is in the production of clothing.

Another very interesting artificial fiber, which at times is referred to as rayon, is cellulose acetate. 5,6,7 Its most

⁵Moncrief, <u>Man-Made Fibers</u>, pp. 184-211.

⁶Cleeland.

⁷J. J. Press, ed., <u>Man-Made</u> <u>Textiles</u> <u>Encyclopedia</u> (New York, 1959), pp. 67-68. common name is simply Acetate; however, it is also produced and marketed in the United States under the trade names, Celanese and Seraceta. Cellulose acetate polymers are produced from the natural cellulose fibers of wood pulp and from cotton linters, cotton of very short staple length which is removed from cotton seeds and which is unsuitable for spinning. The processing procedure is about the same as that used in the production of viscose rayon; however, through an added procedure, most of the hydroxyl groups of the glucose rings are acetylated, as can be seen from the following structure:



The major constituent of the reaction for production of this polymer, other than raw cellulose, is acetic acid from which the acetate radicals are obtained. The resulting polymer is called cellulose triacetate, diacetate, or monoacetate according to the degree of acetylation. The filaments of this long chain of acetylated glucosides are spun by the dry spinning process, and the resulting filaments have a cross-section shape which is lobed.

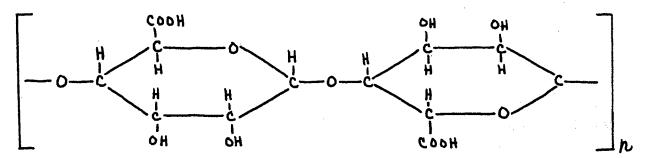
Cellulose acetate has a specific gravity of 1.32, which is very similar to that of wool. Its absorbency is much less than that of viscose rayon because of the esterfication of the hydroxyl groups; however, due to this esterfication, the

filaments are prone to swell or dissolve in certain organic solvents. It is relatively strong and durable, and at up to five per cent stretch, is highly elastic. Acetate has a good resistance to moulds, mildew, and sunlight; but it is a thermoplastic, which means that it softens on heating. Because of this thermoplastic quality, it does not support combustion readily; it melts below its kindling temperature. This melting property makes cellulose acetate very difficult to dye; however, through special processes of cold dyeing, it has been dyed beautifully. It is also very soft in texture; and when it is blended with other fibers, it contributes draping quality and richness to the fabrics produced. Its major use is in the making of luxury fabrics such as satins and taffetas.

In producing artificial or synthetic fibers, the manufacturer is always searching for raw materials which are available in unlimited quantities, easily accessible, and economical. One of the newest types of artificial fibers, which is not yet very popular, fits these specifications perfectly; and because of its future possibilities, deserves discussion here. This relatively new artificial fiber has no well known tradename, and therefore will be referred to as Alginate.^{8,9} Alginate fiber comes from a very familiar and abundant natural source, seaweed. The main component which is used in producing the fiber is a polymer of alginic acid. Its exact chemical

⁸Moncrief, <u>Man-Made Fibers</u>, pp. 241-252. ⁹Press, p. 88.

constitution is still in doubt, but the following structure is acceptable as representing a link in its long chain polymer:



The basic structure of the molecule is that of the disaccharide, mannose, which is composed of two molecules of glucose bonded together by an oxygen bridge. Fibers with desirable properties have been produced by regenerating the alginic acid, and in the process, replacing the hydrogen of the carboxyl group with calcium, which forms calcium alginate. The filaments resulting from the dry spinning method of production have a cross-section shape which is fairly well rounded with slight servations along the edges.

Calcium alginate fibers are reasonably strong, quite absorbent, and sufficiently high in elasticity to meet most textile requirements. The specific gravity of this fiber is 1.75, which is relatively high. Because of its high metal content, the fibers are flameproof; however, this property is offset by the fact that alginate fibers dissolve in slightly alkaline soap golution preventing home cleaning. However, fabrics containing this fiber can be dry cleaned. The fibers are easily dyed because of the high affinity of the many carboxyl groups for basic dyestuffs. The fibers find their main use in the production of medical dressings and bandage material, because they possess a property which aids in the coagulation of blood. They are also used in making clothing, but this is done very infrequently and in small quantities.

One other type of artificial fiber merits a brief discussion, and that is fiber produced from regenerated protein material.^{10,11} The casein fibers constitute the main group of man-made fibers produced from this type of raw material; interest in these fibers developed because of their similarity to wool. The major source of raw material used in the production of casein fibers is a natural product found in milk. Another type of regenerated protein fiber, Vicara, is produced from a natural product of corn; and still another uses soybeans as its natural source of raw materials. Most of these fibers are now in very limited production or have been discontinued. The unpopularity of the regenerated protein fibers results mainly from industry and not from the public. Through a feeling of humanity, the leaders of industry have no desire to utilize needed foodstuffs to make fabric, even though the United States generally shows a large surplus each year of the raw materials necessary for the production of these fibers.

The production of synthetic fibers from waste products of industry and from compounds which are formed in great abundance leaves the conscience of man out of the fiber industry, and utilizes only his ingenuity and skill in the processes involved in synthesizing long chain polymers. The first

10Ibid, pp. 69-70.

¹¹Moncrief, <u>Man-Made</u> Fibers, pp. 255-265.

synthetic fiber produced, and still the major one on the textile market is nylon. There are many different types of nylon fiber, each with slightly different chemical constitution and properties. 12,13,14,15 Normal nylon, which is referred to as Nylon 66, is made by condensation polymerization from amines and acids, and has the following structural formula:

As can be seen, the chemical bond between the main molecules of the chain joins carbon and nitrogen forming what is known as the peptide or amide linkage. The resulting macromolecules are called polyamides. Nylon 66 filaments are spun by the melt extrussion process, and the cross-section shape of the resulting filaments is almost perfectly circular.

Nylon is a very strong material, and is highly durable. Its high elasticity can be noted by the fact that, when it is not stretched more than eight per cent of its original length, it recovers completely its original condition. Nylon is one of the least absorbent of all the synthetic fibers, which points to its well known fast drying ability. It has a

¹²Ibid, pp. 291-323.

13 Rowland Hill, ed., Fibers From Synthetic Polymers (New York, 1953), pp. 414-435.

14 Cleeland.

15Press, pp. 111-116.

specific gravity of 1.14, which is much lower than that of most other fibers. Nylon 66 will not support combustion; it is not easily attacked by chemicals; and it shows almost complete immunity to mildew, bacteria, and moths. However, it is degraded by the action of sunlight.

Nylon dyes easily; but, if done with basic dyestuffs, it will give very poor fastness with respect to light and to washing. Pleats and creases can be durably set into the fabric by heat. Its uses range from parachute material to lingerie because of its versatility with respect to setting in tailor-made qualities.

Nylon, as it was first produced, was not a polyamide, but was a polyester. This polyester form of nylon, however, was not suitable for the desired properties of the material. Improvement of the properties of these polyester fibers brought a new fiber, Dacron, into commercial production.^{16,17,18,19,20} A polymeric ester is produced by the condensation polymerization of an acid and an alcohol. In the case of Dacron, terephthalic acid and ethylene glycol are reacted and combined to produce a chain of molecules of the following structure:

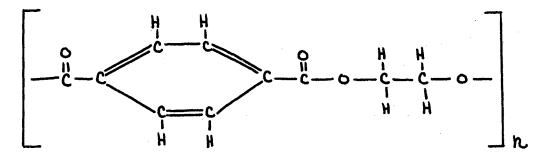
¹⁶Moncrief, <u>Man-Made Fibers</u>, pp. 340-365.

¹⁷Hill, pp. 435-453.

18_{Cleeland}.

¹⁹Charles H. Rutledge, "Dacron; Its Properties, Uses, Performance, and Care", <u>Practical Home Economics</u>, Vol. 2, (April, 1957) p. 27.

²⁰Press, pp. 111-116.

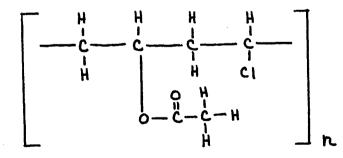


The ring structure represented here is that of benzene, the basic ring structure of the terephthalic acid involved in the synthesis of Dacron polymers. The molecules of the long chain polymer are linked together by oxygen-carbon bonds, which are produced by the replacement of hydrogen in the carboxyl groups involved. The compound split off in this condensation polymerization reaction is water.

Dacron filament is produced by the melt extrussion process, and the resulting filament has a round cross-section shape. This very durable fiber has a specific gravity of 1.38. It is relatively nonabsorbent with respect to water, has a high elasticity rating, and is very strong. Dacron fiber loses strength when exposed to sunlight over long periods of time; however, it is not attacked by bacteria, moulds, mildew, or insects. Dacron fabric is noncombustible, can be pleated and creased durably by heat, and is outstandingly wrinkle resistant when wet of dry. This fiber is very difficult to dye because of its very low absorbative ability. The main uses of Dacron are found in the production of wearing apparel, in industrial filters, and in industrial machinery parts.

The synthesis of fibers has been an achievement that has presented the possibility of making fibers with specified

properties. It is not always possible to meet desired specifications, but it is possible to some extent to modify the physical properties of synthetic fibers by suitably adjusting their chemical compositions. It may be found that one substance when polymerized gives fibers which are unsatisfactory with respect to some quality, and another substance of different structure and/or constitution may react in a similar manner with respect to some other very desirable quality. Yet, when these two substances are polymerized together, copolymerized, the properties of the fiber produced may be satisfactory in all respects. Such a fiber as this is Vinyon. which is produced by the co-polymerization of vinyl chloride and vinyl acetate through heating in the presence of a catalyst.^{21,22,23} The resulting polymer, formed by addition polymerization, is eighty-eight per cent vinyl chloride and twelve per cent vinyl acetate, and has the following chemical structure:



²¹Moncrief, <u>Man-Made Fibers</u>, pp. 366-380. ²²Hill, pp. 454-503.

²³F. Howlett, "The Structure of Textile Fibers", <u>Journal</u> of the <u>Textile Institute</u>, Vol. 41, (1950) p. 124.

The bonding between molecules in the polymer is a regular carbon-carbon linkage. The vinyl acetate serves to plasticize internally the vinyl chloride producing a fiber of very good quality.

Vinyon filament is produced by dry spinning, and has a cross-section shape like that of a dumb-bell or dogbone. It has a very low absorbency with respect to water, is reasonably strong, and is in the medium range with respect to elasticity. The fiber has a specific gravity of 1.37, which is very similar to wool and cellulose acetate. It is unattacked by moths, fungi, bacteria, and carpet beetles; and it is reasonably stable toward chemicals and sunlight. Vinyon is a thermoplastic, and will not support combustion. Because of its high resistance to water, it is very difficult to dye. The major uses of Vinyon are found in the production of protective clothing for chemical workers, and in the production of felts, carpets, and filter fabrics. It is not used in making material for clothing because its low melting point prevents home laundering.

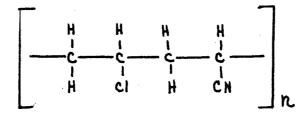
Another fiber of the co-polymer group is Dynel, which is made by the addition polymerization of vinyl chloride and vinyl cyanide.^{24,25,26} The latter compound, vinyl cyanide, is often referred to as acrylonitrile, and will be discussed in detail

²⁴Moncrief, <u>Man-Made Fibers</u>, pp. 373-380.

²⁵Hill, pp. 454-503.

²⁶Hugh L. Carolan, "Dynel; Its Properties, Uses, Performance, and Care", <u>Practical Home Economics</u>, Vol. 2, (February, 1957) p. 38.

later in this chapter. Dynel co-polymer has a chemical structure as follows:



As in Vinyon, Dynel molecules are linked by carbon-carbon bonding. The filament is produced by the dry spinning technique, and has an irregular, ribbon-shaped cross-section similar to that of cotten. Dynel fiber has a specific gravity of 1.31; it is relatively nonabsorbent, mediumly elastic, and very strong. It is resistant to moths, mildew, and fungi. Dynel fabric buried in soil in tropical conditions was unchanged after six months, whereas a heavy cotton duck disintegrated after ten days. Dynel will not burn, but it will shrink when exposed to extensive heat because of its thermoplastic nature. This property, along with its resistance to water, makes dyeing very difficult. Its main uses are in the manufacturing of protective clothing, covers for paint rollers, blankets, coats, and hair for dolls.

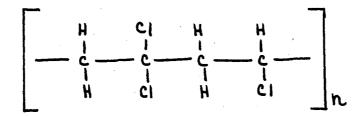
The next fiber to be discussed, Saran, is also a co-polymer.^{27,28,29} Saran is produced by the addition polymerization of vinylidene chloride, an unsaturated compound,

²⁹Moncrief, <u>Man-Made</u> Fibers, pp. 381-386.

²⁷ Cleeland.

²⁸press, p. 132.

and vinyl chloride. The resulting component molecule of the polymer produced has a structural formula as follows:

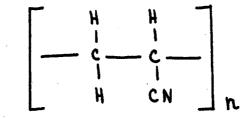


The resulting linkage is the carbon-carbon bond as exhibited by the preceding co-polymers. The word "Saran", like nylon, is simply a generic name referring to the plastic material from which a series of fibers is produced through different manufacturing processes. The major raw materials for the production of saran are ethylene, which is made by cracking petroleum, and chlorine, which is produced by electrolyzing sea water. Saran filament is spun by the melt extrussion process, and has either a flat or elliptical cross-section shape, according to the properties necessary for its specific uses.

Saran fiber has an average specific gravity of 1.71, which is relatively high. It is very strong, and highly resistant to water. The fiber will not support combustion, and it is not affected by sunlight. As are the other co-polymers, it is difficult to dye. Its main use is in upholstery for automobiles and office equipment. Because saran is produced from cheap and abundant materials, petroleum and sea water, and because it is spun by the economical process of melt extrussion, it probably has the best future of any synthetic fiber on the textile market.

One of the most popular synthetic fibers on the commercial

market, Orlon, is produced as a homopolymer, Orlon 81, and as a co-polymer, Orlon 42.^{30,31,32,33,34} Orlon 81 is a polymeric molecule of vinyl cyanide, acrylonitrile, which is formed by addition polymerization and has the following chemical structure:



The fiber produced is often referred to as a polyacrylic fiber. The chemical constitution and structure of the compolymer form of this fiber, Orlon 42, is confidential, although it is known that acrylonitrile makes up about ninety per cent of each polymer. The main reason for the compolymerization of this fiber is to increase its affinity for dyestuffs. Most of the following discussion will be with respect to Orlon 81, unless otherwise specified.

The Orlon 81 fiber is produced by a spinning process which has not been disclosed, and the resultant filaments have a cross-section shape similar to a dogbone, as does Vinyon.

³⁰Moncrief, Man-Made Fibers, pp. 404-427.

³¹Hill, pp. 454-503.

³²Charles H. Rutledge, "Orlon; Its Properties, Uses, Performance, and Care", <u>Practical Home Economics</u>, Vol. 2, (March, 1957) p. 35.

33_{Howlett}.

³⁴William E. Larson et al., "Orlon Acrylic Fiber", <u>Scientific Monthly</u>, Vol. 69, (December, 1949) p. 414.

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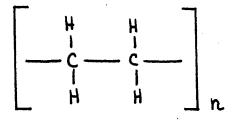
Its specific gravity is 1.17, which is relatively low when considering the heavy feel and appearance of Orlon fabric. Orlon 81 is a very strong fiber with a high elasticity rating. and nearly a complete resistance to water. This absorbency resistance, which is found in most synthetic fibers, contributes directly to the great difficulties met in dyeing operation, The fabric of Orlon is very durable owing to its resistance to most chemicals, moulds, mildew, and sunlight. It will not support combustion, but upon heating to high temperature, it turns black. Because of these properties, plus its draping quality and resistance to creasing, Orlon finds many uses. Some of these are found in the manufacture of tops for convertible automobiles, upholstery for both outdoor and indoor furniture, awnings, carpets, and many other things. Orlon 42, the mystery fiber, finds its main use in the manufacture of knitwear such as dresses, shirts, socks, and underwear. It is usually blended with wool, cotton, or Dynel for utilization of its best qualities.

Another fiber which is very similar to Orlon 42 is Acrilan.^{35,36,37} Acrilan is a compolymer of acrylonitrile and an undisclosed compound. As a result, it has good affinity for dyestuffs. One of the major differences between Orlon 42 and Acrilan is in the method of spinning. Acrilan filament is spun by the wet spinning process, and the resulting shape

35_{Moncrief, Man-Made Fibers, pp. 428-438.} 36_{Hill, pp. 454-503.} 37_{Cleeland.}

of cross-section is round, very unlike the flat cross-section shape of Orlon 42. In respect to other properties and uses, Acrilan and Orlon 42 are very similar. The main uses of Acrilan are in the manufacture of knitwear and blankets.

The last two synthetic fibers to be discussed are very similar in chemical structure and properties. They are polyethylene and Teflon. Polyethylene is produced by the addition polymerization of ethylene under conditions of high temperature and pressure.^{38,39,40,41} The polymer has the following chemical structure:

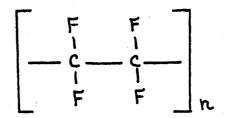


Polyethylene filament is produced by the melt extrussion method, and has a melting point only slightly above the boiling point of water. It has a waxy feel, and is completely resistant to water; and it is the only synthetic fiber which has a specific gravity lower than that of water. Its main uses are in the production of protective clothing because of its great chemical resistance, and in the production of automobile upholstery. It also finds many uses in packaging and storage.

Teflon, which is very similar to polyethylene, is produced

³⁸Moncrief, <u>Man-Made Fibers</u>, pp. 451-454. ³⁹Hill, pp. 47-55. ⁴⁰Cleeland. ⁴¹Howlett.

by the addition polymerization of tetrafluoroethylene, and has the following structural formula: 42,43,44



Teflon filament is produced by a process called emulsion spinning, which refers to the fact that the filament is spun from the same medium in which the polymerization of the molecules takes place. The resulting filament has a round shape of cross-section. Teflon has the highest heat resistance of all synthetic fibers, but is is only medium in quality with respect to strength and elasticity. Also, it is completely resistant to water. The most unique property of the fiber is its chemical stability. It can be boiled in aqua regia. mineral acids, or concentrated caustic soda without decomposition chemically or physically. It is also registant to all of the usual strong oxidizing agents. It is soluble only in fluorine compounds at high temperatures. The main uses of Teflon are found in the industrial field; however, these are at a minimum because of its high price. Regardless of this, the future of this unique and important fiber seems excellent.

⁴²Moncrief, <u>Man-Made Fibers</u>, pp. 455-461.

⁴³R. J. W. Reynolds, "Fibers From New Polymers", <u>Journal</u> of the <u>Textile</u> <u>Institute</u>, Vol. 46, (1955) p. 328.

44Press, p. 46.

CHAPTER V

ECONOMIC, SOCIAL, AND FUTURE ASPECTS OF MAN-MADE FIBERS

Contrary to the thought of many people, man-made fibers are not so much competitive as they are complementary to the natural fibers. The general advent of the new fibers has not been to reduce the quantity of natural fibers used, but so far rather the reverse. Today there is five or six times as much natural fiber used as there is artificial and synthetic; however, this position is very likely to change in the future. It seems certain that man-made fibers will become better, cheaper, and easier to make as time passes; and as these occurrances come to pass the consumption of natural fibers will naturally diminish.¹

One of the first and still very prominent uses of manmade fiber is the production of fabrics by blending with natural fiber.² The material produced by these blended yarns has opened many new doors for the application of natural fibers. Many of the fibers produced by man are used strictly for

¹R. W. Dennison and L. L. Leach, "Blends Containing the New Man-Made Fibers", <u>Journal of the Textile Institute</u>, Vol. 43, (1952) p. 473.

²John Campbell, "Man-Made Fiber Roundup", <u>Journal of Home</u> <u>Economics</u>, Vol. 44, (December, 1952) p. 812.

blending purposes in order to endow the materials produced with new and better properties. The production of these blended yarns has proved important in many ways. The expensiveness and often scarcity of wool has been curbed in many cases by the blending of wool with regenerated protein fiber. Another facter which is advantageous in blends of man-made fibers and natural fibers, is that the price of man-made fibers is usually more stable than that of natural fibers, which varies from year to year according to harvest; consequently, the price of blends is much more stable than that of natural fibers alone.

There is, of course, another side to the picture of the competition between man-made fibers and natural fibers. The best will win, and in some cases, a man-made fiber has already become better than its natural fiber competitor, and some, such as rayon, which is very popular, have reached a peak and will not get much better. Eventually the synthetic fibers of the nylon family may supercede cotton and linen; after all, the nylon fibers are produced from petroleum products, which are much easier to obtain than good crops of cotton and flax. In addition, the better all-round properties of nylon will help to oust its natural fiber competitors.³ This superiority is apparent, and eventually, nylon will take the bulk of the trade for this type of fiber, and cotton and linen will be used only for special purposes. The gradual fall of such

³"War of Fibers", <u>Science News Letter</u>, Vol. 61, (May 3, 1952) p. 280.

popular natural fibers will be very similar to the now notable gradual rise of the new synthetic fibers.⁴

There is one natural fiber, wool, which will present a different proposition, for it is very unlikely that a synthetic fiber with better all-round properties will be spun within the next several years. The time will come though when wool will be restricted to special uses only. So far as can be seen at present, however, the man-made fibers industry will do nothing but good for wool. The number of sheep in the world today is about the same as it was in 1920, and the production of wool has remained fairly constant over the years. The major effect that artificial and synthetic fibers have had on the wool industry is that their threat to the wool market, however minor it has been, has kept the price of wool from going completely out of reason.

The production of man-made fibers is led by rayon, which is second in production only to cotton in the world textile markets.⁶ Among other artificial fibers being produced are the regenerated protein fibers, but the output and consumption of these fibers is very small. The synthetic fiber parade is led by the nylon fibers. Dacron and Orlon are very close for second place among the synthetic fibers produced

⁴E. I. du Pont de Nemours Company, Inc., ed., "From Formula to Fiber", <u>Senior Scholastic</u>, Vol. 62, (May 18, 1953) p. 24.

⁵Roland H. Wright, "Battle of the Fibers", <u>American</u> <u>Mercury</u>, Vol. 87, (November, 1958) p. 93.

⁶R. Robson, <u>The Man-Made Fibers Industry</u> (New York, 1950) pp. 3-8.

and sold, but they are far behind the leader in this field. Although the synthetic fibers have attracted a great deal of attention, they have added only a small amount to the bulk of textile fibers produced over the world. Two factors which will cause a step forward in the production of synthetic fibers are: improvement until they are better in all-round properties; and reduction of the cost of some of the raw materials necessary for their production. These improvements will come, however, only through great expense and long years of research by the synthetic textile industry.

The outlook for production in the future is bright both economically and socially, but great good has already come from the development and manufacture of these new fibers,⁷ the greatest good having come, appropriately enough, to the people who have made these fibers. By this is not meant the few who by outstanding ability have amassed great personal fortunes, but the thousands of men and women who have given their labor and thought to make the fibers. The employees who worked in the first rayon factories did so under far better conditions than those which they had met in the old textile mills. They had shorter work days, better wages, and a much better working environment than had their predecessors. The standards of living and degree of comfort to these workers far overshadowed that of the textile workers of the late nineteenth and earlier twentieth centuries. A good look at some

⁷R. W. Moncrief, <u>Man-Made Fibers</u> (3rd ed., New York, 1959), pp. 632-634.

of our modern chemical plants which engage in the textile industry, and the homes and habits of its employees will give evidence of the outstanding social advancement brought about by the advent of the man-made fiber industry.

The revolution in the textile industry has brought no less to the public than it has to its own workers. Since the introduction of artificial and synthetic fibers, the appearance and durability of clothing, upholstery, and other fabric endowed products has been improved to a great extent; and as research continues, so is the economical aspect of the final fabric products improved. This new and growing industry, which will be expanding for years to come, promises its buying public many new, better, and more economical fibers to be produced in both the near and extended future.

The main advancements in the field of cellulose fibers will probably be the development of high tenacity fibers, and the increasing use of new raw materials such as bamboo, special grasses and seaweed.⁸ The future development of a good, allround fiber from seaweed will be a minor revolution in itself. Protein fibers are due an enormous expansion, and with this will come a change in raw material from edibles such as milk, nuts, and corn, to waste products such as horn, hoofs, scrap leather, feathers, claws, and any inedible animal protein.

The future of the synthetic fiber industry is open; for despite the astounding advances already made, the surface of

⁸Simon Williams, "Synthetic Fibers", <u>Scientific American</u>, Vol. 185, (July, 1951) p. 37.

the field has only been scratched. Although these fibers have valuable properties by themselves, and have increased the strength and durability of natural fibers by blending, a good, all-purpose fiber has yet to be produced. Most of the synthetic fibers produced are strong, durable, and chemical resistant; but none has the capacity for absorbing moisture that is so desirable for intimate wear, none has the natural waterproof character of wool, none has the affinity for dyestuffs exhibited by wool and cotton, and none has the enormous wet extensibility and recovering ability of wool. So far. chemists have produced fibrous molecules that are relatively easy to synthesize, and not one of these is like a natural fiber.⁹ In the future the trend will be to impart hydrophillic properties, absorbency, to present fibers by substitution of different chemical groups into the molecular chains.¹⁰ Also. one of the main aims of basic research in the synthetic field is to discover methods of synthesis that will yield polymers which have this much desired hydrophillic characteristic. As can be seen, the possibilities of man-made fibers are ennumerable; and the things that come to the public in the future from this great industry should be a surprise to no one.

⁹William G. Ashmore, "Surge of New Fiber Activity", <u>Textile World</u>, Vol. 109, pt. 2, (September, 1959) p. 69.

10_{Moncrief}, p. 631.

CHAPTER VI

SUMMARY AND CONCLUSIONS

It is very evident that the work of Hooke, Schoenbein, Chardonnet, and Carothers, among the many men involved in this field of science, has left its mark on the society of our world. The discovery and development of the artificial and synthetic fibers will certainly be a credit to this era of civilization in the ultimate history of the world. The production of fabrics from petroleum, milk, wood, seaweed, and other such materials gives some idea of the development of man's ingenuity and ability to cope with his environment. The story of the man-made fibers, however, is only one of the many histories that can give the same picture of the growth of the human mind and its utilization through the past centuries. First came the idea, then later the production of an artificial fiber from naturally synthesized, long chain molecules. Now man has made his own long chain molecules, and the incorporation of permanent creases, or of wrinkle resistance, or of some other such property through chemistry has gained these fibers the name, "miracle fibers", and rightly so: for some of their properties are relative miracles. The ultimate fulfillment of the promises of the future with repect to these new fibers may be even more amazing.

Through the study of man-made fibers and their properties

and characteristics a definite knowledge of the chemistry involved has been gained by the author of this report. The organization and vocabulary utilized in discussing the subject matter should prove very valuable in the presentation of such material to a group of high school students with a basic knowledge of chemistry. Although the entire treatment of the subject would seem very simple to an expert in the field of man-made fibers, the modern aspects of this presentation with respect to this relatively new phase of chemical industry should offer new knowledge of chemistry and possible inspiration to the young, intelligent mind searching for a career. With this in mind this report has been written.

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