

# NYLON TECHNOLOGY

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## FOREWORD

Nylon is a textile fiber with a success story unparalleled in textile history. Soon after this book appears, nylon will be manufactured by two huge companies in the United States and by numerous companies abroad. Production will be measured in the hundreds of millions of pounds. Its importance, however, has been greater than the tonnage would indicate. No one questions the essentiality of nylon to the military or its essentiality for ladies' hosiery, but its use goes infinitely beyond. It is a fiber with a combination of excellent properties that is not found in any other.

Important segments of the textile industry are completely dependent upon this fiber in order to continue operation—others are dependent upon it for their major profits. Each year many more new textile companies are finding that nylon fits into their operations. Despite such prominence and importance, no one, up to now, had the courage to gather independently the technical processing information concerning this fiber.

In compiling the material for this book, Karl Inderfurth has done an outstanding job that is a credit to him and a major contribution to the industry he has served beginning with his days in the textile school at Clemson College. Mr. Inderfurth has had wide experience in the textile industry, especially with continuous-filament synthetic fibers. Even during his war service he worked on textiles in the Quartermaster Corps—one of the few persons who found himself serving the army in his chosen field.

Mr. Inderfurth has a knack for presenting technical textile information in a clear and interesting manner. He knows without guessing what information is important and how best to present it. He has prepared many technical pamphlets and technical publications as well as articles for trade journals. He has shown wisdom in realizing that no one person could write all the pertinent technology of handling nylon in textile mills. His wealth of friends in the industry has been most helpful in broadening the scope of this book. He has been painstaking in

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having all the material thoroughly checked, realizing, however, that changes in technology are constantly occurring.

This important addition to the Textile Technology Series can serve as a reference point for all persons now engaged in manufacturing textile articles from nylon fiber or as a starting point for the technologists and mill men contemplating its use.

Karl Inderfurth never lost patience regardless of new tasks suggested as the manuscript was developing. As consulting editor of the Textile Technology Series, it has been a pleasure to be associated with him.

C. W. BENDIGO  
*Consulting Editor,*  
Textile Technology Series

New York, N.Y.  
January, 1953

## PREFACE

This book presents, through data gathered from many sources, the methods employed to process nylon in the various segments of the textile industry.

It should be immediately obvious that a book encompassing such a wide scope could not be adequately covered by one individual. Therefore, aid was solicited and received in the form of technical data, operating approaches, and procedures from men familiar with nylon processing throughout the textile industry—from yarn producer to finisher.

Perhaps the most difficult condition which had to be contended with was revising certain material after it was written in order to stay abreast of the constantly changing processing techniques.

The material as put forth in this book is in many instances a consensus of the best-known methods of processing nylon.

The author is extremely grateful to the following persons and companies for their aid in making this book first a possibility and then a reality:

E. I. du Pont de Nemours & Company, without whose aid this book could not have been written

The National Association of Hosiery Manufacturers, Inc.

The Independent Association of Stocking Manufacturers

The National Knitted Outerwear Association

Karl Lieberknecht, Inc.

Mr. John K. Stearns, Director, School of Textiles, International Correspondence Schools, who prepared Chaps. 3 and 4, Spinning Nylon Staple on the Worsted System and Spinning Nylon Staple on the Woolen System

Mr. L. F. Ryan, Technical Demonstrator, Dyes and Chemical Division, E. I. du Pont de Nemours & Company, who prepared Chap. 13, The Dyeing of Nylon

Mr. Newell E. Rollins, Group Leader, Textile Printing Division, E. I. du Pont de Nemours & Company, who prepared Chap. 14, The Printing of Nylon

Dr. J. E. Smith, Head of the Chemical Division, Technical Laboratory, E. I. du Pont de Nemours & Company, who prepared Chap. 15, Finishing of Nylon Fabrics

and to the following men for their help in outlining and reviewing the chapters applicable to their industries:

Mr. John Mason, III, Cheney Brothers (Weaving)

Mr. W. W. Saunders, Jr., Wiscasset Mills, Knitting Department (Full-fashioned)

Mr. Kenneth Horne and Mr. Fred Wood, Hornwood Warp Knitting Corp. (Tricot)

Mr. William Newell, Research Coordinator, North Carolina State College (General)

Mr. D. J. Bringardner, Nylon Technical Service, E. I. du Pont de Nemours & Company (General)

Several other chapters were partially written and wholly reviewed by outstanding men in their chosen line of textile endeavor.

It is hoped that this book will serve as a ready reference and be of some small service to each and every reader; it was in this spirit that it was written.

KARL H. Inderfurth

Charlotte, N.C.  
January, 1953

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## INTRODUCTION: THE DEVELOPMENT OF NYLON

The development of nylon was a triumph of fundamental research, and only after many years of painstaking and exhaustive effort was the objective accomplished.

In 1927, the du Pont organization established an organic chemistry research program to develop fundamental information concerning chemical processes and products. The findings would eventually, perhaps, prove valuable in opening up new avenues for applied research. In many cases, however, the data established by the fundamental research group had little or no immediate practical value.

As early as 1929 an objective of this program was to create, if possible, a distinctly new fiber. To this end cellulose ethers and esters were thoroughly evaluated; and it was found that these materials, while capable of being produced into yarns, offered no outstanding advantages over other types of synthetics then on the market. In addition to the work carried on with the ether and ester derivatives of cellulose, investigations were also conducted on certain nitrogen-containing derivatives of cellulose to determine what effect amino or substituted amino groups might exert on the properties of cellulose, particularly its dyeing characteristics. These projects were carried on during the years of 1927 to 1929 and were not significant in producing the sought-after new fiber.

During the year 1928, Dr. Wallace Hume Carothers was prevailed upon to vacate his instructorship at Harvard University in order to direct the work in organic chemistry of the fundamental research group. From the outset, Dr. Carothers and his small group of organic research chemists were encouraged to select projects of their choice. Dr. Carothers chose as the basic project the polymerization by condensation in conjunction with the structure of substances of high molecular weight. Approximately 7 years later the superpolymer produced from hexamethylenediamine and adipic acid was first synthesized, resulting in Polymer 66, which was to become known throughout the world as nylon.

In 1942, Dr. E. K. Bolton, Chemical Director of E. I. du Pont, prepared a paper on The Development of Nylon which told of the tremendous scope of the over-all nylon project.<sup>1</sup>

Dr. Bolton wrote:

"The research activities preceding the manufacture of nylon yarn may be divided into three periods:

"1. Fundamental research activities which provided the foundation for the development

"2. Concentration of attention on polyamides, which led to the synthesis of a polymer having properties suitable for use as a new fiber

"3. The development of practical processes for the manufacture of intermediates and polymer and for the spinning of fibers.

### Fundamental Research

"Dr. Carothers first directed his attention to polycondensation involving the reaction of difunctional molecules. He chose as his first attack the condensation of dibasic acids with glycols and selected reacting materials which would preclude the formation of five- or six-membered rings. He obtained, without exception, polymers characterized by recurring structural units which might be crudely pictured as hooked together like a chain of paper clips. Dibasic acids (such as malonic, sebacic, maleic, fumaric, and phthalic acids) were condensed with glycols (such as ethylene, hexamethylene, and decamethylene glycols) and esters of a highly polymeric character were obtained as reaction products. By a study of their physical properties and molecular weights, Carothers proved that these esters were not monomeric large-membered rings. The lowest molecular weight observed for any of the solid esters was 2,300 and the highest 5,000.

"After investigating the preparation and properties of many different polyesters, Carothers next turned his attention to the study of the amide of  $\Sigma$ -aminocaproic acid. Upon heating, molecules of this material reacted with one another to form, as the principal product, a polycondensation polymer containing at least 10 molecules of the amino acid. The polymer was a hard waxlike material, insoluble in most organic solvents.

"After work had been under way less than 2 years, a significant advance in the preparation of linear polymers, particularly the poly-

<sup>1</sup> This paper, which was published in *Industrial and Engineering Chemistry*, vol. 34, p. 53, January, 1942, was presented by Dr. Bolton on the occasion of the award to him of the Chemical Industry Medal of the Society of Chemical Industry.



esters, was achieved through the use of the molecular still. This tool made it possible to carry polymerization more nearly to completion by the elimination of water formed by the condensation reaction. The molecular still proved to be a valuable tool in obtaining products of higher molecular weight than were heretofore attainable with ordinary

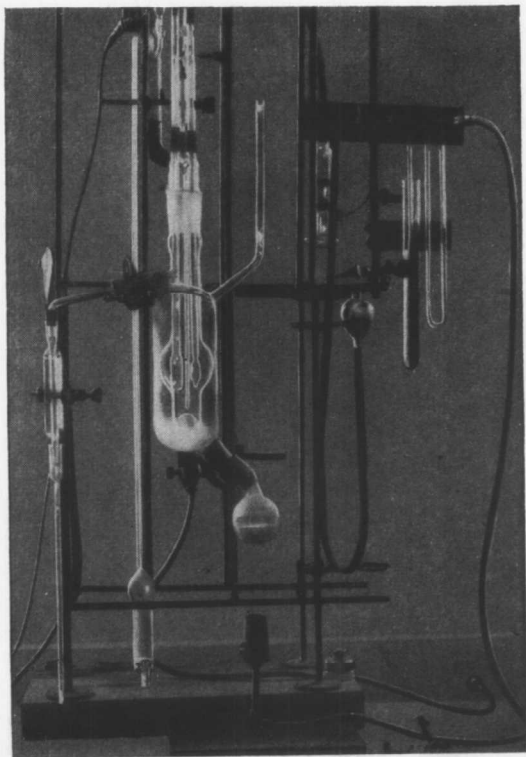


Fig. 1. 1930—The actual equipment used to polymerize chemicals that resulted in nylon.

vacuum distillation equipment. Without this technique Carothers might have failed in his search for superpolymers.

“From this time on, attention was concentrated on the so-called superpolymers. By placing the polymeric esters having molecular weights up to 5,000 in the molecular still, and heating by means of a bath at  $200^{\circ}\text{C}$  for a total of 12 days, Carothers and his associates were able to increase the molecular weights substantially, obtaining values from above 10,000 to 25,000. At this time he applied the term ‘superpolymer’ to materials having a molecular weight of 10,000 or higher.

“The new superpolyesters derived from the condensation of glycols

and dibasic acids were tough, opaque solids which, at an elevated temperature, became transparent viscous liquids. The important observation was made that filaments could be obtained by pulling threads from the molten polymer with a rod. Of still greater importance, however, was the observation that, after the superpolyester filaments had cooled, they could be further drawn to several times their original length, and that such cold-drawn fibers were quite different in physical properties from the initial mass of polymer or from undrawn fibers, that is, fibers pulled from the molten polymer with a minimum of tension and not subjected to further stress.

"For example, cold-drawing developed transparency and a high degree of luster. Furthermore, and this was the really significant difference, cold-drawn filaments had a much higher tensile strength and elasticity than undrawn filaments. They were sufficiently pliable and tough to be tied into hard knots, whereas undrawn filaments were inelastic and fragile.

"The further striking observation was made that, unlike the ordinary textile fibers, the wet tenacity or tensile strength of these superpolyester fibers was approximately equal to the dry tenacity. Moreover, drawn polyester fibers were very superior to rayon in elastic properties.

"X-ray diffraction patterns indicated that superpolyester fibers in the undrawn state were crystalline, but that the crystals had a random orientation. Cold-drawn filaments, on the other hand, gave a fiber pattern which indicated a considerable degree of orientation parallel to the fiber axis. The character of this pattern, incidentally, is similar to that obtained from natural silk fibers or from rayon filaments spun under tension.

"In addition to forming filaments by pulling a thread of the molten polyester with a rod, it was later found that filaments might also be formed by dissolving the superpolymer in chloroform and dry spinning it like cellulose acetate rayon. Such fibers, like undrawn fibers pulled from the molten polymer, exhibited random orientation of the crystals, but again as in the case of melt-spun fibers, cold-drawing produced orientation along the fiber axis.

"Up to the time that the above superpolymers were made, this study was wholly fundamental in character and was designed to throw further light on certain aspects of polymerization. The rather striking properties of fibers obtained from the superpolyesters aroused the hope that it might be possible to make a fiber of commercial utility from some type of synthetic linear superpolymer. Research was accordingly

directed to this practical end. Continued investigation showed, however, that fibers from the polyesters were of only theoretical interest, as their melting points were too low for general textile purposes and their solubilities were too great.

"A linear polyamide had been made earlier from  $\Sigma$ -aminocaproic acid by the condensation of molecules by dehydration at atmospheric pressure or under diminished pressure in the usual distillation equipment. This material had, however, a low molecular weight. When this same polyamide was heated in the molecular still for 48 hr at 200°C, the product became harder and tougher than before this treatment. Like the low-molecular-weight polyamide, it was insoluble in common organic solvents with the exceptions of hot phenol and hot formamide. The change in properties indicated a considerable change in molecular weight but no actual measurements of molecular weight were made, owing to the lack of any sufficiently reliable method. It was concluded that the polyamide so formed was too infusible and insoluble to allow a ready test of its spinnability.

"In the hope of obtaining a compromise between the properties of the polyesters and the polyamides, mixed polyester-polyamides were next prepared by heating together trimethylene glycol, hexadecamethylene dicarboxylic acid, and  $\Sigma$ -aminocaproic acid. On account of the high solubility and the low melting points of the mixed polyester-polyamides, they were not, however, of practical interest from the standpoint of textile fibers.

"A brief summary of the work to this point shows that by means of a molecular still Carothers was able to prepare linear superpolyesters having molecular weights above 10,000 from which fibers could be formed. These fibers were only of theoretical interest, however, because of their low melting points and wide solubility and had no utility as textile fibers. The mixed polyester-polyamides exhibited the same deficiencies. In this early period Carothers had made a superpolyamide from  $\Sigma$ -aminocaproic acid but no fibers were prepared from this polymer. The refractory qualities of the polyamide, in Carothers' opinion, made it difficult to prepare satisfactory fibers.

### Polyamide Synthesis

"The second period of the research leading to nylon was characterized by a concentration of effort in the laboratory to synthesize a polyamide which might form the basis for a commercial textile fiber.

"In the earlier work Carothers had not been successful in preparing a superpolymer having the necessary properties for this purpose. Other

research work on cellulose derivatives to obtain a distinctly new fiber had reached a stage where little hope was held of attaining the objective. A large amount of time and money had been spent on the various phases of the fiber program, but the results were chiefly of theoretical interest. It was therefore a matter of considerable concern to determine what practical use could be made of the scientific information that had been acquired on superpolymers. The possibility of laying the foundation for a new commercial fiber development appeared to be remote, with the result that research work in this field was discontinued for a number of months.

"Carothers, however, was encouraged to direct his work on superpolymers specifically toward the development of a product which could be spun into practicable fibers. On the basis of a survey of his scientific work in this field, he wisely decided to resume work on the superpolyamides. Polyamide formation with 9-aminononanoic acid was selected for study. The polyamide from this acid, after treatment in the molecular still, was spun into fibers which had a melting point of  $195^{\circ}\text{C}$  and, after cold-drawing, were equal to silk in strength and pliability. These observations renewed the hope of making an entirely new type of textile fiber from a synthetic material of the polyamide type, and clearly indicated the possibility of obtaining from Carothers' fundamental work on linear polymers a material for fibers of commercial utility.

"Following these observations, Carothers prepared polyamides from a variety of amino acids and also from dibasic acids and diamines. On Feb. 28, 1935, the first superpolymer from hexamethylenediamine and adipic acid was first synthesized. The resulting polymer, polyhexamethylene adipamide, was called 66, the first digit indicating the number of carbon atoms in the diamine and the second digit the number of carbon atoms in the dibasic acid. Just as in the case of the polyesters previously mentioned, fibers could be formed from this new 66 polyamide by melt spinning or by dry spinning from a solution of the polyamide in a solvent such as phenol. Also, as in the case of the polyesters, undrawn fibers of the polyamide underwent a remarkable change in physical properties on cold drawing. The cold-drawn 66 fibers possessed a high tensile strength and elasticity. Moreover, these polyamide fibers were insoluble in common solvents and melted at  $263^{\circ}\text{C}$ , which gave a margin of safety above commonly employed ironing temperatures. Polymer 66 was selected for initial manufacture because it had the best balance of properties and manufacturing cost of the polyamides then known.

“Although adipic acid was produced commercially in Germany, it was necessary to develop a new process to meet the conditions at the du Pont Company’s plant at Belle, W.Va., where, because of the catalytic technique involved, it was decided to make this intermediate. Hexamethylenediamine was only a laboratory curiosity and a process for its commercial production had to be worked out. It was felt, how-

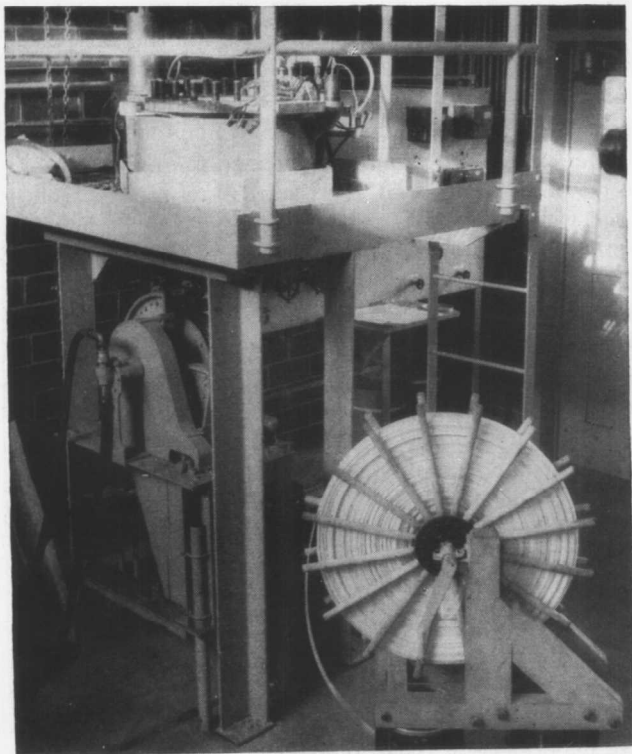


Fig. 2. 1935—This autoclave was developed during the middle thirties to produce small poundages of nylon fiber.

ever, that it should be possible by new catalytic processes to make this material from adipic acid. After the polyamide to be made was selected, development of a practical manufacturing process was turned over to other groups and Carothers was encouraged to explore other types of polyamides inasmuch as this selection of 66 was made when only a small number of the many theoretically possible superpolyamides had been examined. He and his associates prepared and studied many different kinds of polyamides from diamines and dibasic acids, from

amino acids, and from interpolymers of dibasic acids, amino acids and diamines, but polyhexamethylene adipamide continued to appear the most attractive for textile purposes. His further work therefore confirmed the wisdom of this selection.

### Development of Practical Processes

"The third period of research covered the development on a laboratory scale of the manufacturing processes for the intermediates, the polymer and nylon yarn, and the development on a semiworks scale of the chemical and engineering data for the erection and operation of a large-scale plant. The task was enormous and therefore a large force of some of the most competent chemists and chemical engineers available (some of whom were temporarily transferred from the Engineering and Rayon Departments) was assigned to the project.

"The development of the process for the manufacture of adipic acid from phenol was under Roger Williams, chemical director of the Ammonia Department. The Chemical Department had the responsibility for the laboratory work on hexamethylenediamine, but the semiworks investigation was carried out at the company's Belle plant. The Chemical Department developed the laboratory and semiworks process for the preparation of the 66 polymer and the spinning of the fiber. The work within the department was under the general supervision of C. H. Greenewalt.<sup>1</sup> Associated with him were W. A. Lazier, who directly supervised the laboratory work on the process for hexamethylenediamine, and G. D. Graves, who directly supervised the work of a large group on the polymer and the spinning.

"E. B. Bengel, at that time general assistant chemical director, and A. P. Tanberg, director of the Experimental Station, contributed to the progress of this work by advice, encouragement, selection of personnel, and assistance in the organization of these activities. In view of the long experience of the Rayon Department in textile operations of this type, the development of procedures and equipment for the cold-drawing, sizing, twisting, and packaging of the yarn was under the direct supervision of G. P. Hoff, who was then assistant director of the Rayon Research Division. The Engineering Department, under E. G. Ackart, had the responsibility for the construction of the pilot and large-scale plants.

"Many difficulties in working out the process elements of all these operations on a laboratory and semiworks scale were encountered. No similar previous experience with the types of processes employed for these intermediates existed in the company. Nylon polymer was an

<sup>1</sup> Became president of E. I. du Pont de Nemours & Company in 1948.

entirely new material with properties different from those of any previous synthetic product, and spinning it from the molten polymer was entirely different from spinning either acetate or viscose rayon. Information was therefore acquired only by painstaking experimentation at each step. The ingenuity and talents of some of the best chemists and chemical engineers within the company were needed to bring the development work to a successful conclusion.

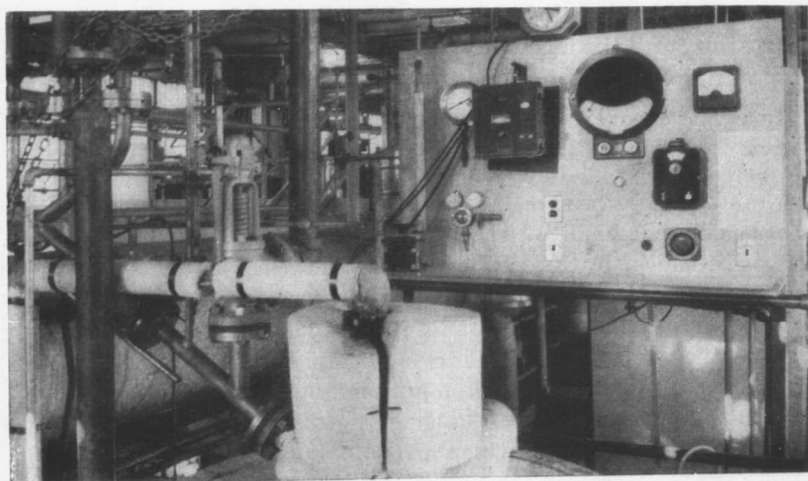


Fig. 3. 1938—A pilot-plant autoclave was the next step. This autoclave permitted the first production of large amounts of fiber for mill evaluation in production runs.

### Final Process

“The process as finally developed for the manufacture of nylon and its fabrication into yarn may be briefly outlined as follows: For the present type of nylon, adipic acid and hexamethylenediamine are combined to form a salt which is charged into an autoclave where polymerization is carried out. Stabilizers are added to control molecular weight and viscosity. In this reaction a long-chain linear polymer is formed with a molecular weight of 10,000 or higher.

“After polymerization, the molten nylon is extruded as a ribbon onto a chilled roll, and the ribbon is cut into small chips. This is a convenient form for storing, handling, and subsequently blending various batches to ensure uniformity of the product.

“The nylon chips are charged into the hopper of the spinning unit and drop onto a specially designed heated grid where the polymer melts. The melt is pumped and metered by specially designed pumps

and finally filtered through special filter packs before passing through the spinneret to form filaments. All parts of the equipment must obviously be maintained at a temperature above the melting point of the polymer, which is blanketed with an inert gas to prevent any undesirable effects from oxidation at the elevated temperature.

"By the pressure of the pumps, the molten nylon is extruded through spinnerets. The filaments, which harden quickly on striking the air outside the spinneret, are wound up on bobbins by special take-up and traverse devices operated at a thread speed of over 2,500 ft per min.

"At this stage the filaments are in an undrawn condition, and do not exhibit the excellent tensile strength and elasticity inherent in the superpolyamides. By the application of a suitable force, however, the nylon filaments are drawn out to about four times their original length. During drawing each filament 'necks down' and takes a smaller diameter, and after drawing retains this new dimension permanently. The fiber has become highly oriented and has a different physical structure, as can be shown by X-ray diagrams. It now has extremely desirable textile properties, particularly a high degree of true elasticity, combined with a tensile strength greater than that of any of the commonly used textile fibers. This cold-drawing of nylon yarn is done on equipment specially developed for the purpose.

"No complete picture can be given here of the numerous chemical and engineering problems which had to be solved in this development. Many types of spinning-cell melting grids were designed and tried before one was finally accepted which overcame difficulties incident to the very poor thermal conductivity of the polymer, coupled with the requirement that heated surfaces be maintained at a minimum operable temperature. Pumps for the molten polymer represent a development in their own right, inasmuch as they must be operated under severe conditions at the high temperature of 285°C, with small clearances and with no lubricant other than the polymer itself. Special abrasion-resistant steels that do not soften or warp at the temperature of operation were required.

"The entire spinning assembly involved radically new engineering developments to produce fibers of the required uniformity and with the other necessary qualities. Five different spinning units, each one embodying the newest ideas, were constructed before the pilot plant was erected."

In 1938 the first large-scale plant for producing nylon was started at Seaford, Del., and except for size, this plant "was practically a duplication of the semiworks plant in all details. Each step of the process and



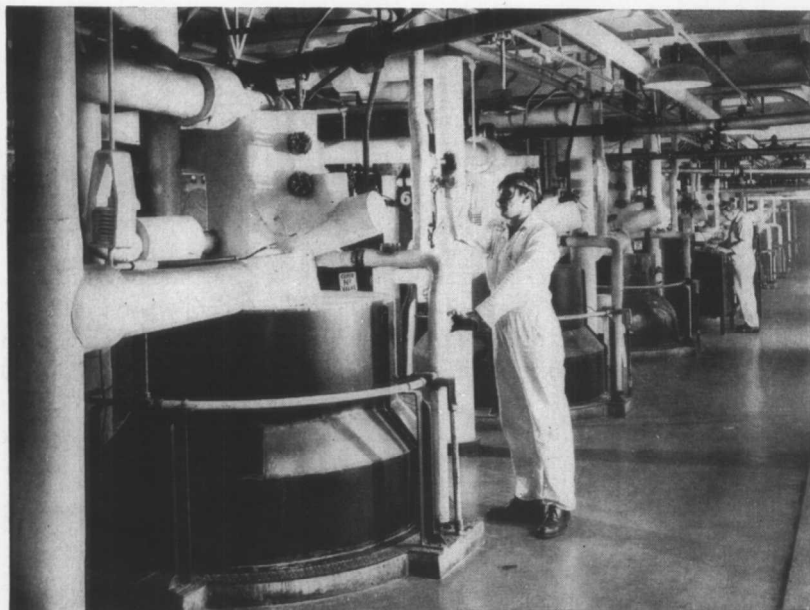


Fig. 4. 1939—Full-scale polymerization in tonnage quantities was the result of these huge auto-claves. They are a far cry from the glassware used by Carothers in 1930.

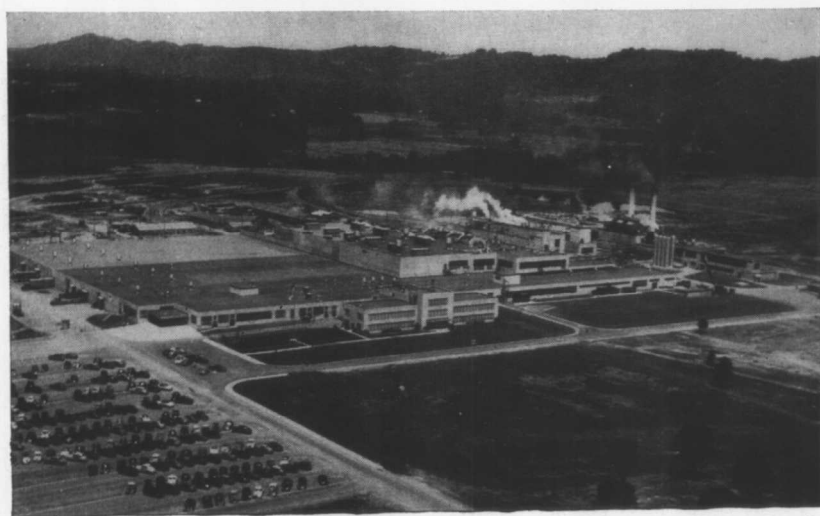


Fig. 5. 1948—Du Pont's third nylon plant, located at Chattanooga, Tenn., went into commercial production. The size of this plant was virtually doubled in 1950.