

# NYLON

## Industrial Chemistry's Glamour Girl

**N**YLON, a peacetime product which was ready for military service when the need arose, is an illustration of what can be accomplished by coordination of scientific research, engineering skill and industrial imagination. The specific product was the result of an expanded program of fundamental research in chemistry which was instituted by the Du Pont Company in 1928.

The original aim was to fill some of the gaps in the knowledge of important chemical processes and to explore new fields in this division of science—let the results be what they may. As head of a group to engage in this type of research, the late Wallace H. Carothers, a chemistry teacher at Harvard University, was chosen. He was surrounded by a small team of well-trained organic chemists and was encouraged to work on problems of his own selection. He chose the subject of polymerization, the process by which small molecules of a chemical unite to form larger molecules with new and different physical properties. This is a process found frequently in nature; for example, in the formation of rubber, the muscle of men and animals, certain other proteins such as casein of milk, and cellulose, the building material of the plant kingdom.

Dr. Carothers was particularly interested in long-chain polymers. One of the first practical results to come out of the studies of his group was neoprene, the synthetic rubber-like material now performing vital tasks in military equipment and production machinery. The researches of the late Father Julius A. Nieuwland on acetylene were an essential contribution to the development of neoprene.

Another phase of this research, more closely related to the eventual synthesis of nylon, involved a group of ring compounds known as macrocyclic esters, most of which were derived from castor oil. It was noticed that some of them had an appealing musk odor, and the work resulted in the production of synthetic perfume chemicals which are now produced commercially.

The group also worked with certain dibasic acids, including sebacic acid from castor oil, and alcohols of the type of ethylene glycol (used in radiator anti-freeze).

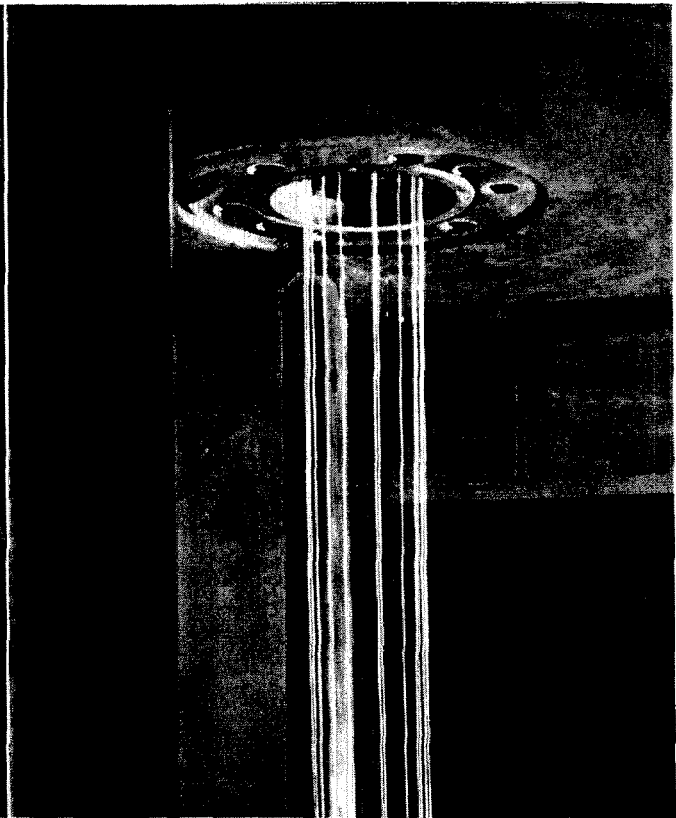
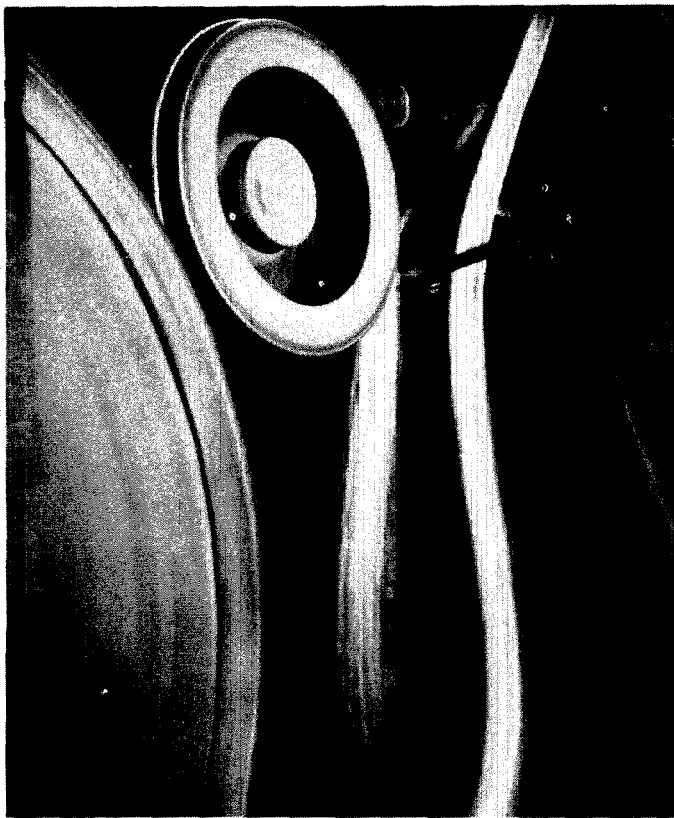
By G. L. BUSSARD

When heated in a molecular still, the acid and alcohol combined to form polyesters having molecular weights up to 25,000. Dr. Carothers called these "superpolymers." In the spring of 1930, in removing one of the "superpolymers" from the still, Dr. Julian W. Hill, one of Dr. Carothers' associates, noted that it could be drawn out into a thin strand, like taffy candy. But unlike taffy, it was not brittle when it cooled. In fact, the cooled strand could be further drawn out to several times its original length. This cold-drawing made the fiber more transparent and lustrous, and what is more important, imparted increased strength and elasticity. It could now be tied in knots without breaking.

At this point the course of the Carothers group, which was working under the direction of the chemical department, left the somewhat meandering path of theoretical research for the specific road of practical development. This was the real beginning, back in 1930, of nylon. But while the road to successful production of this synthetic product was straight, it was by no means smooth. Many different chemicals were tried out and finally a combination which was practical and potentially available in the United States was chosen for commercial development. This was adipic acid and hexamethylene diamine. Polymer from these chemicals was called "polymer 66," because there are six carbon atoms each in the diamine and the adipic acid.

The first nylon filaments were made by forcing the molten polymer through a hypodermic needle. One might spin a single pair of hosiery for a princess this way, but before yarn in commercial quantities could be produced a whole set of new machinery had to be designed and built.

In 1936, the year after "polymer 66" was developed, the rayon department of the Du Pont Company assumed sponsorship of the research. The laboratory at the experimental station continued to improve and expand its facilities for producing the new material, and each pro-



AT LEFT: Original casting wheel, part of the equipment constructed in 1937 to make some of the first nylon. This original wheel (made over from an engine flywheel) is still operating. Extruded in molten form onto the wheel, a segment of which is seen at the left, the nylon solidifies into a plastic ribbon and is then carried up over the small take-off wheel and between air jets in the "blower offer," which dry it. The ribbon is then chopped into flake, which is in turn spun into yarn. AT RIGHT: The birth of nylon filaments. From tiny holes in this spinneret are extruded filaments of nylon. Filaments shown here will be wound together to form nylon yarn.

cess improvement was acclaimed as proudly as a baby's first steps. In March, 1937, 50 batches were run and 86 hours of continuous spinning were reached. In April the first experimental stockings were knit from the new yarn, which still was known only as "fiber 66."

In January, 1938, a pilot plant was authorized, which meant that the laboratory grew into a small-size factory, while retaining its research organization, facilities and viewpoint. The new building was finished in July and production at once increased. Meanwhile toothbrushes bristled with the new material had been manufactured and they were placed on the market in the fall of 1938. The new material was christened "nylon," a name which itself was "synthesized" after several hundred suggestions had been submitted. It had no special significance. It was merely distinctive and easy to pronounce, and it became a new word in the English language, a name for an entirely new family of chemicals.

The Seaford, Delaware, nylon plant started production in December, 1939; women's nylon hosiery made from nylon produced in the pilot plant was put on trial public sale in Wilmington, Delaware, in October, 1939; was made available in all cities in the country on May 15, 1940, and immediately became a success. Approximately 64,000,000 pairs of nylon hose were sold during the first year. By the close of 1941 enough nylon yarn had been shipped to make approximately 175,000,000 pairs. Nylon was also used for women's undergarments, girdles, and gloves, and neckties, fishlines and leaders, football pants, tennis racket strings, brush bristles, surgical sutures, and other articles.

The above historical sketch is given as a background against which the present activities of the nylon research

laboratory and two nylon plants may be viewed.

Production actually starts, however, at the Du Pont Company's ammonia department plant in West Virginia, where high-pressure synthesis converts coke oven gases and coal tar fractions into adipic acid and hexamethylene diamine. One of the intermediate chemicals used is ammonia, which is also made by high-pressure synthesis. The elements entering into these compounds are carbon (from coal), nitrogen and oxygen (from air) and hydrogen and oxygen (from water). Hence the popular characterization of nylon as a product of coal, air and water.

At the West Virginia plant the adipic acid and diamine solutions are run together, in measured amount, into a stainless steel kettle. A reaction takes place and the two chemicals combine to form nylon salt, the scientific name of which is hexamethylene-diammonium-adipate.

For large-scale production the salt is in water solution to facilitate handling. It is run into tank cars, shipped to the nylon spinning plants and there piped to evaporators on the top floor to be concentrated to a certain salt percentage. The concentrated salt solution is put into a cylindrical autoclave and heated by "Dowtherm" circulating through a jacket and coils. ("Dowtherm" is a fluid which has a very high boiling point, vapors of which can therefore be circulated at high temperatures and low pressures.)

It is in the autoclave that the polymerization or linking together of small molecules into giant ones takes place. The nylon salt in solution is ionized and the diamine and dibasic acid parts are dissociated. Each of these parts may be considered as a short chain with a hook at either end. Under the influence of heat the hooks unite with each other. First a diamine unit hooks

up with a dibasic acid unit. This leaves a diamine type hook at one end and an acid hook at the other end of the new molecule. Again a diamine and an acid hook unite, with the formation of a longer molecule. This linking up continues until extremely long molecular chains or polymers are formed. This particular variety of polymer, containing many amide groups, is known as a polyamide.

Theoretically this polymerization might continue until chains of infinite length were formed. However, the desired consistency can be obtained by carefully controlling the temperature and the duration of the process and by the introduction at the proper moment of a chemical, "a stabilizer," which closes the "hooks" at the ends of the molecules and prevents further linkages.

When polymerization has been completed a slot in the bottom of the autoclave is opened and the viscous material is allowed to flow out on the surface of a broad, slowly-revolving wheel, termed a casting wheel (illustrated). A shower of water causes the polymer to harden into a translucent, milky-white ribbon. Two rows of air jets dry the ribbon as it leaves the casting wheel en route to the rotary cutter, which chips it into flakes. The flake is subsequently dried to a specified moisture content.

The next step is to blend the flake from several autoclave batches, to insure uniformity, and then to pour the blended flake into the spinning hoppers. Each charge of flake in the hopper is purged of oxygen by passing into it a blast of pre-purified nitrogen (nitrogen with an oxygen content of less than five-1000ths of one per cent). The nitrogen is then removed by vacuum and this "washing" process is repeated.

The valve at the lower end of the spinning hopper is now opened and the flake falls onto a melting grid, which looks much like the coiled heating unit of an electric cooking stove. Here again, circulating "Dowtherm" sup-

plies the heat. The molten polymer passes through the grid into a funnel-shaped melt chamber from which it is squeezed by a special gear pump into and through the spinneret assembly.

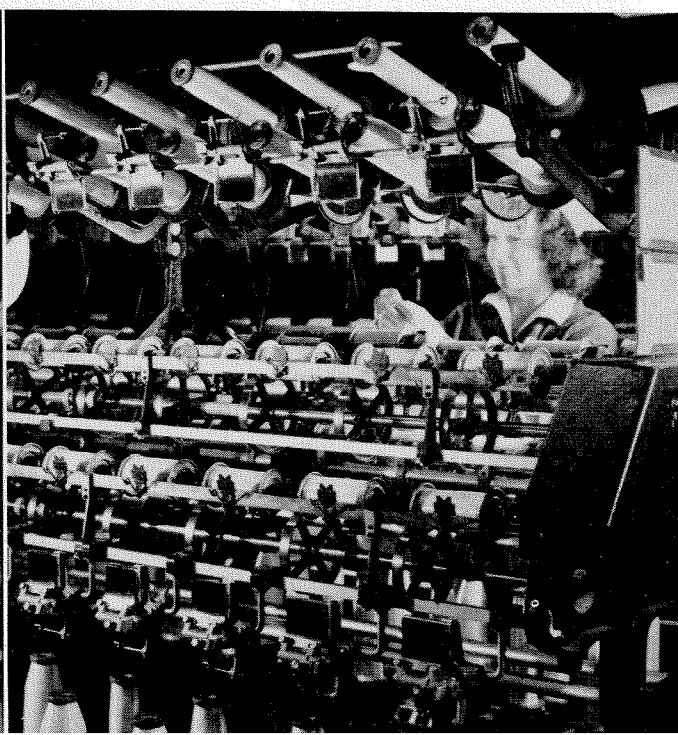
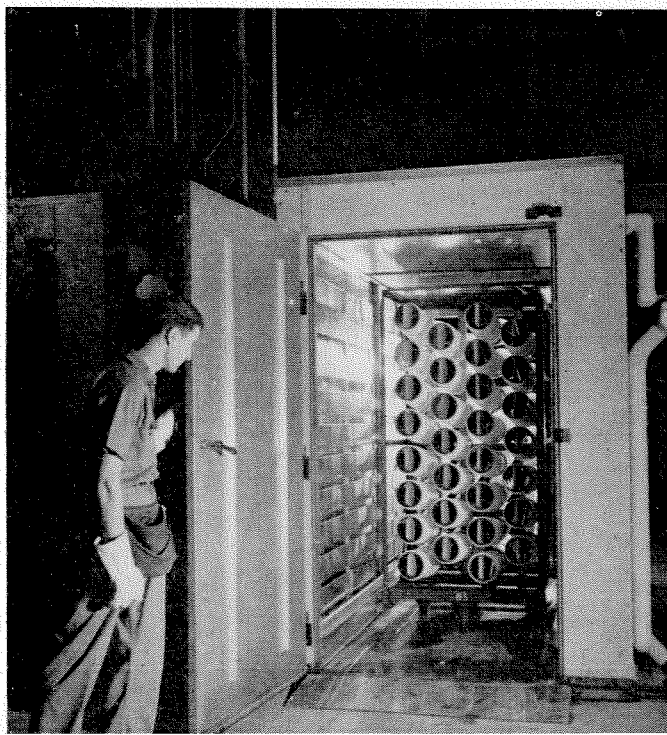
Both the pump and the spinneret are very important parts of the spinning machinery. The pump must squeeze all the bubbles out of the viscous polymer and must deliver it to the spinneret at a constant rate to insure uniform denier or thickness of the filaments. The spinneret itself is a thick disc of metal about the diameter of a silver dollar and it is pierced with fine holes, flaring out like tiny funnels at the upper ends where the polymer starts through. Before the polymer reaches the spinneret plate, however, it is filtered through a layer of sand, to insure smoothness and purity. In early experiments the filter was a layer of phonograph needles, packed together, points up, to give an assemblage of roughly conical passageways. But metal corrodes and is difficult to clean. Cloth filters would be destroyed by heat. Sand was chosen, therefore, because it will withstand high heat and because it is cheap and easy to handle. Spare spinneret packs, already heated, are kept on hand in a heated rack much like a restaurant steam table.

As the thick syrupy polymer is squeezed through the holes of the spinneret (illustrated) the filaments are formed, at the rate of about 1,000 to 3,000 feet per minute, and are air cooled. The filaments then converge and pass into a conditioner which moistens them sufficiently to make them stick together as a single strand.

During the windup process the yarn passes over a lubricating roll, which puts a finish on the surface. This also helps the filaments stick together and prevents the accumulation of static electricity.

The yarn is next pre-twisted, and several strands or "ends" may be plied together at this point to make a heavier denier yarn. Denier is a term relating to the

**AT LEFT:** Batteries of machines (see illustration, page 5) wind nylon yarn onto spools after filaments have been extruded from the spinnerets. Nylon yarn is "baked" in large "twist setting ovens" like the one illustrated, before it is wound on spools and cones for inspection and shipment. **AT RIGHT:** Spools of nylon getting their last windup before being shipped to converters and throwsters. This machine is one of a large battery now engaged in getting the yarn ready for shipment as rapidly as it can be manufactured.



weight, and therefore indirectly the fineness of yarn, particularly synthetic yarns. A one-denier fiber is one of such size that 9,000 meters of it (9,842 yards) weigh only one gram. A one-denier filament of nylon has a diameter of about one 2,500ths of an inch.

Up to this point the yarn has undergone no real physical change since it was first formed upon emergence through the spinneret. But now it is drawn, or stretched, by traveling between rolls revolving at different speeds, so that it becomes several times its original length. This cold-drawing makes the long-chain crystalline molecules of nylon snap out of their helter-skelter arrangement and line up parallel with each other and close together. This increases the opportunity for powerful intermolecular forces to come into play and the result is an exceedingly strong fiber. After the "draw-twisting," as this operation is termed, the yarn is again twisted and then, if desired, it is sized. An important sizing material used to protect the yarn during subsequent textile operations is polyvinyl alcohol, another synthetic polymer. The yarn is then twist-set in a steam oven (illustrated). This relieves the internal stresses, in a manner somewhat similar to the annealing of steel or glass, and prevents the yarn from kinking.

A number of tests are given the nylon to insure maintenance of strict standards. One of them is known as the creel mirror test. Several hundred spools are set up on a rack or creel and the ends are brought down in a broad band of parallel threads. These pass into a darkened booth. Here they are viewed almost end-on in a

raking light, which throws long shadows and thus shows up the little irregularities and snarls that indicate broken filaments. The principle is the same as that which causes small pebbles in the road to stand out prominently in the low, straight-on beam of the headlight. A check is made of the number of broken filaments per 1,000 yards of yarn.

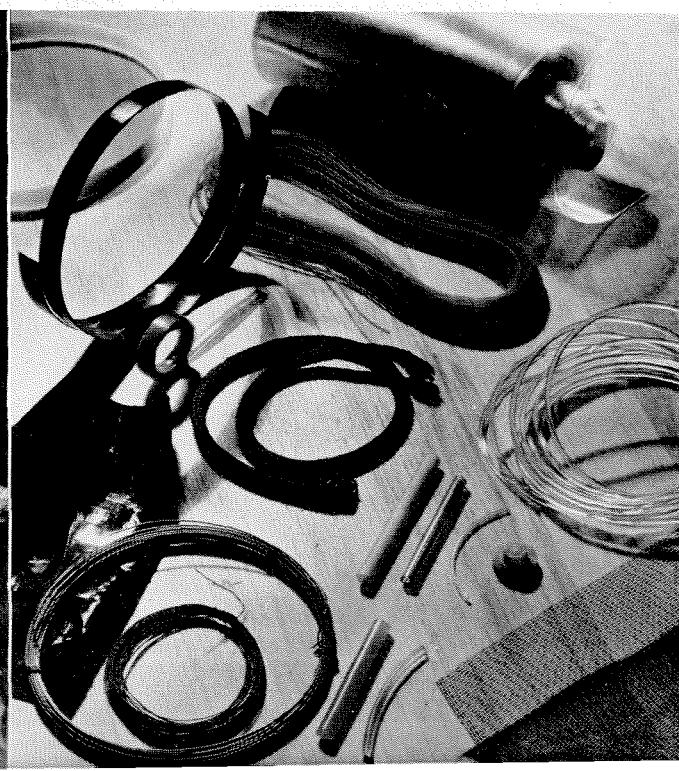
Another test, in which the yarn is made to support a weight attached to an indicating pointer, reveals the strength or tenacity and the percentage of elongation.

The nylon divisions' product development men became interested in nylon as a possible replacement for silk parachutes early in 1940, started an intensive program early in 1941 and had a product ready to do the job when the Pearl Harbor attack December 7, 1941, severed all connection with Japan and Japanese silk. Both nylon plants (a new one began operation at Martinsville, Virginia, in the fall of 1941) were diverted entirely to production for government purposes in February, 1942.

Some of the war uses for nylon are confidential and strategically important. But it is no secret that nylon supplies not only the canopy cloth of parachutes, but also the tapes, shroud lines and certain of the harness webbing and belting. Nylon rope is superior to any other existing fiber with respect to strength, lightness and durability. It has the additional property of elasticity, which makes it suited to such an application as the tow rope for gliders picked up by airplanes in a new maneuver which the Army has tried out. Nylon is also being

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**AT LEFT:** Some of the numerous new nylon products. Arranged clockwise, beginning at the paintbrush with tapered nylon bristles, are: parachute harness webbing, parachute shroud lines, heavy nylon rope for military gliders, cargo parachute cloth, camouflaged Army Air Force escape parachute cloth, and light nylon rope. Centered in the photograph are, left to right: experimental molded nylon plastic bearing, carburetor diaphragms of nylon fabric, and surgical sutures. **AT RIGHT:** Some of the plastic forms nylon takes, together with a few of its newest uses as a synthetic fiber. From top to bottom are shown extruded strips of the plastic, coated fabric made by applying nylon in solution, insulated wire, and a coil spring. In the center, from top to bottom, are: nylon film, extruded rattan, braided machinery packing made from the fiber, various sizes of extruded tubing, and two rods. At the right of this view are a coil of narrow tubing, an electric motor bearing of the plastic, and nylon window screen.



and accurately controlled. The result is a heat-treating technique which is very precise, yet flexible and adaptable to production processes, particularly with small parts.

An entirely different problem which also is solved with the high frequency oscillator is the problem of heating an insulating material such as plywood. In making large thicknesses of plywood, the problem of heating the wood uniformly in order to bond the sections together is rather difficult. However, if the wood is placed in a high frequency, high voltage electric field, heat will be produced uniformly throughout its thickness and bonding will be completed in much less time than with the usual steam press. Since the heating does not come from outside, there will be a uniform treatment throughout the wood and a more satisfactory product should result. Such "dielectric" heating may be applied to plastics of various sorts, and even, on a mild scale, to the human body. Diathermy machines have proven of considerable value to medicine.

Electronic control and measurement devices are too numerous to attempt to give more than a few general ideas as to their nature. First we might mention the direct control of a current by an electronic switch which is opened and closed automatically at precise instants of time. An example is the control used with resistance welding equipment. Second, the direct control of a motor. Various kinds of devices are available to control the speed and direction of small motors. Third, the use of photoelectric devices to operate relays or other equipment when a light is turned on or off, or two colors are matched. All sorts of counting mechanisms operate photoelectrically. Burglar alarms, smoke alarms are often photoelectric. Fourth, the use of amplifiers to

increase a small control-signal up to the point where it can accomplish some desired result. The signal may come from a distant radio station, from a telephone, from the pounding of a fly's footsteps on a microphone, or from any conceivable electrical source. Fifth, electronic means to measure such quantities as time intervals as short as a millionth of a second, dimensional changes as small as a millionth of an inch, or to measure frequency, or count objects at speeds as high as 10,000 per second. Sixth, in a class by itself, the cathode ray oscilloscope, an instrument which can be used to visualize any transient or recurrent electrical phenomena, and which is thus of the utmost value in the analysis of complex electrical circuits. Furthermore, it can be used to great advantage in such diverse applications as the analysis of pressure variations in a gas engine cylinder and the measurement of the speed of rotating machinery, or it can serve as a remote position indicator. In electrical circuits it may be used as voltmeter, ammeter, phase-meter, frequency-meter, and modulation-meter.

As the possibilities of these circuits and gadgets become more widely appreciated, it is reasonable to expect that a great many new applications and devices will appear. When the full story of wartime industrial developments becomes known, it will be found that electronics helped to keep many a production schedule and to break many a production bottleneck.

Among the contributions of the twentieth century to technology, the vacuum tube must surely earn a place near the top of the list. Starting as a scientific curiosity it founded an industry which affected our lives almost as much as the automobile. Now doing its part in winning the war, it will prove useful in peace, not alone in its own field, but as a veritable handmaiden of technology in all its branches.

## Nylon

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made, on an experimental scale, into tire cords, and tests indicate that it is by far the strongest fiber yet found for tire fabrics. In addition it permits the saving of weight and rubber in the manufacture of the tire, and it is particularly suitable where the tire undergoes severe punishment. The strength and adaptability of nylon in various forms—filaments, bristles, "wire" for experimental nylon window screens, sheets and molded plastic articles—indicate that its future should be as brilliant as its past.

One of the most interesting new projects developed in the nylon research laboratory is in connection with the nylon salvage program. This was undertaken because of the urgent need for more nylon for government use. The high-pressure synthesis equipment which makes nylon chemicals from coal, air and water, is already taxed to capacity, and to make additional equipment would require large amounts of strategic metals needed for airplanes, ships and ordnance. The logical alternative was to salvage nylon scrap and make new nylon out of it, and several months ago the Du Pont Company launched such a scrap campaign, offering to buy waste yarn from textile mills and waste dealers. Collection of this material is under government direction.

The waste nylon material is subject to a series of chemical treatments.

It will be, in effect, chemically "unraveled" until you arrive at the original two starting chemicals from which

it was made—adipic acid and hexamethylene diamine.

First step is to boil the nylon scrap in a strong hydrolyzing agent. In the laboratory demonstration this is done in a glass flask, to which is attached a reflux condenser. On a plant scale it is carried out in a lead-lined vessel. By the end of the first hour of boiling the fabric has completely disappeared and the vessel contains only a dark brown solution. A precipitate forms on cooling.

Filtering through a glass fabric separates the precipitate, which contains the adipic acid, from the filtrate, which contains the diamine.

Each of the two components is now purified. The adipic acid, which is a powder and in the unpurified form may be any color depending on the amount of impurities present, is redissolved and recrystallized and is then treated with decolorizing agents. These steps yield a pure final product. The diamine solution is neutralized by addition of lime, which produces a precipitate of calcium sulfate. The mother liquor is drawn off and the water distilled off to leave the diamine. The diamine, which has a higher boiling point than water, is now distilled and it condenses as a colorless liquid, which becomes crystalline on cooling. The "reverse synthesis" of nylon into its chemical components is now complete.

As mentioned previously, the future is expected to find an ever increasing number of uses for this interesting product. For the present, however, all efforts of those concerned with the production and improvement of nylon are centered on making its contribution to the winning of the war as full and complete as possible.