Spring 5-16-1960

An Approach to Plastics with a Discussion of TEFLON and Its Medical Application

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AN APPROACH TO PLASTICS WITH A DISCUSSION OF TEFON
AND ITS MEDICAL APPLICATIONS

by

David Kramish

M.D., University of Colorado, 1943

A Thesis submitted to the Faculty of the Graduate
school of the University of Colorado in partial
fulfillment of the requirements for the Degree
Master of Science
Department of Surgery

1960
This Thesis for the M.S. degree by

David Kramish

has been approved for the

Department of

Surgery

by

[Signature]

David H. Watkins

Date 16 May 1960
As the future in surgery begins to unfold, there is no doubt that synthetics will play an important role. The stage has been set experimentally and the clinical application of these materials will provide as fantastic a finale as any dramatic production. Of all the plastics there singularly exists one material which demands a leading part because of its unlimited medical possibilities—this material is TEFLON.

Within this thesis the stimulating story of "plastics" is revealed in such a manner that historical interest chronologically precedes but is no more significant than definition or classification. One has only to briefly review the chemistry and properties of TEFLON to appraise its superiority and to appreciate my insatiable curiosity to investigate its potential as a prosthesis. Unavailability has lead to the development of methods and the problems associated therefrom. Nevertheless, prostheses of TEFLON were used to bridge defects in various hollow viscera of laboratory animals with gratifying results, and the clinical implication of these successful experiments cannot be underestimated.

This thesis is dedicated to the purpose of associating a knowledge of "plastics" with medical ingenuity in the hope that this combination will lead to visionary advances in the field of medicine which may be of some benefit to mankind.

This abstract of about 200 words is approved as to form and content. I recommend its publication.

Signed

Henry Swan, M.D.
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INTRODUCTION

The plastics industry is a young industry and is growing more rapidly than most other American industries. It is expanding at an astonishing rate both in the number of different materials commercially available and in the fields of their applications. Today, judged by total sales, it comprises one of the few billion dollar industries and its growth has been so rapid in recent years that public acceptance has out-stripped public knowledge.

Few people have any insight into the dramatic and extraordinary roles that plastics have been playing in the field of medicine. Most of us have heard about the pill-boxes of acetyl-cellulose acetate with which soldiers are supplied—containers so strong that a man could stamp on them without crushing them, yet so easily opened that a wounded man can even slide open the cover with his teeth. Many of us are acquainted with the Lucite shields and windows used in incubator covers and oxygen tents, and the Lucite parts for stethoscopes, cystoscopes, sigmoidoscopes, otoscopes and other diagnostic medical instruments. But how many of us know that the development of methyl methacrylate has meant greater eye protection in many more ways for more people than has been possible through the medium of glass. It has made possible the construction of contact lenses—something impossible with glass owing to the risk of breakage and irritation to the eyeball itself, and the development of night-vision goggles for pilots. Industrial eye injuries have been reduced to a vanishing point by the development of non-snar­tering, non-fogging, adjustable lenses made of cellulose acetate used to protect their eyes from dust and flying bits of metal. The price of effective hearing aids has been reduced from about $150 to $40 by the use
of polystyrene to replace metal in the manufacture of the amplifier unit, and methyl methacrylate in the magnetic earphone. Few surgeons realize that the property of fine sensitivity and good elasticity of their rubber gloves was attributed to a new elasto-plastic called Marvinol. Nylon catheters and sutures, vinyl transfusion and drainage tubes, as well as cellulose-acetate brain and tonsil probes and tongue depressors are a few more of the applications now being made with plastics in the medical field.

Plastics subsequently invaded the human body, and medical investigators conducted experiments to test the tissue reactivity and tolerance of the various available materials—namely, nylon, dacron, orlan and ivalon—and investigated various areas of the body and pathological conditions in which synthetic materials could be sued to replace tissues damaged by injury or disease. It soon became clearly evident that synthetic arterial grafts were superior to homografts and less expensive. Since the introduction and success of the Edwards-Tapp nylon artery graft, there has been a drive to find a "superior material"—one that more completely fulfills the criteria of an ideal graft—namely, low tissues reactivity and retention of strength with age. The introduction of tetrafluoroethylene—TEFLON—by E.I. du Pont Nemours and Company fulfilled these requirements. There is voluminous evidence supporting the fact that TEFLON stands out so far beyond any other known "material" that the claim for its unapproachable superiority is made unreservedly.

My interest in the field of "medical plastics" began about two years ago when I made a comprehensive review of all the available literature on commercial plastics in an effort to find a material suitable for bridging defects in the cervical esophagus following radical extirpational surgery
for carcinoma of the larynx and hypopharynx. This survey introduced me to TEFLON and the general field of fluorocarbons. Consequently a considerable amount of time and energy has been expended in evaluating these substances and their applicability for medical research and clinical investigation.

This thesis may, therefore, be said to serve a two-fold purpose: first, to relate the fascinating and interesting story of the plastic industry and to acquaint the reader with the various forms of plastic materials that are available commercially; and second, to present the subject of Fluorocarbons in a semi-technical manner emphasizing their chemistry, properties and projected medical applications.
PART I

THE STORY OF PLASTICS

WHAT ARE PLASTICS?
Three wars and a major depression produced the plastic industry and gradually lifted plastics from the status of a chemical novelty, used in the manufacture of billiard balls, to a new scientific frontier of first rank in our national economy. Today, there are more than thirty-two different kinds of plastics and thousands of articles are manufactured with these magical materials. A billion pounds of plastics are produced each year in the United States alone. Although most of us think this laboratory miracle as a twentieth century discovery, the plastics industry, through a curious strain of circumstances, may be said to owe its existence to the Civil War.

America had few games prior to the Civil War. Golf did not exist. Baseball had been invented but it was still called "rounders" and was chiefly played by boys of teenage. Workingmen labored fourteen hours a day and had neither the time nor energy for games. Country folk tossed horseshoes. "Gentlemen" played croquet with the ladies at garden parties, went hunting or yachting, and during the winter months they played cards or billiards.

The end of the Civil War brought a surge in business, social entertainments became lavish, and every new mansion included a spacious library - with one or more billiard tables. Billiards had been regarded as a gentleman's diversion ever since John Quincy Adams installed a billiard table in the White House in 1828. After the Civil War, the ownership of a billiard table came to be regarded as proof of social distinction, much as the swimming pool later became "de rigueur" for a Hollywood star. This added up to a shortage of billiard balls, which were made of ivory.
Within three years after Abraham Lincoln's death the billiard-ball shortage had grown so acute that Phelan and Collandar, merchants of New York, offered a $10,000 prize to the resourceful person who could invent a satisfactory substitute for ivory. A young man by the name of John Wesley Hyatt of Albany, New York, a printer by trade, heard of the offer and set to work experimenting along lines of his own. By grinding bits of wood, paper and rags, he hoped to produce a pulp which he could mix with shellac or glue and form into balls. He was on the right track. The resiliency and strength of wood lies in the fact that it is composed of tiny cellulose fibers held tightly compressed together by the natural resins of wood. But he needed a more powerful binder than either shellac or glue. In the course of his experiments he mixed cellulose, nitric acid and sulphuric acid, and got nitrocellulose. He was not a chemist and did not know that at this point he might have blown himself and his makeshift laboratory to kingdom come. Nitrocellulose is a satisfactory explosive when sufficient heat and pressure are applied, and it is used in the manufacture of smokeless powder.

A guardian angel seems to hover over young inventors, and Mr. Hyatt was especially favored. At this critical point, he conceived the idea of mixing solid camphor with his preparation. Then he discovered that nitrocellulose becomes solvent in camphor. Thus, when heated, his camphorated cotton pulp could be molded into any desired shape, and when cold, it became strong and hard and could be easily machined. So, in 1868, the first plastic came into being. Mr. Hyatt called it Celluloid. He didn't win the $10,000 prize, but a little later on he did win a new partner, Charles A. Seeley, who was interested in making, not billiard balls, but dental plates. Together, they launched the Albany Dental Plate Company.
Hyatt added pink coloring to his celluloid for the manufacture of dental plates, and overnight the business received an avalanche of orders for not only dental plates but also other articles that could be made with celluloid. A year later the Celluloid Manufacturing Company was organized to handle production. In 1872 the plant moved to Newark, New Jersey, where the manufacture of celluloid collars, cuffs and shirt fronts for men began.

The infant company grew fat with profits, enjoying a virtual monopoly of celluloid articles and a great variety of products were added to its list. Further experimentation revealed that celluloid could be developed as an imitation amber, mother-of-pearl, coral or tortoise shell with equal success. Consequently, the prosperous factory was too busy filling orders for anyone to give much thought to the question of research and study of the basic formula of celluloid. The wondrous secrets of cellulose for other plastic formulas were to remain undiscovered for more than fifty years.

In the meanwhile, Leo Hendrik Baekeland, a student at the University of Ghent in Belgium, was startling his professors by his brilliant work in chemistry. At the age of twenty-four he became professor of chemistry at the University of Bruges, and promptly won the first prize in chemistry in a competition among the alumni. The award included a traveling scholarship, and Dr. Baekeland subsequently sailed to America.

The year was 1889, and young Dr. Baekeland had no thought of becoming the father of plastics in the United States. He was absorbed in photography. He shortly developed Velox, a photographic paper which utilizes a special colloidal chloride of silver, enabling it to be exposed and developed very rapidly and conveniently. Soon afterward
he launched the Nepera Chemical Company to handle the manufacture of Velox. Ten years later he sold George Eastman, the inventor of kodaks, the rights to his process for the interesting sum of $1,000,000.

Dr. Baekland indulged himself to the extent of building a small, makeshift laboratory at his home in Yonkers, New York, and diverted himself with experiments in electro-chemistry. While experimenting with mixtures of phenol and formaldehyde, from which he hoped to produce a synthetic shellac, he found that the last mixture had thickened to the consistency of cold molasses and could not easily be poured from the test tube. He was in the habit of cleaning his tubes after each experiment and using them again and again for new trials. The acquisition of a million dollars had changed his laboratory habits not one iota.

Dr. Baekeland applied heat to the tube and shook it impatiently with the idea of melting the heavy syrup quickly so he might clean the tube. The syrup became as hard as a rock. Disgusted, but still determined to salvage the tube for another test, he applied solvents in an effort to melt the hard substance and wash it from the tube. To his astonishment, he found that he might as well have splashed water over the rigid lump. Now his curiosity was aroused. Manufacturers had long been seeking a shellac that would be impervious to solvents. He went back over his experiment step by step. He had used equal molecular proportions of phenol and formaldehyde in the presence of an alkaline catalyst. Then he had applied heat and shaken the tube. The syrup had become rocklike, and could not be reduced to a syrup again by the application of additional heat or by the use of solvents.

Clearly, if the mixture could be made to harden gradually without the application of heat, he would have the long-sought synthetic shellac.
Further experimentation showed that the formula could not be adapted for this purpose. He was disappointed; however, he began to study the curious, dark, rigid substance he had created. He discovered that it had many virtues. It was lighter in weight than metal or stone. It was very strong and yet could be machined. It was chemically resistant and would not corrode or rust. He found that when the compound was in its liquid state, it could be poured into a mold, and the application of heat to the mold would make the compound "set". The net result was an article exactly the shape of the mold. He also discovered that fillers could be added to his compound that improved its tensile strength, and incidentally, stretched the compound in an economical manner, increasing its bulk at low cost.

In 1907, Richard W. Seabury, the general manager of the Boonton Rubber Company, heard about Dr. Baekeland's curious resin, and asked him for samples. The Boonton Rubber Company was engaged in the manufacture of molded articles made from reclaimed rubber. The resourceful Seabury, himself, a creative chemist of a high order, decided to blend Dr. Baekland's resin with a filler of asbestos fibers and find out if the compound would yield the kind of material needed for the manufacture of electrical parts. The experiment proved eminently successful. Thus, in 1907, Bakelite, as the new substance was called after its creator, made its debut.

An immense step had been taken toward launching the plastic industry, for bakelite was shortly to be used in the manufacturing of telephones and telephone equipment, thereby acquainting the average American with a new substance that was neither metal, stone, wood nor glass, and paving the way for the sale of other articles made of this
material. Most people were favorably impressed by this laboratory product. It did not feel cold and clammy to the touch as did metals, nor chip and break like glassware, nor become worn and splintered like wood. But it was dark and uninteresting in color and texture and did not capture the imagination.

The progress of the industry was to be slow at this period. Cartoonists were making fun of the American celluloid collar and cuffs for men. There had been some unpleasant accidents in connection with the use of celluloid toilet articles in the home. All of the early celluloid products would quickly ignite and explode when exposed to an open flame. Women of this era were in the habit of curling their hair with curling irons which they heated over a lighted gas jet. Now and then a woman would become careless and pick up a curling iron while still holding a celluloid comb in her hand and lift the curling iron to the gas jet, thus bringing the comb too close to the open flame. A serious burn, blindness, a facial disfigurement, and, in some instances, death followed. If these articles were among furnishings that had caught fire, the fumes in the room would become deadly and the firemen would quickly lose consciousness. So many firemen lost their lives in this manner that editorials were written about it. America's first plastic was under a cloud. And bakelite, though as safe as asbestos, had none of the colorful, adaptable qualities of celluloid to win widespread popularity.

Then came World War I, and the picture began to change. The explosives behind the bullets, shells and grenades used in this war were very different from the powders that had been used in the Civil and Spanish-American Wars. The smokeless powder was related to
nitrocellulose compounds which may be adapted to a great number of non-military uses. The old powders were made of sulphur, potassium nitrate and charcoal, and were of little value except for the manufacture of explosives. This development in munitions was to have a critical bearing upon the growth of the plastics industry. E.I. du Pont de Nemours and Company became thoroughly familiar with every phase of the production of nitrocellulose. When the world conflict drew to a close, the chiefs of the giant chemical company were obliged to ponder on the continued activities in a peace time world.

The DuPonts resolved to put their faith in the American woman and her fondness for materials as soft as silk. The shells that burst so effectively over the Marne in France owed their explosive force to nitrocellulose powders which are made by mixing nitric acid, sulphuric acid and cellulose. Rayon, made by the Chardonnet process, is manufactured by mixing cellulose in nitric and sulphuric acid, dissolving this product in alcohol and ether, forcing the final mixture through tiny holes, and hardening the spray in hot air.

E.I. du Pont de Nemours and Company promptly purchased the North American rights of a French company already engaged in the manufacture of viscose rayon, adopted still newer processes that made the final product far less costly to manufacture, and relied on progressive merchandising tactics to induce women to buy more rayon materials. So it turned out that a generous slice of the 1914-1918 munitions profits were spent during the post-war years persuading Mama to buy a new dress to wear to church on Sunday.

Meanwhile, the Du Ponts took a fresh interest in the Arlington Company, makers of a product called Pyralin, another nitrocellulose
plastic. They had taken over the Arlington Company in 1915 during the scramble for materials needed to meet war contracts, and now regarded the organization with new favor. Large research staffs were hired to find new ways of using nitrocellulose plastics. New customers were located for Pyralin products, including Dr. West for toothbrushes, Parker's fountain pens, and the Woolworth Company which had an ever increasing demand for combs, babies' toys and kitchen gadgets.

In 1925 the Du Ponts purchased the Viscoloid Company, makers of another cellulose plastic called Viscoloid and used for manufacturing frames for brushes, mirrors and other dressing-table articles. Once again the average American was being accustomed to the use of a material that was neither metal, glass, stone nor wood. The word "plastic" was not familiar to most Americans in the twenties.

The Du Ponts made dynamic drives in other branches of the plastics field, pioneering a Pyroxylin binder for the manufacture of safety glass; Duco, the marvelous nitrocellulose lacquer for automobile bodies; Fabrikoid, an artificial leather made of cotton treated with a lacquer similar to Duco and used for making handbags, traveling bags, book bindings, etc., and the sparkling merchandising aid - Cellophane - a viscose rayon made in transparent sheets instead of thread form. During the 1930's they promoted the use of plastic door handles and numerous plastic gadgets for automobiles supplied by Fisher Bodies.

All in all, the predicament of the munitions company at the close of World War I proved a blessing to the plastics industry. The tremendously expensive task of promoting and selling plastics to the American people during the 1920's was accomplished chiefly by the Du Pont millions, and other manufacturers took heart and entered the field.
By 1929 four new plastics were placed on the market: Casein, a skimmed-milk product invented by W. Krische and Adolphe Spitteler in 1897 and developed by George Morrell Corporation in 1919 for the manufacture of inexpensive buttons and buckles; the alkyd resins (which revolutionized the paint industry), launched by the General Electric Company in 1926; Cellulose Acetate, a new member of the nitrocellulose family with a few of the explosive, inflammable propensities of its parent, introduced by the Celluloid Corporation in 1927, thus interrupting that organization's fifty-seven-year promotion of celluloid. Most important of all was the presentation of Urea (better known as "beetle") by the American Cyanamid Company in 1929. This powerful plastic has many of the virtues of Bakelite, can be made in brilliant colors, and can be developed also as a translucent material suitable for making electric-light fixtures. By 1930 more than twenty-five million dollars worth of plastic materials was being sold annually in the United States.

The plastic industry was fortunate during the depression years in that the boom in radio was halted only temporarily, and when it regained its momentum, modern low-priced sets in plastic cabinets ran away with sales. The growth of this industry carried plastics on the crest of its wave.

The depression itself created a new demand for plastics. The toothpaste manufacturers, soapmakers, cereal and food processors turned one by one to the plastics field for bright novelties that could be used as premiums to sell their products. In 1932 a toothpaste manufacturer started this trend by buying 2,000,000 bathroom tumblers to be given away with a new antiseptic mouthwash. His sales shot skyward, for the tumbler was attractive and light weight, would not splinter and break
into tiny pieces as would glass, and came in a variety of colors. The purchaser could choose a tint that harmonized with the bathroom color scheme. Most important, the plastic tumbler ended the age-old threat of broken glass or china on the bathroom floor where the bare feet of youngsters might encounter it. The plastic tumbler was safe. American housewives who might never have owned an article made of plastic until now were delighted with this innovation.

General Mills took the hint and ordered a plastic "Skippy" bowl to be given away with the purchase of two packages of Wheaties. Once again its appeal to the customer was the fact that it was safe for young hands and could not be easily broken. Children liked it because it was light weight and colorful. Grocers liked it because it made an effective window-display piece. During the next three years General Mills gave away nearly 30,000,000 plastic premiums - such as measuring spoons, cups, cooky cutters, children's toys— or about one to every home in the United States.

National advertisers began to flock to the doors of plastics firms seeking ingenious articles that could be used for premiums. General Foods ordered 8,400,00 Mickey Mouse cereal bowls. Then they ordered coffee spoons to boost the sales of Maxwell House Coffee. This was followed by measuring spoons for Calumet Baking Powder and Swansdown Cake Flour customers. The B.T. Babbitt Company devised a plastic container for their cleanser cans, which their customers might purchase for an extra twenty-five cents each. Soon the Babbitt container sales were over 1,000,000. Lipton's Tea, the Borden Company, the A & P and Kolynos Tooth Paste were also among those firms that became plastics-conscious and ordered novelties to be given or sold to customers.
This decade of feverish activity had a number of long-range effects. Every large chemical firm prodded its research staffs and advanced precious sums for experimental work. One by one, new plastics made their appearance on the industrial horizon. The Hercules Powder Company came forth with Ethyl Cellulose in 1935 - a flexible lacquer, extremely useful as a tough wire coating owing to its resistance to moisture. Two years later the Dow Chemical Company entered the field with Ethocel and Ethofoil. Then came the dramatic eye-attracting acrylics in 1936.

Dr. Otto Rohm uncovered the acrylic resins when engaged in research in 1901, but did not develop them until 1931, and then only for coatings and for bonding safety glass. Not until 1936 and 1937 did Rohm and Haas Company, Inc., develop Plexiglas and Crystalite. During the same year (1937) E.I. du Pont de Nemours came forth with the magical Lucite. Before the year was out, the Dow Chemical Company presented Styrene, the lightest plastic yet formulated, and the only one that tinkled.

These epochal discoveries rocked the industry, and it seemed as if nothing in plastics could top them. But the following year the Du Ponts presented Nylon and the superlatives that had been used to describe Lucite, Plexiglas and Styrene were now applied to Nylon. Like so many other plastics, Nylon was not merely "as good" as the material for which it had been created as a substitute, but it was, in certain respects, infinitely superior. The greater elasticity and tensile strength of Nylon over any other textile fiber made it the most desirable fabric for the manufacture of stockings and, during World War II, for the production of parachutes, glider tow-lines and other critical items used by the armed forces.

Overshadowed by these dramatic innovations, yet possessing long-
term potentialities of equal importance, were several plastic discoveries made during the next two years. Cellulose Acetate Butyrate arrived on the scene in 1938, a new tough cellulose plastic with greater dimensional stability and weather resistance than other members of the cellulose family. Its resistance to heat and moisture is so high that it can even withstand boiling. The Bakelite Corporation, the Hercules Powder Company and the Tennessee Eastman Corporation all developed it in their own distinctive ways, and soon the national sales passed the 2,000,000-pounds-a-year mark.

Slow in winning attention, but certain to outshine in the future many current favorites, are the vinyl resins which were also advanced importantly during the next two years. Discovered in 1838 by Regnault and forgotten for decades, a vinyl resin was first manufactured in the United States in 1928 by the Carbide and Carbon Chemicals Corporation under the trade name of Vinylite. In 1938 the Du Ponts and the Carbide and Carbon Chemicals Corporation created a stir by developing Polyvinyl Butyral for the manufacture of a safety glass superior to any made up to that time. Overnight cellulose acetate was rendered obsolete in the safety-glass field. In 1940 the Dow Chemical Company stole the spotlight with Saran (vinylidene chloride), a flexible plastic with the highest tensile strength of any plastic on the market.

Almost entirely lost from view, was the debut of Lignin, entitled to honors as the cheapest of all plastics. In 1938 the Masonite Corporation solved the secrets of its manufacture, and thus added a new product to the long list of items that may be made from the wastes of the lumber industry. Since lignin is the resin found in wood which forms the bond for the wood cellulose fibers, the Masonite Corporation really
developed a technique for exploiting wood and its natural resins in such a way as to produce a new plastic; briefly, it taught Nature a new trick with her own materials. The final product has all the uniformity of plastics, will resist moisture as wood will not, and is also superior to wood because it has not grain to cause weakness in one direction. Most relevant - it is cheap.

The year 1940 also witnessed on the plastics horizon the advent of Melamine, launched by the American Cyanamid Company. Superior in heat, oil and moisture resistance, and also tasteless, odorless and possessing a very hard surface, this new plastic gave some of the old-timers a run for their customers. The American Cyanamid Company called it Melmac. Soon it provided the U.S. Navy with a superior non-breakable tableware for rolling ships at sea. The high chemical and electrical resistance of this plastic made it useful for electrical circuit breakers.

With dramatic suddenness, following the debacle at Pearl Harbor, the synthetic rubbers captured the spotlight. All at once newspapers and magazines featured stories about Buna-S, Neoprene, Buna-N, Butyl, Thiokol and other synthetic rubbers. Many people were under the impression that these synthetics were something new and had been developed overnight to meet the war emergency. Actually the search leading to the development of artificial rubber began more than a century ago. Many European countries successfully produced synthetic rubber long before we did. Then in 1932 E.I. du Pont de Nemours and Company achieved the first commercial triumph in the United States in this field with neoprene, an artificial rubber of high quality. Soon afterward several rubber companies offered synthetics of their own. But scant attention was paid to these developments. Incidentally, few people
guessed that all synthetic rubbers were members of the plastics family.

Fluorothenes, fluorocarbons and fluorochemical plastics were an outgrowth of the same Du Pont research that led to the development of the "Freon" series of refrigerants. The commercial production of "Freon" refrigerants compounds consisting of fluorine, carbon, and (usually) chlorine, began in 1931. They are chemicals characterized by having a large percentage of the hydrogen directly attached to carbon replaced by fluorine. One part of the group consists of the polymers of trifluorochloroethylene and includes Bakelite's fluoroethene and Kellogg's Kel-F. These are available as resins and dispersions which have high thermal stability and excellent resistance to chemical attack. Among the unusual properties are the following:

(1) zero moisture absorption
(2) temperature range from --320 to +390°F
(3) high compressive strength
(4) non-wettability
(5) excellent electrical resistance
(6) high inertness

Further research on this family of products lead to the laboratory discovery of tetrafluoroethylene resin in 1938. Semi-plant production began in 1941; and the first commercial plant, at Parkersbury, West Virginia, started operation in 1950. Continuing research has resulted in the development of a variety of forms in which the product can be provided. Tetrafluoroethylene, that is Teflon, has the following properties:

(1) high inertness
(2) excellent dielectric properties
(3) heat-resistance

(4) toughness

(5) low coefficient of friction

Nothing could have been more fortunate than the commercial development of plastics during the World War II years. Plastics were placed one by one, on the list of priorities. Manufacturers were warned that any article made of plastic that could be made with a substitute material must be made with the substitute. The armed forces needed a staggering number of articles made of plastics that could not be made as satisfactorily of any other material. The heat, cold, water and weather resistance of many plastics, plus their lightness in weight, made them the ideal material for use under battle conditions. No other material would serve as well. GI Joe's equipment included plastic goggles, helmet inner liner, comb, brush, toothbrush, razor case, canteen, plastic-treated raincoat and shoes, plastic bayonet scabbard—to name a few articles. Every piece of communications equipment used by every branch of the armed forces included plastic parts. Every plane, tank, jeep and half-track required a certain number of plastic articles in its manufacture. Every base hospital, field hospital, ship and plane used to transport the wounded was outfitted with plastic materials and equipment of every description. Every surgeon, stretcher-bearer, orderly and nurse relied on a very long list of small indispensable articles made of plastic for use under battle conditions.

Some idea of the vast quantity of plastic materials needed for the armed services may be gathered from the order placed with manufacturers for plastic buttons for servicemen and women. The U.S. armed forces required 4,000,000,000 buttons a year! Yet plastic buttons constituted
one of the smallest items on the list of military needs.

More plastics began to appear on the scene—the organosols and plastisols, the epoxy resins, and the urethanes—to fulfill the demands to satisfy the growing commercial need. See Table I.16

TABLE I.
PROGRESS IN PLASTICS DEVELOPMENT

Approximate Dates Covering Introduction of Commercial Plastics

<table>
<thead>
<tr>
<th>Year</th>
<th>Plastic</th>
<th>Typical Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1870</td>
<td>The nitrates (Celluloid)</td>
<td>Eyeglass frames</td>
</tr>
<tr>
<td>1909</td>
<td>The phenolics</td>
<td>Telephone hand set</td>
</tr>
<tr>
<td>1909</td>
<td>Cold molded</td>
<td>Electric heater parts</td>
</tr>
<tr>
<td>1919</td>
<td>Casein</td>
<td>Knitting needles</td>
</tr>
<tr>
<td>1919</td>
<td>Vinyl acetates</td>
<td>Adhesives</td>
</tr>
<tr>
<td>1927</td>
<td>The acetates</td>
<td>Safety glass interlayer</td>
</tr>
<tr>
<td>1928</td>
<td>The ureas</td>
<td>Lighting fixtures</td>
</tr>
<tr>
<td>1931</td>
<td>The acrylics</td>
<td>Brush backs, displays</td>
</tr>
<tr>
<td>1935</td>
<td>Ethyl cellulose</td>
<td>Flashlight cases</td>
</tr>
<tr>
<td>1936</td>
<td>Polyvinyl chloride</td>
<td>Raincoats</td>
</tr>
<tr>
<td>1938</td>
<td>Vinyl butyral</td>
<td>Safety glass</td>
</tr>
<tr>
<td>1938</td>
<td>Polystyrene</td>
<td>Houseware</td>
</tr>
<tr>
<td>1938</td>
<td>Polyamides (nylon)</td>
<td>Fibers</td>
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<tr>
<td>1939</td>
<td>Polyamide molding powders</td>
<td>Gears</td>
</tr>
<tr>
<td>1939</td>
<td>Melamines</td>
<td>Tableware</td>
</tr>
<tr>
<td>1939</td>
<td>Polyvinylidene chloride (saran)</td>
<td>Auto seat covers</td>
</tr>
<tr>
<td>1942</td>
<td>Polyethylene</td>
<td>Squeeze bottles</td>
</tr>
<tr>
<td>1942</td>
<td>Polyesters</td>
<td>Large forms</td>
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</tbody>
</table>
When the truth became known to the war industries, the status of plastics underwent a profound change. For the first time in their history they enjoyed the respect they had always deserved. Manufacturers and the public alike had been inclined to view them as novelties of slight importance, or, at best, as synthetics with the limitations of substitutes. Now at long last they were regarded more in the light of a new precious metal - an indispensable material for which in many cases there was no substitute.
WHAT ARE PLASTICS?

The generic term "plastics" refers to a group of organic synthetic materials which group itself constitutes the best definition of the term. The American Society for Testing Materials has the following rather complicated description: "A plastic is a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and at some stage in its manufacture or in its processing into finished articles, can be shaped by flow."²

Plastics are synthetic in the sense that they do not occur naturally. The molecules are composed principally of carbon, hydrogen, nitrogen and oxygen, which are derived from petroleum, coal, salt, air, and water. Their properties depend to some extent on the size of the molecules of which they are composed. In the early stages of manufacture most plastics are monomers, composed of small single molecules, but under the influence of heat, or of heat and pressure, or of chemical catalysts, these small molecules combine to form long-chained molecules which make up solid or semi-solid structures. This process is called "polymerization".¹⁹

Thus, one of the chief characteristics of plastics is that their molecules are composed of a large number of repeating molecules - monomers. As with certain chemical elements and compounds, a few of these may agglomerate to form a low polymer, but it is not until some 500 to 1,000 of the monomeric units, on an average, combine, that the substance is called a high polymer. Thus, polystyrene averages 1,000 to 2,500 units; polyvinyl acetate, 400 to 1,200; rubber, 2,000 to 4,000.⁰

Plastics are high polymers whose units are linked to each other by carbon atoms. They are said to be of linear structure when these units are attached to each other in a series. Thus, if A represents a monomer
a linear high polymer may be represented schematically as -A-A-A-A-.

Or to cite an actual material, vinylidene chloride monomer (H₂C=CCl₂) polymerizes thus: -H₂C-CCl₂-H₂C-CCl₂-. If two monomers enter into the high polymer, it is called a copolymer, and the linear structure takes the form -A-A-B-A-A-B. This process is called "co-polymerization".

Thus, vinyl chloride (H₂C-CHCl) and vinyl acetate (H₂C=CH-O-CO-CH₃) co-polymerize in this manner: (-H₂C-CHCl-CH₂-CHCl-CH₂-CH-O-CO-CH₃-)ₙ.

In the above examples the line or "backbone" of the polymer is a "straight chain" (or open chain). In the phenolics, cellulose and cellulose-derived plastics, ring structures are the major part of the backbone. In thermosetting materials, these linkages of unit to unit take place in three dimensions, creating a much more complex molecule than an open-chain type.

In any case, the branched side chains are the reactive parts of the molecules. By suitable chemical substitutions in these side chains, the molecule can be modified, and with it the properties of the material. This has given rise to the concept of the "tailored molecule"—one made to order with desired properties. Thus, to obtain a material with the general characteristics of polystyrene but without its flammability and with a higher softening temperature, two chlorine atoms are substituted for two hydrogen atoms in the polystyrene molecule. The addition to a plastic of a substance which is attracted to and held between the chain molecules tends to weaken the force of attraction between the chains, giving the plastic a rubber-like quality. This is one explanation of how plasticizers work.

The use of the term "resin" is sometimes confusing. It may be synonymous with "plastic" but it usually refers to the liquid polymers
which are the starting materials in the production of molded or fabricated solid or semi-solid products.19

Some materials which belong to the broad family of plastics are based on inorganic rather than organic molecules, and this further complicates the definition for plastics. Typical of the inorganic group are the silicones.13 Their stability is contributed to their unique molecular structure of alternate silicone and oxygen atoms. In contrast to organic materials based on a carbon-to-carbon linkage, the silicones, due to the bond energy of their silicones-to-oxygen backbone, are held together with a force half again as strong. As a result, they show excellent resistance to the effects of heat, oxidation and weathering. Furthermore, their unusual chemical structure and composition make them water repellent, incompatible with most organic polymers, notably indifferent to temperature variation, and resistant to electrical breakdown.

As stated earlier, the best definition of "plastics" is the total list of materials designated in Table II now generally accepted as such.14 If one knows these materials he has a pretty good idea of the meaning of the word "plastics", but he may still have a far from complete understanding of the entire plastics industry in which the methods of fabrication and the intermediate shapes and forms play such an important role.

Most basic materials for the plastics industry—the resins and molding powders—are produced by a branch of a chemical industry, and thus both industries—plastics and chemical—are closely associated. Many resins are filled or reinforced or are extended by non-plastic
materials, chief of which are wood flour used in phenolics and in some of the other thermosetting plastics, and glass fibers and fabrics used in connection with several of the newer thermoplastic resins. These materials, known as "fillers" play an important part in the over-all plastics picture.

TABLE II.

<table>
<thead>
<tr>
<th>TYPES OF PLASTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Acetates</td>
</tr>
<tr>
<td>2. Acrylates</td>
</tr>
<tr>
<td>3. Alkyds</td>
</tr>
<tr>
<td>5. Butyrates</td>
</tr>
<tr>
<td>6. Casein</td>
</tr>
<tr>
<td>7. Cellophane</td>
</tr>
<tr>
<td>8. Cellulose nitrate</td>
</tr>
<tr>
<td>10. Cold-molded compounds</td>
</tr>
<tr>
<td>12. Ethyl cellulose</td>
</tr>
<tr>
<td>14. Fluorocarbons</td>
</tr>
<tr>
<td>15. Furans</td>
</tr>
</tbody>
</table>

At this point the terms thermosetting and thermoplastic should be explained. Thermosetting is a term applied to resins (plastics)
which solidify or set on heating and cannot be remelted, nor will the application of any known solvent break down their molecular structure. The thermosetting property usually is associated with a cross-linking reaction which forms a three-dimensional network of polymer molecules. Typical of the thermosetting materials are the following plastics listed in Table III. In general, thermoset materials cannot be reshaped once they have been fully cured.

**TABLE III.**

The Common Thermosetting Plastics
(Non-remeltable)

<table>
<thead>
<tr>
<th>Term</th>
<th>Features</th>
<th>Some Trade Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxies</td>
<td>coatings, tooling and for reinforced materials</td>
<td>Epon-Shell Chemical C-8 epoxy-Bakelite</td>
</tr>
<tr>
<td>Melamines</td>
<td>sturdy, hard, rich, durable</td>
<td>Melmac-American Cyanamid Resimene-Monsanto</td>
</tr>
<tr>
<td>Phenolics</td>
<td>extra strong, durable, good insulator</td>
<td>Resinox-Monsanto Bakelite Phenolic—Bakelite</td>
</tr>
<tr>
<td>Polyesters</td>
<td>weather resistant, choice for reinforced material</td>
<td>Laminac-American Cyanamid Vibrin-Naugatuck Chemical</td>
</tr>
<tr>
<td>Ureas</td>
<td>hard, smooth surfaced, colorful, stable</td>
<td>Beetle-American Cyanamid Plaskon Urea-Barrett Division</td>
</tr>
</tbody>
</table>
Thermoplastic is a term applied to resins (plastics) that may be softened by heat and which, upon cooling, regain their original properties, even if the process is repeated. They can be fused by heat and dissolved in certain solvents because their chains are not interconnected. Plastics typical of this group are listed in Table IV. All of the

**TABLE IV.**

The Common Thermoplastics
(Remelttable)

<table>
<thead>
<tr>
<th>Term</th>
<th>Features</th>
<th>Some Trade Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrytics</td>
<td>crystal-like, warm</td>
<td>Lucite-Du Pont</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plexiglas-Rohm &amp; Haas</td>
</tr>
<tr>
<td>Acetates</td>
<td>tough, hard, easily colored</td>
<td>Lumarith-Celanese</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plastacele-Du Pont</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Vuepak-Monsanto</td>
</tr>
<tr>
<td>Butyrates</td>
<td>tough, good weatherability</td>
<td>Tenite Butyrate-Eastman</td>
</tr>
<tr>
<td>Cellulose propionate</td>
<td>no odor, stable, bright finish</td>
<td>Forticel-Celanese</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>tough, hard surface, inflammmable</td>
<td>Nixon C/N-Nixon Nitration. Herculoid-Hercules Powder</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>tough, stands hard treatment</td>
<td>Hercocel E-Hercules Powder. Nixon E/C-Nixon Nitration</td>
</tr>
<tr>
<td>Polyamides (nylon)</td>
<td>strong, extra tough, stands high temperature</td>
<td>Zytel-Du Pont Plaskon-Barrett Division</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>light weight, squeezable</td>
<td>Poly-eth-Spencer</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alathon-Du Pont</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>brilliant, rigid, colorful</td>
<td>Styron-Dow Lustrex-Monsanto</td>
</tr>
<tr>
<td>Vinyls</td>
<td>versatile, multi-purpose, colorful</td>
<td>Exxon-Firestone Marvinol-Naugatuck</td>
</tr>
</tbody>
</table>
thermoplastic products have a greater resistance to shock and impact than the thermosetting materials. But the latter have a higher resistance to moisture than the thermoplastics. Both basic types of plastics have virtues of their own. Thermoplastics are more useful for certain applications, the thermosetting compounds for others. The "best" plastic depends entirely upon the article to be made and the condition under which it will be used.

The most common over-all advantages of plastics as a group are: good physical properties, good range of color, adaptability to mass production methods, and, often, lower cost. Generally speaking, plastics are light in weight; however, for their weight, they are prodigiously strong. Of the thirty-two commercial varieties of plastics, each one has its own individual characteristic properties. With a knowledge of these properties and the individual application of each plastic, it is usually possible to select the one type which is best suitable for a given job. A recent case in the medical field may emphasize the value of securing the right plastic. Charles Holter, seeking a material for a small valve used in draining fluid from the brain in treating hydrocephalic infants, tried several plastics which failed for one reason or another. Finally, engineers from Lee Rubber and Tire Company suggested silicone, which proved successful, thereby solving a problem which had baffled surgeons for many years.

Except for a few of the more common types, it is a difficult task to identify plastics by any simple test. A person with a good sense of smell and some knowledge of chemical odors can identify any of several plastics by holding a match to them. Some precaution should be used, however, because cellulose nitrate is almost explosive when dry and in
thin sections. An electric soldering iron is a good tool to use for identification. Before it gets red hot, press it against the unknown sample. If it sinks in, the sample is thermoplastic; if not, it is thermosetting. This locates the sample as belonging to one of the groups shown in Tables III and IV as being either thermoplastic or thermosetting.

A more extensive examination can be made with a Bunsen burner. If the sample will not burn (after 10 seconds at the edge of flame), it is a vinyl or a fluorocarbon if it was found to be thermosetting. A fish-like odor is indicative of a melamine and a phenol odor is, of course, a phenolic. The absence of either odor should indicate a urea. If the sample burns with a blue flame and dies after removal, a polyamide is indicated. However, if the dying flame is yellow, it may indicate any of the following: a casein if the odor is of burning milk, and the material was thermosetting; a vinyl, if the odor is acrid, for a thermoplastic. If there is an acetic odor, a flame-resistant type of cellulose acetate is indicated.

If the sample had a dying flame and was found to be thermosetting, it probably was a laminated phenolic. In this case, in addition to the characteristic phenol odor, it would have an odor of burning cellulose or of some other filler material. If the sample continued to burn after removal from the flame and was found to be thermosetting, an allyl is indicated.

The search has now been narrowed to perhaps six thermoplastic materials, but these are the hardest to identify accurately. An odor of burnt sugar points to ethyl cellulose; an odor of rancid butter means a butyrate. A yellow flame and an acetic odor indicates a standard
type of cellulose acetate or a vinyl acetate. The vinyl acetate has a
darker smoke. An odor of illuminating gas indicates polystyrene.
PART II

CHEMISTRY AND PREPARATION OF TETRAFLUOROETHYLENE

PROPERTIES OF "TEFLON" TETRAFLUOROETHYLENE RESINS

WHY TEFLON?
CHEMISTRY AND PREPARATION OF TETRAFLUOROETHYLENE

It was not until 1933 that the isolation of tetrafluoroethylene was reported. The monomer is a colorless, odorless gas which liquefies at -76.3°C. The commercial synthesis of tetrafluoroethylene is of a very unusual type for an olefinic monomer. This is the pyrolysis of monochlorodifluoromethane which can be obtained by the Swarts-type liquid-phase fluorination of chloroform:

\[
\text{CHCl}_2 = \text{HF} \quad \text{(anhydrous)} \quad \text{SbCl}_5 \quad \text{or other catalyst} \quad \text{at 65°C or above}
\]

\[
\text{H} \quad \text{FCCl}_2 + \text{F}_2\text{CCl} + \text{CCl}_2\text{F}_2 + \text{HCl} \quad \text{(recycled)}
\]

\[
\text{F}_2\text{CCl} + \text{CHCl}_3 \quad \text{at 650-800°C}
\]

\[
\text{H} \quad \text{Cl} \quad \text{H}_2\text{C} \quad \text{F} \quad \text{H} \quad \text{F}_2\text{C} = \text{CF}_2 + 2\text{HCl}
\]

In a preferred laboratory pyrolysis about 180 g gaseous chlorodifluoromethane was passed through a platinum tube at 700°C at a rate of 120 g per hr at atmospheric pressure and with a contact time of 0.3-0.4 sec. At a conversion to 25-30% tetrafluoroethylene a yield of 90% was obtained. The side products consist of higher-boiling compounds of the types H(CF\(_2\))\(_n\)Cl, and (CF\(_2\))\(_n\) cyclic compounds. Some of the cyclic compounds are highly toxic. Small amounts of hydrogen fluoride are also formed. TFE, as well as higher perfluoro-olefins, has been prepared by decomposition salts of perfluoro acids.

Tetrafluoroethylene reacts very readily with bromine and chlorine. It has the surprising property of burning in air or oxygen to give carbon dioxide and carbon tetrafluoride: 

\[
\text{CF}_2 = \text{CF}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{CF}_4
\]

The monomer reacts readily with hydrogen halides. Tetrafluoroethylene...
undergoes additional reactions with alcohols to give ethers and reacts readily with many other compounds containing active hydrogen atoms.\(^9\)

The tetrafluoroethylene monomer and polymers have been reviewed by Renfrew and Lewis, who give the data in Table V.\(^{44}\)

**TABLE V.**

TFE Monomer Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point, °C</td>
<td>-76.3</td>
</tr>
<tr>
<td>Freezing point, °C</td>
<td>-142.5</td>
</tr>
<tr>
<td>Critical density, g/cc</td>
<td>0.52</td>
</tr>
<tr>
<td>Critical temperature, °C</td>
<td>33.3</td>
</tr>
<tr>
<td>Critical pressure, psi</td>
<td>572</td>
</tr>
<tr>
<td>Dielectric constant at 28°C</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vapor pressure (log/p), atm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>At -76.3-0°C</td>
<td>5.6210 - (875.14/t)</td>
</tr>
<tr>
<td>At 0-33°C</td>
<td>5.5906 - (866.34/t)</td>
</tr>
</tbody>
</table>

| Liquid density, g/cc at -100 to -40°C | 1.202 - 0.00414t |
| Thermal conductivity at 30°C, cal/cm²/sec/°C/cm | 0.0000037 |

The infrared absorption spectrum of the gaseous monomer has been studied.\(^{37}\) An olefinic CF\(_2\) group can be identified by frequencies near 1,750 and 1,325\(^-1\). The monomer seems to be non-toxic.

For storage of the monomer, compounds may be added which preferentially react with oxygen, such as 0.5% dipentene, tetrahydronaphthalene, benzaldehyde, octene-1 or methyl methacrylate. The safe handling of tetrafluoroethylene under pressure requires avoiding contact with oxygen and preventing the formation of its oxidation products. By reducing the oxygen content below 20 ppm the monomer may be stored at 25°C under pressure as a liquid. For removal of oxygen the monomer may be scrubbed with a chromous salt, alkaline hydrosulfite or sodium B-anthraquinone sulfonate solution.\(^{18}\)
POLYMERIZATION OF TETRAFLUOROETHYLENE

The discovery in 1941 by Plunkett that gaseous tetrafluoroethylene monomer under pressure polymerizes readily was a great surprise. Until ethylene high polymers had been prepared by Fawcett and coworkers, it had been supposed that one or two substituents had to replace hydrogen atoms in ethylene to disturb the charge or symmetry in order to permit polymerization. Ethylene had been polymerized readily to products of high molecular weight only at high temperature, e.g., 200°C. Tetrachloroethylene shows no tendency to homopolymerize.

Tetrafluoroethylene had been evaluated as a refrigerant in the Kinetic Chemicals Laboratories. The compound proved of little interest for this purpose. The story is told that a pressure cylinder of material which had been stored for some time was examined as part of a safety inspection. Little gas escaped when the valve was opened. A check of the cylinder weight showed that the tetrafluoroethylene had not leaked out during storage. The steel cylinder was then cut open, revealing a white, opaque solid with a waxy feel.

The basic reactions for the commercial production of polytetrafluoroethylene are illustrated in Table VI. Pure uninhibited tetrafluoroethylene can polymerize with violence, starting even below room temperature. The high temperatures generated by uncontrolled polymerization can lead to the explosive disproportionation reaction forming carbon and carbon tetrafluoride. Several lives were lost in the wartime development of polytetrafluoroethylene before the extreme dangers in handling the monomer were fully appreciated.

As well as polymerization on storage without catalyst, Plunkett observed faster polymerization of tetrafluoroethylene at 25°C in the
TABLE VI. Some of the more important steps in the manufacture of "Teflon" molding powder.

(1) \[ \text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HF} + \text{CaSO}_4 \] (fluorspar) (hydrogen fluoride)

(2) \[ 2\text{HF} + \text{CHCl}_3 \rightarrow \text{CHClF}_2 + 2\text{HCl} \] (chloroform) (chlorodifluoromethane)

(3) \[ 2\text{CHClF}_2 \rightarrow \text{CF}_2\text{CF}_2 + 2\text{HCl} \] (pyrolysis) (tetrafluoroethylene monomer)

(4) \[ n \begin{bmatrix} F & F \\ C & C \\ F & F \end{bmatrix} \rightarrow \begin{bmatrix} F & F & F & F & F \\ F & C & C & C & C \\ F & F & F & F & F \end{bmatrix} \] (x) "Teflon" molding powder
presence of silver nitrate and methanol. Later studies showed that better control often could be obtained using aqueous media with persulfate or bulk polymerization with free-radical catalysts. Many organic emulsifiers and peroxide catalysts were objectionable because the residues charred or decomposed, giving spots or holes at the high temperatures necessary to shape the polymers.

In one patent a silver-lined pressure vessel was charged with 100 parts 5% aqueous sodium hydroxide solution. It was then evacuated, and 200 parts tetrafluoroethylene added along with 0.04% oxygen based on the monomer. The reactor was agitated with heating at 148-151°C for 8 hr, during which time the pressure fell from 2,200 to 1,600 psi. The reactor was cooled, the pressure released and 82 parts granular white polymer was obtained. With 0.2% benzoyl peroxide in an aqueous phase brought to pH 3.3 by adding formic acid, only 8.5% polymerization was obtained by reaction at 84°C for 9 hr. The polymerization of tetrafluoroethylene with hydrogen peroxide catalyst at 60°C and initial pressure 700 psi has been described.

Faster controlled polymerizations at comparatively low temperatures were accomplished, using aqueous persulfate systems along with alkaline buffers. High pressures such as 1,000 atm gave faster polymerization. In one patent a stainless steel reactor was one-fourth filled with 100 parts water, 0.2 part potassium persulfate and 0.5 part borax. The reactor was closed and evacuated. There was forced in under pressure 30 parts tetrafluoroethylene. The system was agitated for 1 hr at 80°C. The yield was 26 parts white, granular tetrafluoroethylene polymer. Under similar conditions but without borax only 16% polymer was obtained after 6 hr at 80°C. A suspensoid of 6.5% TFE polymer in water was
obtained using 0.1% disuccinic acid peroxide with rapid agitation at 55°C. The monomer pressure was 350 psi, and less than 50% conversion to polymer occurred during 8 hr. Improvements have been made also in the bulk polymerization.

In large plant-scale polymerization of tetrafluoroethylene special precautions must be taken to dissipate the heat of polymerization, which has been estimated to be as high as 20-25 kcal.

Irradiation of gaseous tetrafluoroethylene containing mercury vapor by the mercury resonance light of 2,536 A has given hexafluorocyclopropane along with some white solid polymer.²

POLYTETRAFLUOROETHYLENE appears to be a chain polymer (—CF₂—)ₚ of very high molecular weight, of the order of half a million.⁵ The powdered material, as produced in the polymerization reaction, is highly crystalline below 20°C. The 'melting point'—the first order transition from a partly crystalline to a completely amorphous structure—is about 330°C., very much higher than that of the corresponding hydrocarbon polymer—132°C., 136.5°C.; but at 20°C. the fluorocarbon polymer shows another first-order transition involving a 1 per cent change of density, which is shown by X-ray diffraction patterns to be due to a partial disordering of the crystalline regions. The occurrence of a reversible first-order transition involving disordering at a temperature so far below the 'melting point' (actually about half the absolute 'melting point') is unique among polymers, and directs increased attention to the structure of the molecules and of the crystals, both below and above the 20°C. transition.⁵⁴

In studying the structure of molecules and crystals of fluorocarbons, Bunn and Howells observed that the fluorocarbon molecules
have a helical chain with a 13-atom repeating unit, while the corresponding hydrocarbon molecules have a plane zigzag carbon chain; and that fluorocarbon crystals disordered far below their melting points. 11

In the plane zigzag chain found in the hydrocarbons, the span of the zigzag is 2.539 Å. Hydrogen atoms attached to next-but-one carbon atoms are also at this distance from each other. Since the van der Walls radius of hydrogen is 1.1–1.2 Å., there is ample room for these atoms—in fact, they are not in contact but separated by a gap; but the van der Walls radius of fluorine is 1.35 Å.; double this figure is 2.70 Å., so that fluorine atoms attached to a plane zigzag carbon chain would be overcrowded. The helical structure is presumably due to rotation around the chain-bonds which takes place to increase the distance between the fluorine atoms. It is interesting to find, however, that although satisfactory distances between fluorine atoms could be attained by a rotation which would bring one fluorine atom (F_3 in Fig. 1-a) equidistant from the two (F_1 and F_2) on the next-but-one carbon atom, this

![Diagram](image)

**Fig. 1.** (a) Configuration giving equal F—F distances (F_1F_3 = F_2F_3); (b) Configuration actually found.
is not what actually happens; instead, a smaller rotation occurs (giving unequal F—F distances), and the remainder of the required increase of the shortest distance is provided by an increase of the zigzag span from 2.539 A. (the figure for hydrocarbons) to a 2.595 A., an increase which is presumably due to an opening of the bond angle to (to 116°), since this is much easier than stretching the C—C bonds. The limitation of the rotation may be due to repulsion between fluorine atoms and next-but-one chain carbon atoms (F₃ and C₁ in Fig. 1-b) or to a bond-orientation effect (as distinct from atom repulsions) which favors staggered configurations of which the plane zigzag chain is the most simple example.

The order-disorder transition which occurs at room temperature in the high polymer is evidently not a phenomenon peculiar to the polymer, for the same type of transition is found in perfluorocetane, again at a temperature far below the absolute melting point; it is evidently due to some feature of the structure of a fluorocarbon chain. The transition may be analogous to the change that occurs in paraffin hydrocarbons from C₂₁ to C₂₇ (but not in the high polymer) a few degrees below the melting point, a change that is thought to be due to the onset of rotation of the molecules about their long axes (though the only evidence is the change to hexagonal symmetry). In the fluorocarbons we have much more definite evidence for disorder, and, above all, the transition occurs far below the melting point. Molecular models show that the fluorocarbon chain is more 'streamlined' than the hydrocarbon chain (see Fig. 2) in the sense that the general shape is more nearly cylindrical and the projections and depressions in the profile are smaller in relation to the cross-sectional area of the
molecule. The close approach to cylindrical shape may be the simple explanation of the existence of disordered crystals at such low temperatures. Both rotations around the chain axis and longitudinal translations would be facilitated by such a streamlined shape.

Left: twisted zigzag chain found in fluorocarbons. Centre: fluorocarbon molecule (side and end views). Right: hydrocarbon molecule

FIGURE 2.
Tetrafluoroethylene copolymerizes with many ethenoid monomers under conditions somewhat similar to those used in the homopolymerization. Of special interest are copolymers which are comparatively transparent and non-crystalline. In one patent example a polymer of tetrafluoroethylene, vinyl fluoride and vinylidene fluoride was prepared at 80°C under pressure of 2,600 psi, using benzoyl peroxide in oxygen-free aqueous system. A copolymer containing about 36% TFE, 37% vinyl fluoride and 27% vinylidene chloride had a tack temperature of 45°C and good clarity. Some of these copolymers illustrate the reduced crystallinity, lower softening temperature and improved solubility which result from random distribution of polar substituents on the carbon chain.

Copolymerizations of tetrafluoroethylene with ethylene, with vinyl esters, and with other vinyl compounds have been disclosed. In one example a mixture of TFE-ethylene (10-90) with benzoyl peroxide catalyst was copolymerized at 78°C and 800 atm. A polymer containing a 1 to 8.6 molar ratio of monomer units was obtained. It was soluble in hot xylene and could be molded at 150°C to clear, tough films. Tetrafluoroethylene forms copolymers with sulfur dioxide and telomers with chloroform and other chain-transfer halogen compounds.
The high polymers of tetrafluoroethylene not only are the least thermoplastic of vinyl plastics, but also are remarkable in resistance to solvents and corrosive chemical in strength and flexibility over an extremely wide temperature range and in chemical stability. In fact, the behavior of polytetrafluoroethylene departs in many respects from that characteristic of organic substances. When heated in air at 450°C the polymers are degraded slowly but without any charring. (These polymers are derived from a monomer boiling at -76°C.)

Although flexible and subject to some cold flow or deformation under pressure, the tetrafluoroethylene polymers are not as soft or as rubber-like as chlorotrifluoroethylene polymers. The polymers are white or light gray in color and waxy in appearance. Teflon is highly crystalline, and translucent or opaque except above its transition point at 327°C. Quenched tapes and foils, however, have fair transparency. Since there is no solvent for the polymers molecular weight and viscosity data cannot be obtained. Differences in mechanical properties, however, indicate differences in the degree of polymerization.

The following account of tetrafluoroethylene polymer properties is derived largely from Du Pont papers and trade literature. Table VII summarizes the more important physical properties of "Teflon" tetrafluoroethylene resins.

"Teflon" tetrafluoroethylene resins have practically universal chemical inertness. Of the chemicals encountered in commercial practice only alkali metals such as sodium, halogens such as fluorine and some halogen compounds show any sign of attack on these resins.
<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>UNITS</th>
<th>A.S.T.M. METHOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, 73°F.</td>
<td>lb./sq.in.</td>
<td>D638—52T</td>
</tr>
<tr>
<td>Elongation, 73°F.</td>
<td>%</td>
<td>D638—52T</td>
</tr>
<tr>
<td>Flexural strength, 73°F.</td>
<td>lb./sq.in.</td>
<td>D790—49T</td>
</tr>
<tr>
<td>Flexural modulus, 73°F.</td>
<td>lb./sq.in.</td>
<td>D747—50</td>
</tr>
<tr>
<td>Impact strength, Izod, —40°F.</td>
<td>ft.-lb./in.</td>
<td>D256—47T</td>
</tr>
<tr>
<td></td>
<td>%</td>
<td>D256—47T</td>
</tr>
<tr>
<td>Hardness, Durometer</td>
<td>ft.-lb./in.</td>
<td>D676—49T</td>
</tr>
<tr>
<td>at 1% offset, 73°F.</td>
<td>lb./sq.in.</td>
<td>D695—52T</td>
</tr>
<tr>
<td>Coefficient of linear thermal expansion per °F., 73—140°F.</td>
<td></td>
<td>D696—44</td>
</tr>
<tr>
<td>Thermal conductivity, 0.18 in.</td>
<td>B.T.U./hr./sq.ft./°F./in.</td>
<td>(2) 1.7</td>
</tr>
<tr>
<td>Specific heat</td>
<td>B.T.U./lb./°F.</td>
<td>0.25</td>
</tr>
<tr>
<td>Deformation under load, 122°F., 1200 lb./sq.in., 24 hrs.</td>
<td>%</td>
<td>D621—51</td>
</tr>
<tr>
<td>122°F., 2000 lb./sq.in., 24 hrs.</td>
<td>%</td>
<td>D621—51</td>
</tr>
<tr>
<td>Heat-distortion temperature, 66 lb./sq.in.</td>
<td>°F.</td>
<td>D648B—45T</td>
</tr>
<tr>
<td>Dielectric strength, short-time, 0.080 in.</td>
<td>v/mil</td>
<td>D149—44</td>
</tr>
<tr>
<td>Surface arc-resistance</td>
<td>sec.</td>
<td>D495—48T</td>
</tr>
<tr>
<td>Volume resistivity</td>
<td>ohm-cm.</td>
<td>D257—52T</td>
</tr>
<tr>
<td>Surface resistivity, 100% R.H.</td>
<td>megohms</td>
<td>D257—52T</td>
</tr>
<tr>
<td>Dielectric constant, 60 to 3 x 10⁹ cycles</td>
<td></td>
<td>D150—54T</td>
</tr>
<tr>
<td>Dissipation factor, 60 to 3 x 10⁹ cycles</td>
<td></td>
<td>D150—54T</td>
</tr>
<tr>
<td>Water-absorption</td>
<td>%</td>
<td>D570—42</td>
</tr>
<tr>
<td>Flammability</td>
<td>in./min.</td>
<td>D635—44</td>
</tr>
<tr>
<td>Specific gravity</td>
<td></td>
<td>D792—50</td>
</tr>
<tr>
<td>Resistance to weathering</td>
<td></td>
<td>2.1—2.3</td>
</tr>
<tr>
<td>Static or kinetic coefficient of friction against polished steel</td>
<td></td>
<td>0.04</td>
</tr>
</tbody>
</table>

Data shown are average values and should not be used for specifications.

1) Tensile strength in oriented film may be as high as 15,000 lb./sq. in.
2) Measured by Cenco-Fitch apparatus.
3) Value is 1000-2000 volts/mil in thicknesses of 12 to 5 mils, 4000 volts/mil for ¼ mil.
4) Does not track.
5) Various methods used.
6) Unaffected by 10 years' exposure in Florida.

**TABLE VII.**

Properties of molded "Teflon" tetrafluoroethylene resins
Even with these, special conditions such as elevated temperatures or pressures or both are required for a noticeable effect. "Teflon" tetrafluoroethylene resins have been tested in many boiling solvents, including a variety of halogenated hydrocarbons, ketones, esters, and alcohols, without swelling or change in weight. It has been immersed in boiling aqua regia, and in hydrofluoric, nitric, and sulfuric acids with no change in weight or properties. It is equally resistant to attack by alkalies in all concentrations. Fluorine and chlorine trifluoride will react with it at elevated temperatures and pressures. 27 Although tetrafluoroethylene resins are successfully used in chlorine and bromine service, under certain conditions the halogens and halogenated compounds may affect them.

Insolubility in organic solvents at room temperature and a waxy feel are properties common to polyethylene and polytetrafluoroethylene. On heating, polyethylene chains become more flexible and the polymer dissolves in a wide variety of solvents. Not so with tetrafluoroethylene high polymers which resist attack even above their transition temperature. Perhaps the space between chains is too small for solvent molecules to penetrate readily. At high temperatures polytetrafluoroethylene is swollen or slightly dissolved by only a few agents such as fluorine, certain inorganic fluorides and certain fluorocarbon oils. The properties of tetrafluoroethylene resin are compared with those of polyethylene resins in Table VIII. 49

In addition to its outstanding chemical inertness tetrafluoroethylene resins are relatively impermeable to many chemicals. Metal coated with a thin layer of "Teflon" tetrafluoroethylene resin is considerably superior in chemical resistance to uncoated metal. However, on long
immersion, materials such as hydrochloric acid may diffuse through the film and attack the metal substrate. In the case of thick coating, the rate of permeability is so low as to be negligible.

TABLE VIII.

Properties of Tetrafluoroethylene and Polyethylene Resins

(Average Values) *

<table>
<thead>
<tr>
<th>Properties</th>
<th>Tetrafluoroethylene &quot;Teflon&quot;</th>
<th>Polyethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>2.15</td>
<td>0.92</td>
</tr>
<tr>
<td>Tensile strength, psi</td>
<td>2500</td>
<td>1750</td>
</tr>
<tr>
<td>Compressive strength, psi</td>
<td>1700</td>
<td>low</td>
</tr>
<tr>
<td>Continuous heat resistance, °F</td>
<td>500</td>
<td>220</td>
</tr>
<tr>
<td>Heat distortion temp.*, °F(66psi)</td>
<td>250</td>
<td>121</td>
</tr>
<tr>
<td>Dielectric strength, v./mil</td>
<td>500</td>
<td>460</td>
</tr>
<tr>
<td>Machining qualities</td>
<td>Excellent</td>
<td>Fair to good</td>
</tr>
<tr>
<td>Effect of sunlight</td>
<td>None</td>
<td>Some crazing</td>
</tr>
<tr>
<td>% Water absorption, 24 hr.</td>
<td>0.005</td>
<td>0.014</td>
</tr>
<tr>
<td>Resistance to strong acids</td>
<td>Excellent</td>
<td>Poor to fair</td>
</tr>
<tr>
<td>Resistance to weak acids</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Resistance to strong alkalies</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Resistance to weak alkalies</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Clarity</td>
<td>Opaque</td>
<td>Opaque to translucent</td>
</tr>
</tbody>
</table>

"Teflon" tetrafluoroethylene resin is nonflammable and practically unaffected by water. It has less than 0.01% water absorption by A.S.T.M. test. It will not absorb moisture, a property which adds greatly to its
value as an electrical insulator, since its dielectric strength is not diminished by immersion in fresh or salt water. Above 200°C water may very slowly react with the finely divided polymer, giving traces of hydrogen fluoride.48

So stable is tetrafluoroethylene high polymer to heating that samples maintained at 300°C for a month showed only a loss of 10-20% in tensile strength. However, there is evidence of some reduction in molecular weight by such treatment. Only above 400°C does loss of weight by chain cracking become important. By pyrolysis at 600-700°C and 150 mm pressure there were obtained 80% TFE monomer, 14% hexafluoropropene and 5% octafluorocyclobutane. Under other conditions of heating at 500°C microcrystalline fluorocarbon waxes may be obtained.42

The electrical properties of "Teflon" tetrafluoroethylene resins are exceptional and surpass all other organic insulation products. Their dissipation factor is less than 0.0003 over the entire spectrum measured to date, 60 cycles to 3,000 megacycles. Their volume resistivity is greater than $10^{18}$ ohm-cm, even after prolonged soaking in water. Their surface resistivity is greater than $10^{17}$ ohms/sq. even at 100% relative humidity. Tetrafluoroethylene resins also have excellent arc-resistance. On exposure to an arc, material made of the resins is decomposed to a vapor which leaves no carbonized path, regardless of time of exposure to the arc.34 Short-time dielectric strengths are high. These values range from 500-4,000 volts per mil, depending on thickness. However, recommended working stresses are in the range of 50-100 volts per mil, typical voltages used in motor and generators.12,28

The electrical properties of "Teflon" tetrafluoroethylene resins are essentially unchanged at temperatures up to at least 480°F.
Outdoor exposure of 6 years produces no detectable change in TEFLON. Because of low thermal conductivity, frictional heat from mechanical working of the compact polymers can sometimes result in local high temperatures and dangerous vapors which should not be allowed to accumulate.

"Teflon" tetrafluoroethylene resins have an appreciable degree of elasticity, and have a perfect "plastic memory", or tendency to return to their original shape when heated. This property of "plastic memory" is used to advantage in making tight joints between these resins and metal. A component made of TEFLON is pressed into a metal assembly at a low temperature in such a manner that there is some deformation of the component. As the temperature is increased and the component of TEFLON tends to recover its original shape, a tight joint is produced.

"Teflon" tetrafluoroethylene resins can be "oriented", as indicated by the fact that they do not recover completely when a deforming load is removed (at normal temperatures). Whether deformed by a tensile or compressive force, internal stresses are introduced that will remain unless relieved by heating. Such internal stresses, often termed orientation, have a marked effect on the physical properties of these resins. This is typified by molded sheets that are cold-rolled to increase length and width with a corresponding reduction in thickness. Rolling of sheet stock increases tensile strength and reduces the tendency to deform under compressive load. On the other hand, when sheets processed in this manner are heated, without restraint, they shrink in length and width and increase in thickness, because of the stress-relief that takes place. Any article of TEFLON may contain internal stresses. To obtain maximum dimensional stability, it is necessary
to remove such stresses by heating at a temperature above that which will be encountered in service, before finishing to the final dimensions. 8, 53

When clear tetrafluoroethylene polymer (not melted) is cooled from 350°C, a double transition seems to occur at about 320°C. Below this temperature the polymer becomes opaque or translucent. Like acrylonitrile high polymers, the TFE polymers never give a flowable melt or become readily thermoplastic at any high temperature. However, there is sufficient chain mobility for very slow flowing under pressure, and for orientation and quenching effect. Quenching tapes and films from above 327°C to cold water gives improved clarity and toughness. In measuring tensile strength, TEFLON specimens begin to cold-draw when loads of 1,500-2,000 psi are reached. The material can be extended 300-450% before breaking occurs at 2,500-4,000 psi (original cross section). In oriented tapes tensile strength as 25,000 psi have been measured along the line of orientation. 35

Although showing some delayed elasticity or recovery, TFE polymers are subject to considerable cold flow at moderately elevated temperatures. This accounts for the moderately low heat-distortion temperature and is one of the important limitations of the material. In some cases shaped masses undergo at room temperature density changes of about 1% which seem to result from an internal transition to a different crystalline state more stable below 25°C. 38

The properties of tetrafluoroethylene polymers have given considerable food for thought to those interested in the relation of properties of the fine structure of macromolecules. The resistance to flow when heated may be attributed to stiffness of the chain segments. The
latter probably results from the tightness with which the fluorine atoms are held, repulsive forces between fluorine atoms, restriction of rotation about the chains, and steric constraints from the close packing. The chain segments have maximum symmetry and compactness. The inertness of polyfluorides has been attributed in part to the fact that the normal carbon-fluorine bond distance of 1.42 Å is reduced to 1.35 Å when two fluorine atoms are attached to a single carbon. The C—F bond strength may be as high as 120 kcal per mole. Since chain branching would involve the breaking of C—F bonds, it seems improbable that polytetrafluoroethylene should have much branching.

The value of "Teflon" tetrafluoroethylene resins in some applications can be considerably enhanced by the use of additives. Such modification improves certain mechanical properties of these resins, and permits compositions based on them to be "tailored" to a wide variety of chemical, mechanical and electrical applications. Any material which can tolerate the processing temperatures required for tetrafluoroethylene resins can be used. This temperature requirement eliminates organic additives, but most inorganic materials are sufficiently heat-stable. Types of additives that are generally suitable included metallic copper and bronzes, glass fiber, graphite, coke flour, molybdenum disulfide, clay, talc, silica, asbestos and calcium fluoride powder. The choice of a specific additive and concentration depends on the needs of the particular application for which the composition is intended. As a general rule, the additive should be used in the smallest particle size in which it is available, to obtain the maximum physical properties. However, exceptions may be found in the cases of materials of extremely fine particle size.

In general, "Teflon" tetrafluoroethylene resins can be compounded
to increase these properties:

1) Resistance to deformation under load by a factor of 10.
2) Resistance to wear by rotating shafts, by as much as 500 times.
3) Stiffness by a factor of 4 to 5.
4) Thermal conductivity by a factor of 5 to 10.
5) Compressive strength by a factor of 3 to 4.
6) Hardness by about 10%

Furthermore the modified compositions retain these outstanding properties of uncompounded TEFLON:

1) Low coefficient of friction.
2) Heat-resistance (up to 500°F.)
3) Excellent outdoor durability.
4) Non-flammability.
5) Zero water-absorption
6) High flexural strength
7) Excellent electrical properties.

The properties of polytetrafluoroethylene, nylon, polyethylene and the acrylics are compared in Table IX.
### TABLE IX. *

Comparative Characteristics Chart

<table>
<thead>
<tr>
<th></th>
<th>Fluorocarbons</th>
<th>Nylon</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical</strong></td>
<td>Completely inert to all chemicals and solvents normally encountered in industry, Impervious to water.</td>
<td>Unaffected by common solvents, alkalies, dilute mineral acids and most organic acids.</td>
</tr>
<tr>
<td><strong>Mechanical</strong></td>
<td>Tough over a range of temperatures from −450 to 500°F. Non-adhesive. Low friction coefficient. Self lubricating.</td>
<td>Tough and resilient at low temperatures. Requires little or no lubrication. Resists abrasion.</td>
</tr>
<tr>
<td><strong>Electrical</strong></td>
<td>Excellent in electrical properties at all frequencies.</td>
<td>Good dielectric properties at commercial power frequencies.</td>
</tr>
<tr>
<td><strong>Structural</strong></td>
<td>Tough and resilient. Resistant to impact. Impervious to weather.</td>
<td>Strong and durable. Good form stability. Light in weight.</td>
</tr>
<tr>
<td><strong>Decorative</strong></td>
<td>Can be colored. Useful for color coatings to aid identification.</td>
<td>Good color stability. Attractive texture.</td>
</tr>
</tbody>
</table>

* Comparative chart continued on page 50.
### TABLE IX.

Comparative Characteristics Chart

<table>
<thead>
<tr>
<th></th>
<th>Polyethylene</th>
<th>Acrylcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Excellent chemical and water resistance.</td>
<td>Resistant to dilute alkalies, many strong acids and other chemicals.</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Tough and flexible over wide range of temperatures.</td>
<td>Rigid, good dimensional stability.</td>
</tr>
<tr>
<td>Electrical</td>
<td>Excellent dielectric properties over wide frequency and temperature range.</td>
<td>Good dielectric properties at all commercial power frequencies.</td>
</tr>
</tbody>
</table>
WHY TEFLON????

For the past two years I have made an intensive investigation of all the available plastic materials in an effort to find the "superior or ideal material" for implantation studies in both the experimental animal and the human being. I've traced the origin of these plastics; and, as each new plastic became commercially available, I studied its physical and chemical properties with the meticulous and concise care that I would use in evaluating a surgical patient.

In choosing any synthetic plastic substance for permanent placement in the human body it is imperative that the material fulfill certain select criteria. The implant must:

1) Not be physically modified by tissue fluids.
2) Be chemically inert.
3) Not excite an inflammatory or foreign body cell response in the tissues.
4) Be non-carcinogenic.
5) Not produce an allergy or hypersensitivity.
6) Be capable of standing up to mechanical strains imposed on it.
7) Be capable of being fabricated in the form required with reasonable ease at a relatively low cost.
8) Be capable of being sterilized.

Theoretically, TEFLON unequivocally fulfills these criteria for a satisfactory synthetic prosthesis better than any plastic reported to date. It is flexible, elastic and has a high mechanical strength over a wide range of temperatures. It has a high degree of chemical inertness. Chemists who have worked with TEFLON find it hard to
realize that any material could have such unbelievable properties of chemical resistance and inertness, and it has been given the name "Dragon Fur". It is practically indestructible for it will not deteriorate by hydrolysis, oxidation, degradation by acids, alkalis, organic chemicals or fluids. There is no known solvent for TEFLON. It is non-wettable, impermeable and has zero moisture absorption. According to Table X the tensile strength of TEFLON is less than other materials; in reality, it retains or even gains in strength with age. Tensile strength studies with other plastics have shown that the rate of loss of strength is highest during the first six months. Nylon loses 83% of its strength in the first half-year; while TEFLON gains in strength after it has been implanted. Harrison has shown that the TEFLON gained in strength after 208 days as an artery graft and 301 days as a pericardial graft. It is easily sterilized by autoclaving—which is the most certain method of sterilization—and can be repeatedly

TABLE X.

Comparative Tensile Strengths
(in grams per denier)

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon</td>
<td>7.8</td>
</tr>
<tr>
<td>Dacron</td>
<td>4.5</td>
</tr>
<tr>
<td>Orlon</td>
<td>3.0-4.5</td>
</tr>
<tr>
<td>Vinyon N</td>
<td>3.0</td>
</tr>
<tr>
<td>TEFLON</td>
<td>1.3-1.5</td>
</tr>
</tbody>
</table>
autoclaved any number of times with full assurance that it will be unaffected. Nothing will adhere to it; and, once formed, it cannot be cemented to any other known material.

Most of all, TEFLON incites minimal tissue reaction. LaVeen and Barberio instilled fine granular particles of TEFLON into the peritoneal cavity of experimental animals; and, comparing the reactions produced by nylon, celluloid, and lucite, found very striking differences. The finely divided chips of TEFLON were seen to be lying free in the peritoneal cavity. There were no acute inflammatory changes and no gross evidence of tissue reaction. Occasionally, chips could be seen encased in the omentum, but the extent of the peritoneal reaction was certainly no more than would be expected from simple surgical manipulation. At the end of 70 days most of the chips were surrounded by omentum. There was no fibroblastic reaction and the chips could be easily removed from the flimsy omental adhesions which were broken with ease. A thin, fibrous sheath of mature fibroblasts surrounded the plastic by the end of 70 days; and no proliferative foreign body reaction was present. By the end of six months, the delicate fibrous capsule surrounding the plastic has not increased in thickness. An intact mesothelial-like layer on the omentum exposed to the plastic emphasized the plastic's inability to produce tissue changes, and suggested that the fibrous capsule was caused by trauma rather than by tissue reaction. In contradistinction to all of the other plastics, the surface of TEFLON in all sections was free of absorbed protein. All of the other plastics studied produced an intense fibrinoplastic, inflammatory reaction. This minimal host response to TEFLON in terms of fibroblastic reaction has been substantiated by others, including Harrison, Merendino, Girvin, Usher, Pitts and Pinkham.
With all of the evidence cited above in support of TEFLOMN as an "ideal material", the question arises as to why anything but TEFLOMN was ever considered as a material for synthetic arterial grafts. One cannot under-emphasize the significant role that homografts played in arterial replacement surgery. However, the limited supply, time involved in procurement and preservation, and the disappointing evidence that there was disruption and degeneration after long periods of implantation made them less than ideal as a source of available grafts. Efforts were directed toward developing satisfactorily a synthetic prosthesis that could be readily available in any number, size, or shape, and would not degenerate over a long period of time. Since the report in 1952 by Voorhees with grafts of vynlon "N", others have reported favorable results with a variety of synthetic materials, including nylon, Dacron, Orlon and Ivalon. The answer to this question is very simple—namely, that the problems involved in the routine production of TEFLOMN grafts had not been solved. TEFLOMN fiber was not available in a purified form and no practical and safe method for purifying TEFLOMN was known at this time. The cost to purify TEFLOMN added to its already high price of $17 per pound compared to about $1.50 for nylon or Dacron made it expensive to experiment with and a pound of TEFLOMN had only about half the volume of a pound of the other yarn. It was definitely an expensive material. Very little data was available on handling TEFLOMN fiber for knitting or braiding. Due to its extremely inert properties there seemed little that could be done to make it hold corrugations or to treat it for porosity control. TEFLOMN was not available in various types of yarn constructions such as we find for Dacron and nylon in their Helanca, Fluflon, Superloft and Banlon forms.
Thus, it is easy to see why nylon and Dacron, even though they do not have the ideal properties of TEFLON, were the first in this very new field of synthetic arterial grafts. However, it has been clear to many of us for some time that TEFLON would have to become available as a graft and that the problems of routine production would soon be solved. Today we have the Edwards Artery Graft of Du Pont's TEFLON, and it is the nearest to the ideal graft that we will see in a long time.\textsuperscript{52} Harrison has shown that the low tissue reaction of TEFLON results in the following advantages for its use as an arterial graft:\textsuperscript{20,24}

1) More rapid healing of the graft with the formation of a fibrin lining which is gradually replaced by fibrous tissue growing through the interstices of the graft. The thickness of the fibrin lining deposited on the inner surface of the graft is not over 1\,mm, but with Dacron or nylon it is 2-3\,mm, and in an artery these are significant figures.

2) Lower rate of thrombosis.

3) Incidence of occlusion lower than any other material, including homografts.

4) Formation of a thinner fibrous enclosure with more pliability of the healed graft.

5) Walls of the graft retain their original strength to prevent aneurysm or rupture.

Although it has been in the field of arterial replacement surgery that TEFLON has reached universal acclaim, there are many other problems and conditions in surgery where this material may find extremely useful applications. The bridging of defects in the esophagus, common bile duct, and trachea with a tubular prosthesis is being evaluated, and the short-term results are very encouraging. Non-permeable and non-wettable arterial grafts are being investigated in an effort to improve the poor results obtained in small vessel surgery with our present methods. TEFLON auditory struts are being used in our
institution following stapes mobilization procedures. In over 50 clinical cases to date, the results have been excellent. Micropore film is being used to line the middle ear following procedures for adhesive otitis media, and to repair perforation in the tympanic membrane. Skull-caps are being fashioned to replace defects in the skull left by neurosurgical procedures. TEFLON is an ideal material to be used as a substitute for cartilage, and has excellent possibilities in reconstructive procedures of the nose and ear.

The future of this material in orthopedics is unlimited. Reconstruction of diseased and damaged joints, construction of femoral and condylar heads and digits, as well as intramedullary splints for the treatment of fractures are future possibilities. Tracheal stoma cannu-las as well as gastrostomy and suprapubic cystotomy appliances are now being manufactured by our department. The properties of TEFLON lend this substance suitably for the construction of heart valves, intracardiac sounding devices, millipore membranes and a large variety of instruments and machines of a scientific nature.

All in all, we have barely invaded the domain of TEFLON, and there is no doubt that the future holds unlimited possibilities of this material in medicine.
PART III

METHODS UTILIZED IN THE PRODUCTION OF A
TEFLON PROSTHESIS
For a considerable length of time I have been interested in the applicability of synthetic materials to bridge defects in the human body resulting from radical extirpational surgery for neoplastic disease. An intensive review of all available plastic materials, and a diligent investigation of their properties and tissue reactivity lead us to the conclusion that TEFLON deserved top-priority in our experimental study. Unfortunately, this substance was not available in a form that was suitable for our work. The commercial production of "Teflon" tetrafluoroethylene resins is centered around such products as coated fabrics and laminates, extruded rods, sheets or cylinders, tape, enamels and finishes, granular molding powders, and aqueous dispersions. None of these products—individually or collectively—adequately fulfilled the requirements of a good prosthesis.

A prosthesis—to be of any value—must be one that is readily available in all sizes, shapes, and forms. Its tubular or cylindrical wall should have good tensile strength despite its thinness and flexibility. Variations in diameter, length, thickness, and flexural components must be adequately controlled by methods of production which are simple, rapid and inexpensive. It must be adaptable to the suture technique of anastomosis and, most of all, be tolerated by the tissues and producing a minimal amount of tissue reaction. Insolubility in body fluids, along with impermeability, non-wettability, and non-carcinogenicity are other desirable properties. An "ideal" prosthesis is one that can expeditiously be "tailor-made" to bridge a specific defect produced by the surgical procedure.
Two methods of production were evaluated in order to obtain a suitable prosthesis of TEFLON. These included the following processes:

1) **ELECTRODEPOSITION.**

2) **LOW PRESSURE LAMINATION.**

Both processes have been described in the technical literature and therefore, we do not claim originality. However, the application of them in the production of a specific TEFLON product which was not available commercially, and the modifications in technique required to produce prostheses of variable characteristics is unique to our laboratory.

**PROCESS OF ELECTRODEPOSITION**

The overall advantage of this method is that it is possible to obtain a wide variety of forms and shapes from the polytetrafluoroethylene resins that cannot be obtained by any other method. The rubber industry has used this method for a number of years in the production of surgical gloves in which latex is electrically deposited onto highly polished metal mandrels.

The principle is simply a matter of **electrophoresis.** When a direct current is passed through an aqueous suspension of TEFLON (T-30 or T-41X), the negatively charged dispersed particles migrate toward the positive electrode (anode) while the water phase has a tendency to move towards the negative electrode (cathode). The negatively charged dispersed particles of TEFLON arriving at the anode by electrophoretic migration are discharged and deposited there. Certain positive ions (e.g., Cu++, Al+++, etc.) are oxidized at the anode. These are actually contaminants within the solution and migrate toward the cathode. The metal cations...
contact the negatively charged particles of TEFLON at the anode and cause them to coagulate by neutralizing their charge. Since the ratio of charge to particle size for the metal ions is much greater than that for the dispersed particles, this coagulation accounts for the very high rate of electrodeposition of TEFLON from the aqueous dispersion. Hydrogen gas and the formation of hydroxyl ions may occur at the cathode. These may produce an uneven current of deposition, and interfere with the result of the final product. This can be overcome by the use of a porous membrane, as asbestos cloth.

The apparatus utilized in our laboratory for this process is illustrated in Figure 4.
The required equipment includes the following items:

1) A direct source of current with a variable and reproducible emf ranging from 0 to 100 volts and a current capacity up to 25 milliamperes per square centimeter.

2) A constant temperature waterbath in which the TEFLON bath container is immersed.

3) pH meter.

4) Ion exchange column.

5) Analytical balance.

6) An accurate timing device to control the duration of deposition.

7) A pre-shaped mandrel to be used as a conductive anode upon which the TEFLON will be deposited.

8) A deposition bath lined circumferentially with a conductive cathode.

9) A permeable membrane (as, asbestos cloth, doubled, 80 mesh) located about ½ inch distant from the cathode lining, completely shielding it from the centrally positioned anode.

10) An oven with close temperature control ranging from 100 to 750°F.

A large number of problems required diligent and careful investigation before a satisfactory solution to them could be found. These included:

1) Concentration of solids in the TEFLON dispersion and its ratio to the stabilizing agent, Triton X-100.

2) Optimum pH, temperature, current and time of deposition.

3) Control of foreign ions (contaminants) in the bath.

4) Production of suitable mandrels.

5) Careful temperature control of the sintering oven.

6) Stripping of the finished product from the mandrel.

All of these problems had been faced individually, and a satisfactory solution to them has lead to the development of a process which appeared to be unique and substantially different from the process of electro-deposition as described in the technical literature from the E. I. Du Pont
The principle of electrophoresis is the same; but there have been modifications in the overall technique to make this procedure adaptable to the specific needs of this project.

The Teflon dispersions are obtained from the Du Pont Company and come in two different preparations:

1) **Teflon-30**—an aqueous dispersion containing 59-61% polytetrafluoroethylene resins by weight and stabilized with 5.5 to 6.5% non-ionic wetting agent of Triton X-100.

2) **Teflon 41X**—an aqueous dispersion containing 33-35.5% polytetrafluoroethylene resins by weight and stabalized with 1.35% of the wetting agent.

By repeated serial determinations, it was found that the ideal solid resin content of the dispersion bath should be around 33-35% polytetrafluoroethylene resin to which additional stabilizing agent—Triton X-100—was added in the amount of 9% of the solid content. This codispersion was checked periodically for concentration of solid content to be certain of its accuracy. The optimum pH was found to be 6.8—although a pH range between 6.5 to 7.0 was considered acceptable. The adjustment of the pH of the codispersion was done in an ion exchange column which contained an ion exchange resin (Amberlite IRC-50) and exchange resin beads (glass) that were confined to the chamber by the placement of a screen of tantalum mesh at either end of the column. The column is first flushed with a buffered citric acid sodium phosphate (dibasic)-sulphuric acid (10%) solution to convert it to a pH range of 6.5 to 7.0. It was then back-flushed with neutral distilled water (pH 7). The Teflon codispersion is then flushed through this column until the pH of the codispersion reaches 6.8. This solution is now allowed to set at room temperature.
for 12-24 hours before it is used. This codispersion bath will maintain its solid content and pH for a considerable length of time provided that periodic agitation of the solution is done.

When depositions are to be made, the constant temperature bath is adjusted to a temperature slightly above ambient (40°C). Once the temperature is constant, the buffered codispersion bath of polytetrafluoroethylene resins is transferred to the deposition tank and immersed until its temperature is equivalent to that of the constant temperature bath. A chemically clean mandrel (anode) is then inserted into the codispersion bath and a permeable membrane (asbestos cloth, doubled, 80 mesh) is placed ¼th inch distance from the cathode lining (deposition tank). Leads are now connected to the power supply—a special current source built especially for this project—and deposition of the polytetrafluoroethylene resins on the anode will proceed when the current is instituted. The voltage, amperage, and duration of deposition have been meticulously evaluated. Since the deposition rate of the polytetrafluoroethylene resins out of aqueous dispersion is extraordinarily high (several times that of metallic electroplating baths), low current densities and short deposition times are needed.

The mandrels are machine from stock metals, and correspond in dimension and configuration to the desired prosthesis. (Figures 5 & 6). These are made from a metal having the least amount of foreign ionic contamination of the codispersion bath during the deposition procedure. They are machined in such a fashion that the grooves have a screw-type affect—a necessity to facilitate stripping procedures.

After the electrophoretic process has been completed, the electrodeposited mandrel is removed from the dispersion bath, and placed in an
FIGURE 5.
Mandrels for Esophageal Prosthesis

FIGURE 6.
Mandrels for Tracheal Prosthesis
oven where the polytetrafluoroethylene resins are cured by a process of sintering. This is an important part of the procedure and requires careful control of the temperature of the oven. An improper temperature profile during the sintering operation will result in cracked coatings of low dielectric strength. Drying is accomplished by gradually increasing the environmental temperature of the coated mandrel in the oven from 100°F to 390°F. By the time 390°F is reached, the entrained water has been removed, and the fragile raw deposit becomes tough enough so that mechanical failure through handling is minimized. The temperature is then more rapidly increased to 620°F during which time the stabilizer is evaporated. This is the transition temperature, and the temperature is more slowly raised to an ultimate of 698°F – 716°F. From this peak value the oven is permitted to slowly drop to 400°F – at which time the finished product can be removed and permitted to air cool to handling temperature or it may be cold-quenched. The TEFLOH prosthesis is then stripped from the mandrel; and, after adequate sterilization by autoclaving, is ready for implantation. The entire time involved from the deposition to cure of the prosthesis is no more than 5 minutes.

Although this process had considerable possibilities, there were too many variable factors that required meticulous control. Any deviation in these variables resulted in an imperfect prosthesis. The most difficulty encountered was in the stripping or removal of the finished product from the mandrel. Despite cold-quenching it was difficult to remove the finished product from the mandrel without producing imperfections in its wall. An attempt to overcome this problem involved tightly wrapping the mandrel with aluminum foil and electrodepositing the polytetrafluoroethylene resin on the foil wrapping.
Following the cure phase, the foil was removed from the mandrel and easily stripped from the prosthesis. This method was soon discarded since the foreign ionic contamination of the codispersion bath with Al\textsuperscript{+++} ions interfered with the passage and complete deposition of the polytetrafluoroethylene resin ions at the anode. Another solution to this problem was the advocacy of mandrels made of metals having known melting points. A wide variety of "wood's metals" were tried—the principle being that the metal would melt at a certain temperature after the polytetrafluoroethylene resin had been cured, i.e., shortly after its transition temperature. Thus, a prosthesis having the configuration of the mandrel would be left free in the oven. However, this method soon was also abandoned since the cost of machining and re-machining mandrels became a serious problem.

There soon became available on the commercial market a form of cast "Teflon" film—Type CSC. After studying the possibilities of this material, we ceased our experiments with electrodeposition of aqueous dispersions, and concentrated our attention on a method of production that was less complicated—namely, low pressure lamination.

**PROCESS OF LOW PRESSURE LAMINATION**

Type CSC Cast "Teflon" Film is a multi-laminate of individually cast thin TEFLON films superimposed and completely fused together into a high impermeable, void-free film. Over this base of fused and stress-free film is cast an additional layer of TEFLON in particulate form; however, the superfacial layers are not fused but are sufficiently heated to cause a medium bond between the unfused layers and the base fused film. These unfused layers of TEFLON will resist normal handling.
and may be easily detected by applying a strip of pressure sensitive cellophane tape against either side of the CSC Film and stripping. The unfused layer comes away readily.

At normal temperatures TEFLON has a crystalline structure but when heated above 620°F changes into an amorphous transparent gel. At these temperatures TEFLON is sticky and has the ability to weld itself together. The presence of unfused TEFLON seems to enhance this welding characteristic, particularly in film form. Therefore, when wrapped upon itself and subjected to sintering temperatures of 620-660°F, the Type CSC Films readily fuse into a coherent and firm mass.

Thus, the process of lamination by low pressure involves the wrapping of a highly polished mandrel having a diameter equivalent to the finished I.D. requirements of the prosthesis. The mandrel is first treated with a thin layer of mold release agent—silicone; and is then tightly wrapped with Type CSC TEFLON cast film. The mandrel is deeply grooved in screw-fashion with about 1/16th inch pitch and distance between spirals in order to allow for flexibility of the prosthesis. The thickness of the tube will depend upon the number of layers of film used in the wrapping process and the film thickness. Attention is directed to applying the film as tightly as possible in spiral fashion using a minimum of a single overlay. Asbestos cord or glass impregnated fiber is then used as a wrapping to be certain that the film is pressed deeply into the grooves of the mandrel. The casted mandrel is placed in an oven and sintered at a temperature of 680°F, producing solid fusion of the layers of the film. Dwell time within the oven depends upon the thickness of the TEFLON and the diameter of the mandrel. In our laboratory we use change in color to transparency as a guide to complete
fusion. When fully cured, the mandrel is taken from the oven and immediately cold-quenched. The cord is removed and the finished prosthesis is unscrewed from the mandrel.

This method has proved very successful and produced a prosthesis rapidly and conveniently within a matter of minutes. The prosthesis and its flexural characteristics are illustrated in Figure 7.

FIGURE 7.

Flexural Properties of TEFLON Prosthesis

Since TEFLON per se produces a minimum amount of tissue reaction, it was necessary to incorporate in the final prosthesis a material which was capable of fibroblastic reaction in order to allow for complete fixation and prevention of leakage due to disruption of the anastomotic
site. Strips of Marlex mesh—a linear or high density polyethylene—were anchored to the center of the prosthesis by a TEFLOn ring. (Figure 8) A "skirted" prosthesis of TEFLOn with Marlex strips therefore was used in our esophageal and tracheal experimental projects, while a smooth "pure" TEFLOn tube was utilized in our common duct experiments. (Figure 9)
FIGURE 9.

TEFLON Common Duct Prosthesis
PART IV
EXPERIMENTAL PROJECTS

THE BRIDGING OF DEFECTS IN THE COMMON BILE DUCT BY THE USE OF A TEFLOMN PROSTHESIS
(Comprehensive Presentation)

A SUCCESSFUL METHOD FOR BRIDGING THORACIC ESOPHAGEAL DEFECTS IN THE DOG
(Brief Review)

THE BRIDGING OF SURGICAL PRODUCED DEFECTS IN THE TRACHEA OF EXPERIMENTAL ANIMALS USING A "TEFLOMN" PROSTHESIS
(Brief Review)
INTRODUCTION

It has long been apparent that reconstructive procedures on the common bile duct have been a tax on the ingenuity of many a notable surgeon. The difficult problem of restoration of ductal continuity following resectional therapy for either benign or malignant conditions has been a great challenge; unfortunately, the results have not been too fruitful. So many procedures have been advocated that there now exists considerable confusion over the choice of a suitable one for the unfortunate patient.

From all of the procedures that have been suggested and performed during the past many years, end-to-end anastomosis is the most desirable repair if this is technically feasible. The suggestions of Cattell, Cole, and Lahey for mobilizing the duodenum in order to compensate for the loss in length of the duct will increase the number of cases in which primary union of the duct may be performed. An essential function of the sphincteric action of the papilla of Vater is the prevention of ascending cholangitis and its severe secondary sequelae. Therefore, restoration of the flow of bile from the proximal common duct through the distal segment to save the function of the sphincter of Oddi should be considered. However, if the defect between the two ends does not allow primary union, then a prosthesis to adequately bridge this defect should be considered.

It is true that a large number of ductal prostheses have been advocated and tried in the past. These have varied from viable grafts to non-viable, artificial appliances; but all have been short-lived in
their applicability. Most of these have failed due to the high percentage of occlusion secondary to inflammatory reaction, cicatricial contracture, or the deposition of foreign material within the lumen of the tube, thereby producing obstruction with secondary ascending cholangitis. Loss of the tube with subsequent fibrous contracture was common due to failure of fixation of the prosthesis. It has been for these reasons that the shunting procedures have been recommended. But even in these procedures, the problems of patency of the anastomatic stoma and ascending cholangitis have been serious ones.

Perhaps, one of the reasons for the failure of prosthetic appliances in the past has been the fact that an ideal material for such a prosthesis had not been available. Our experience with TEFLON during the past two years in bridging defects in other hollow viscera in the body has lead us to believe that this substance may be suitable for such a prosthesis. Consequently, the purpose of this project has been to evaluate the applicability of a prosthesis produced from TEFLON to bridge defects in the common bile duct of the experimental animal.

**MATERIALS**

Using a method developed in our laboratory a small, smooth tubular prosthesis was constructed from TEFLON. This ranged in thickness from \(\frac{1}{2}\) to 1 mil, and had an average length of 25 mm. with an inside diameter varying from 3 to 5 mm. Our previous work with this material has shown that this substance is inert when implanted into various areas of the body. This lack of tissue reactivity is advantageous since it eliminates the element of cicatricial contracture which was a major factor in the failure of previous materials. Whereas other anastomoses in the gastro-
intestinal tract proper heal well with a minimum of constriction, anastomosis of the common duct carries a high potentiality for subsequent stricture formation. This material should eliminate this potentiality. In addition, it has many other properties that are advantageous, namely, non-wettable, non-permeable, resistant to heat, acids, and alkalis, and has excellent tensile strength which does not diminish with age. It supports a suture firmly, and can be sterilized by autoclaving. Tubes varying in size, shape, rigidity, and flexibility may be produced within a matter of minutes so that a "tailor-made" prosthesis may be made during the operative procedure to bridge the resultant defect.

PROCEDURE

A total of nineteen animals were used in this experiment, and these were divided into the following groups:

Group I: Seven dogs in which a 20 mm. segment of the common bile duct was resected, and the defect bridged by the insertion of a TEFLOK prosthesis measuring 24 mm. in length. The inside diameter of the prosthesis averaged 2 mm.

Group II: Seven dogs in which a cholecystectomy had been performed; and then at a later date, a 20 mm. segment of the secondarily dilated common duct was resected and replaced by a 24 mm. TEFLOK prosthesis. The inside diameter averaged 5 mm.

Group III: Five cholecystectomized dogs in which the common bile duct was purposefully injured. After icterus was fully developed, the strictured area (25 mm.) was resected, and
a 30 mm. prosthesis having an inside diameter of 5 mm. was inserted.

All animals were anaesthetized with intravenous sodium nembutal and were intubated. Transabdominal approach was used, and all wounds were closed without drainage. The prosthesis was invaginated into the ends of the common duct for a short distance, and fixation was accomplished by a purse-string of 4-0 silk suture. No supporting splints, such as T-tubes, were used. Antibiotics were given 24 hours preoperatively, and continued for three postoperative days. The degree of icterus present, and its response to the corrective procedure was followed by the usual liver function tests—particularly, the alkaline phosphatase; and cholangiograms were obtained when feasible.

RESULTS

Fifteen animals survived the operative procedure and exhibited no evidence of biliary tract obstruction. Four dogs expired from various causes allowing autopsy evaluation.

In Group I there were 5 successful procedures. In an observation period ranging from 9 to 20 months, there was no evidence of jaundice in any of these animals. The oldest was recently explored, and it was found that the prosthesis was still in place with a minimal amount of fibrous tissue encompassing it but without adherence to its wall. There was no evidence of dilatation of the common bile duct, and aspiration revealed an absence of debris within its lumen. The anastomotic site was still patent. Laparotomy on the subsequent animals revealed similar findings. Two dogs expired from extraneous causes on
the 18th and 60th POD, respectively, and autopsy revealed the prosthesis to be encased in a very thin fibrous sheath. When this was opened the prosthesis was not adherent to its wall; the anastomotic sites were intact and no debris was present within its lumen.

![Specimen of common duct and duodenum in which the prosthesis is still in situ. Common duct is normal in size, and there is a lack of tissue reaction in this region.](image)

**FIGURE 10**

Specimen of common duct and duodenum in which the prosthesis is still in situ. Common duct is normal in size, and there is a lack of tissue reaction in this region.

All of the animals in Group II survived; and, in an observation period from 9 to 20 months, they have remained free of jaundice. Cholangiographic studies revealed a normal biliary tree without evidence of dilatation of the ductal system, and with a free flow of bile into the intestinal tract.
FIGURE 11

Common duct has been opened revealing ductal continuity with the prosthesis in place. A thin layer of fibrous tissue encompasses the prosthesis but is not adherent to it. There is no evidence of cicatricial contracture or disruption of the suture site.

Only 3 dogs survived in Group III. Short-term observation of 4 to 5 months has revealed all animals to have fully recovered from their preoperative icteric state. Within the first two weeks, the alkaline phosphatase levels dropped from 438, 292, and 362 units to 6.8, 163, and 53.2 units respectively. X-rays revealed good ductal continuity without evidence of obstruction. One dog expired on the 13th POD from bile peritonitis secondary to severance of an accessory bile duct while the other expired on the 45th POD from an intrahepatic
abscess with recent exsanguinating hemorrhage. Both animals had completely recovered from their preoperative icteric state. Autopsy revealed the prosthesis to be in place without disruption of the anastomotic site or fibrous contracture of the ends of the duct despite the extensive inflammatory reaction present.

**DISCUSSION**

There have been many problems involved in the reconstruction of the common bile duct following injury. Many procedures have been advocated but the results have been discouraging. The best procedure is still primary repair of the ends of the duct by end-to-end anastomosis over a splint whenever this is feasible. Preservation of the ampulla of Vater is one important aspect of the prevention of ascending cholangitis and functional continuity of the biliary ductal system. To bypass this area by the use of the various shunting procedures often does not offer a satisfactory solution to the problem. Even though a Roux-Y arm of jejunum is used, as practiced by Whipple, Cole, and others, Colp has aptly pointed out that this type of repair does not eliminate entirely the subsequent occurrence of cholangitis from infection ascending the jejunal segment into the common duct; and, there is also no assurance that the anastomotic stoma will remain patent.\(^2,3,7,24\)

A preferable method is to bridge the defect in the duct with a prosthesis providing both ends can be identified. The suggestions of Lahey\(^7\) and Cattell\(^1\) in finding the distal segment of the duct should be of considerable value in its identification.

It is true that in the past a wide variety of substances and materials have been utilized to bridge the ductal defect. Autogenous
and homologous free grafts of skin, veins, arteries, fascia, appendix, intestine, fallopian tube, ureter, and even common duct itself — both fresh and preserved — have been tried and proved unsuccessful. Necrosis with disruption of the anastomotic site, and occlusion by cicatricial contracture were responsible for these failures. Viable pedicle grafts have yielded a few satisfactory results — but, by and large, most of these have also met with failure. Various artificial appliances have been inserted — including tubes made of rubber, vitallium, polyethylene, nylon, and other forms of plastic materials — with disappointing results. Occlusion of the tubes with biliary sediment and loss of fixation and ductal continuity followed by fibrous contracture presented a serious problem.

To date, an ideal prosthesis has not been found which is suitable for reconstructive procedures in this area. Our work with TEFLON has been very encouraging, and has lead us to believe that this material may adequately fulfill the requirements of an ideal prosthesis. The potentiality of cicatricial contracture is eliminated since this substance produces a minimum of tissue reaction thereby obviating stricture formation. Its properties of chemical inertness, non-wettability, and non-permeability are advantageous in the prevention of occlusion of the lumen by biliary debris or sediment. Anastomosis is easily performed without utilization of special techniques, and its tensile strength prevents fragmentation and deterioration with the passage of time. Prosthetics varying in size, shape, and flexibility may be expeditiously and inexpensively produced within a few minutes.

Although the results of our experiment are on a relatively short-
term basis -- the period of observation being 9 to 20 months -- 15 animals have remained alive and well. There has been no evidence of biliary tract obstruction. Liver function tests and cholangiograms are all within normal limits.

SUMMARY

A prosthesis made of TEFLON was used to bridge defects in the common bile duct of 19 animals. Excellent results were obtained in 15 dogs, while 4 of them expired from various extraneous causes. There was no evidence of obstructive jaundice or secondary cholangitis in any of the surviving animals. In these the prosthesis had maintained its integrity and functioned without evidence of cicatricial contracture or occlusion by debris. Although the period of observation has been short-termed -- from 9 to 20 months -- the animals are being preserved for long term observation.
A SUCCESSFUL METHOD FOR BRIDGING THORACIC ESOPHAGEAL DEFECTS IN THE DOG

Surgeons have long sought a successful method for restoring esophageal continuity following radical ablative procedures. Our efforts to solve this problem have centered around a TEFLON prosthesis which can be simply made in our laboratory. Briefly, our experiments can be divided into two phases.

Phase I experiments numbered 34 animals and involved reliance of suture fixation to maintain the prosthesis in place. Our result in this group was total failure to achieve permanent anchorage of the prosthesis resulting in death due to disruption of the anastomotic site with leakage into the pleural cavity and stricture formation.

Phase II experiments were based on the concept that suture fixation must be augmented by another factor—namely, host reaction about the prosthesis in the form of fibroblastic adhesions if success were to be achieved. To the TEFLON prosthesis (which by itself is so inactive that host fixation will not occur) were added strips of Marlex mesh through the interstices of which the hosts' fibroblasts would grow and anchor the prosthesis. Sixteen animals had their mid-thoracic esophagus resected and restored with this scheme. (Figure 12)

Five of them died from the operative procedure; but of the remaining 11 dogs, 9 are alive and well one year postoperatively — 87.5% survivability. They are maintaining their preoperative weight and have no difficulty in swallowing. Of the two dogs which were lost during the postoperative period, it is interesting to note that autopsy specimens revealed good fibroblastic reaction around the Marlex strips.
TEFLON-MARLEX ESOPHAGEAL PROSTHESIS

proximal esophagus

distal esophagus

Teflon prosthesis in position with Marlex strips sutured to esophagus
providing firm fixation of the prosthesis. (Figure 13) There was minimal reaction around the TEFLON where it was encompassed in a thin fibrous sheath of mesothelial cells which was not adherent to its wall. (Figure 14) Our success with this scheme has been sufficiently good to encourage its use in human subjects.

**FIGURE 13**
Anatomical specimen showing good fibroblastic reaction around Marlex strips.

**FIGURE 14**
Fibrosis sheath opened. No adherence to wall of prosthesis. Mesothelial cells in their layers.
Initial work consisted of resecting the cervical or thoracic trachea in dogs and inserting various types of TEFLON prostheses to bridge the defect. In this phase of the project fixation was accomplished by either direct suture technique or fixation rings. Little success was achieved due to ultimate loss of the prosthesis with subsequent leakage of air into the pleural cavity along with its secondary complications and tracheal stenosis. Based on earlier work with esophageal prostheses, all later experiments were designed to supplement suture fixation with host fibroblastic reaction with resultant striking improvement.

The prosthesis that has given our best results consists of a helical - coil TEFLON tube to which are fixed Marlex strips. An end-to-end anastomosis of the tracheal ends to the prosthesis is first performed and the Marlex strips are then tacked to the trachea beyond the anastomotic site. Suture fixation will care for the immediate anchoring of the prosthesis, but permanent fixation is dependent upon subsequent growth of fibrous tissue through and about the Marlex strips. The experimental animals were divided into three groups.

In Group I a segment of the cervical trachea was resected in six dogs. Four of these animals survived the operative procedure and are asymptomatic. Of the dogs that expired there was loss of fixation during the first postoperative week in one dog with a secondary fistula in the trachea, and the other dog expired from hemoptysis of unknown origin. There is a 66-2/3% survivability of these animals at the present time which is 5 months postoperatively.
In Group II a segment of thoracic trachea was resected and the defect bridged with a prosthesis. Of these six animals there was one mortality due to loss of fixation of the prosthesis during the immediate postoperative period. All of the other five animals are living and well 3 to 4 months postoperatively which gives 83-1/3% survivability.

In Group III there were eight dogs in which a right pneumonectomy was performed along with resection of the carina and lower thoracic trachea. A prosthesis was inserted from the upper thoracic trachea to the left main stem bronchus. Six animals survived this procedure and two died postoperatively. These have been observed for 2 months giving a survivability of 75%.

These results are encouraging and should have considerable clinical application in allowing a more radical approach to the problem of bronchogenic carcinoma.
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