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BIOGRAPHICAL MEMOIR

OF

WALLACE HUME CAROTHERS

1896–1937

BY

ROGER ADAMS

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Wallace H Carothers

## WALLACE HUME CAROTHERS

1896-1937

BY ROGER ADAMS

Wallace Hume Carothers, who died on April 29, 1937, was born in Burlington, Iowa, on April 27, 1896. His contributions to organic chemistry were recognized as outstanding and, in spite of the relatively short span of time for his productive accomplishments, he became a leader in his field with an enviable international reputation.

His paternal forbears were of Scotch origin and settled in Pennsylvania in prerevolutionary days. They were farmers and artisans. His father, Ira Hume Carothers, who was born in 1869 on a farm in Illinois, taught country school at the age of 19. Later he entered the field of commercial education and for forty-five years has been engaged in that type of work as teacher and vice-president in the Capital City Commercial College, Des Moines, Iowa. Wallace Hume Carothers was the first scientist in the family.

His maternal ancestors were of Scotch-Irish stock and were also, for the most part, farmers and artisans. They were great lovers of music, and this may account for the intense interest in and appreciation of music which Carothers possessed. His mother, who was Mary Evalina McMullin of Burlington, Iowa, exerted a powerful influence and guidance in the earlier years of his life.

To his sister Isobel (Mrs. Isobel Carothers Berolzheimer), of radio fame as Lu in the trio Clara, Lu and Em, he was especially devoted. Her death in January, 1936, was a staggering shock to him and he was never able to reconcile himself completely to her loss.

On February 21, 1936, he married Helen Everett Sweetman of Wilmington, Delaware. Her father is Willard Sweetman, an accountant, and her mother, Bertha Everett. The family is of English-Welsh descent. Mrs. Carothers received her bachelor's degree in chemistry at the University of Delaware in 1933 and was employed in the patent division of the chemical depart-

ment of the du Pont Company from 1933-1936. A daughter, Jane, was born November 27, 1937.

Wallace was the oldest of four children. His education began in the public schools of Des Moines, Iowa, to which city his parents moved when he was five years of age. In 1914 he graduated from the North High School. As a growing boy he had zest for work as well as play. He enjoyed tools and mechanical things and spent much time in experimenting. His school work was characterized by thoroughness and his high school classmates testify that when he was called upon to recite his answers revealed careful preparation. It was his habit to leave no task unfinished or done in a careless manner. To begin a task was to complete it.

He entered the Capital City Commercial College in the fall of 1914 and graduated in the accountancy and secretarial curriculum in July, 1915, taking considerably less time than the average. He entered Tarkio College, Tarkio, Missouri, in September, 1915, to pursue a scientific course, and simultaneously accepted a position as assistant in the Commercial Department. He continued in this capacity for two years and then was made an assistant in English, although he had specialized in chemistry from the time he entered college. During the World War the head of the department of chemistry, Dr. Arthur M. Pardee, was called to another institution, and Tarkio College found it impossible to secure a fully equipped teacher of chemistry. Carothers, who previously had taken all of the chemistry courses offered, was appointed to take over the instruction. Since he was rejected as a soldier on account of a slight physical defect, he was free to serve in this capacity during his junior and senior years. It is interesting that during his senior year there were four senior chemistry-major students in his class and every one of them later completed work for the doctorate, studying in the universities of this country and abroad. Today they bear testimony to the fact that as undergraduates they owed much to the inspiration and leadership of Carothers.

Upon entering college his interest in chemistry and physical sciences was immediate and lasting, and he rapidly outdistanced his classmates in accomplishment. As a student he showed

mature judgment and was always regarded by his fellow students as an exceptional person. Invariably he was the brightest student in the class regardless of the subject. Financial necessity required that he earn a large portion of his educational expenses. He always found time, however, to associate with the other students, though he showed little interest for the boisterous enthusiasms of the average underclassman. During his last two years in college he was entrusted with a number of student offices to which he gave freely of his time and energy.

Leaving Tarkio College in 1920 with his bachelor of science degree, he enrolled in the chemistry department of the University of Illinois where he completed the requirements for the master of arts degree in the summer of 1921. His former instructor at Tarkio College, then head of the chemistry department at the University of South Dakota, desired a young instructor to handle courses in analytical and physical chemistry and was fortunate in securing Carothers for this position during the school year, 1921-1922. He went to South Dakota only with the intention of securing sufficient funds to enable him to complete his graduate work, but the careful and adequate preparation of his courses, as well as his care of the students under his direction, showed that he could be a very successful teacher of chemistry. He was still the same quiet, methodical worker and scholar, not forceful as a lecturer, but careful and systematic in his contact with the students. He always required adequate preparation of assigned work and was able to get a large volume in student accomplishment.

Simultaneously with his teaching work he started to develop some independent research problems. He was especially interested in the 1916 paper of Irving Langmuir on valence electrons and desired to investigate some of the implications it held in organic chemistry. Pursuing this idea he carried out laboratory studies which were reported in his first independent contribution to the *Journal of the American Chemical Society*, "The Isosterism of Phenyl Isocyanate and Diazobenzene-Imide." His second independent paper, published while still a student, was that on "The Double Bond." In this he presented the first clear, definite application of the electronic theory to organic

chemistry on a workable basis. He described the electronic characteristics of the double bond and in essence included in his discussion everything that has since been written on this particular subject.

It was evident, even at this stage of his career, that teaching was not his forte. Literally he spent all of his spare time on research problems in which he became interested. A number of his newly found friends in South Dakota tried to induce him to relax somewhat from his constant and sustained application to work, but without avail. He appeared to be driven by the many things that occurred to him as worthy of investigation in the laboratory.

He returned to the University of Illinois in 1922 to complete his studies for the degree of doctor of philosophy, which he received in 1924. His major work was in organic chemistry with a thesis under the direction of Dr. Roger Adams, on the catalytic reduction of aldehydes with platinum-oxide platinum-black and on the effect of promoters and poisons on this catalyst in the reduction of various organic compounds. His minors were physical chemistry and mathematics. He exhibited the same brilliance in all of his courses and in research which characterized his earlier accomplishments. Although specializing in organic chemistry, he was considered by the physical chemists to have a more comprehensive knowledge of physical chemistry than any of the students majoring in that field. In 1920-1921 he held an assistantship for one semester in inorganic chemistry and for one semester in organic chemistry. He was a research assistant during 1922-1923, and during 1923-1924 held the Carr Fellowship, the highest award offered at that time by the department of chemistry at Illinois. During these two years his seminar reports demonstrated his wide grasp of chemical subjects. The frequency with which his student colleagues sought his advice and help was indicative of his outstanding ability. At graduation he was considered by the staff as one of the most brilliant students who had ever been awarded the doctor's degree. A vacancy on the staff of the chemistry department of the University of Illinois made it possible to appoint him as an instructor in organic chemistry in the fall of 1924. In this

capacity he continued with unusual success for two years, teaching qualitative organic analysis and two organic laboratory courses, one for premedical students and the other for chemists.

Harvard University, in 1926, was in need of an instructor in organic chemistry. After carefully surveying the available candidates from the various universities of the country, Carothers was selected. In this new position he taught during the first year a course in experimental organic chemistry and an advanced course in structural chemistry, and during the second year he gave the lectures and laboratory instruction in elementary organic chemistry.

President James B. Conant, of Harvard University, was professor of organic chemistry at the time that Carothers was instructor. He says of him—

“Dr. Carothers’ stay at Harvard was all too short. In the brief space of time during which he was a member of the chemistry department, he greatly impressed both his colleagues and the students. He presented elementary organic chemistry to a large class with distinction. Although he was always loath to speak in public even at scientific meetings, his diffidence seemed to disappear in the classroom. His lectures were well ordered, interesting, and enthusiastically received by a body of students only few of whom planned to make chemistry a career. In his research, Dr. Carothers showed even at this time that high degree of originality which marked his later work. He was never content to follow the beaten track or to accept the usual interpretations of organic reactions. His first thinking about polymerization and the structure of substances of high molecular weight began while he was at Harvard. His resignation from the faculty to accept an important position in the research laboratory of the du Pont Company, was Harvard’s loss but chemistry’s gain. Under the new conditions at Wilmington, he had facilities for carrying on his research on a scale that would be difficult or impossible to duplicate in most university laboratories. Those of us in academic life, however, always cherished the hope that some day he would return to university work. In his death, academic chemistry, quite as much as industrial chemistry, has suffered a severe loss.”

In 1928 the du Pont Company had completed plans to embark on a new program of fundamental research at their central laboratory, the Experimental Station at Wilmington, Delaware. Carothers was selected to head the research in organic chemistry. The decision to leave his academic position was a difficult one. The new place demanded only research and offered

the opportunity of trained research men as assistants. This overbalanced the freedom of university life and he accepted. From then on until his death his accomplishments were numerous and significant. He had the rare quality of recognizing the significant points in each problem he undertook, and unusual ability for presenting his results in a most explicit and precise way, which led to clarity and understanding. In these nine years he made several major contributions to the theory of organic chemistry and discoveries which led to materials of significant commercial importance. Dr. Elmer K. Bolton, Chemical Director of the du Pont Company, writes concerning Carothers—

“At the time the du Pont Company embarked upon its program of fundamental research in organic chemistry in the Chemical Department, Dr. Carothers was selected to direct this activity, because he had received the highest recommendations from Harvard University and the University of Illinois, and was considered to have unusual potentiality for future development. There was placed under his direction a small group of excellently trained chemists to work on problems of his own selection. The results of his work, extending over a period of nine years, have been of outstanding scientific interest and have been considered of great value to the Company as they have laid the foundation for several basically new developments of commercial importance.

“In our association with Dr. Carothers, we were always impressed by the breadth and depth of his knowledge. He not only provided inspiration and guidance to men under his immediate direction, but gave freely of his knowledge to the chemists of the department engaged in applied research. In addition, he was a brilliant experimentalist. Regarding his personal characteristics, he was modest, unassuming to a fault, most uncomplaining, a tireless worker—deeply absorbed in his work, and was greatly respected by his associates. He suffered, however, from a nervous condition which in his later years was reflected in poor health and which became progressively worse in spite of the best medical advice and care, and the untiring efforts of his friends and associates. His death has been a great loss to chemistry and particularly to the Chemical Department. In my judgment, he was one of the most brilliant organic chemists ever employed by the du Pont Company.”

His reputation spread rapidly; his advice was sought continually, not only by his colleagues but also by chemists throughout the world. In 1929 he was elected Associate Editor of the *Journal of the American Chemical Society*; in 1930 he became

an editor of *Organic Syntheses*. He took an active part in the meetings of the organic division of the American Chemical Society. He was invited frequently to speak before various chemical groups. He addressed the Johns Hopkins summer colloquium in 1935 on "Polymers and the Theory of Polymerization." That year he also spoke on the same subject before the Faraday Society in London, when his paper was considered one of the outstanding presentations on the program. His achievements were recognized by his election to the National Academy of Sciences in 1936—the first organic chemist associated with industry to be elected to that organization. During these years from 1928-1937 several attractive academic positions were offered him but he chose to remain to the end with the company which had given him his opportunity for accomplishment.

Very early in life he displayed a love for books. From the time when *Gulliver's Travels* interest a boy on through Mark Twain's books, *Life of Edison*, and on up to the masters of English literature, he was a great reader. He possessed a singing voice that might have developed under training into something very worthwhile. Though he had no technical training in music, he was a lover of the great masters, and possessed a large and much-used collection of phonograph records of their works. He said occasionally that were he to start over he would devote his life to music.

Carothers was deeply emotional, generous and modest. He had a lovable personality. Although generally silent in a group of people, he was a brilliant conversationalist when with a single individual, and quickly displayed his broad education, his wide fund of information on all problems of current life, and his critical analysis of politics, labor problems and business, as well as of music, art, and philosophy. With all his fine physique he had an extremely sensitive nature and suffered from periods of depression which grew more pronounced as he grew older, despite the best efforts of his friends and medical advisors.

### SCIENTIFIC WORK

His early scientific work involved an extension to organic compounds of Langmuir's idea of isosterism. He demonstrated

that it was valid in the case of phenyl isocyanate and azoimide. Reactions of the double bond were interpreted in terms of the electronic theory, using a point of view that has since gained wide acceptance.

His next efforts were devoted to demonstrating that any idea of "negativity" alone is inherently incapable of accounting for the relative reactivity of organic halides. He measured the base strength of a series of amines. His work on the thermal decomposition of alkali alkyls threw light on the inherent properties of the simplest organic anions.

The first field of which he was in a position to make an exhaustive study was that of acetylene polymers and their derivatives. With vinylacetylene and divinylacetylene made available to him, he completed a detailed study of these substances. It was his discovery that it was possible to add hydrogen chloride to monovinylacetylene with formation of 2-chloro-1,3-butadiene, called chloroprene. This substance is analogous structurally to isoprene but polymerizes several hundreds of times more rapidly and leads to a product much superior to all previously known synthetic rubbers. It was the first synthetic material to show rubber's curious property of developing fibrous orientation when stretched and instantly reverting to the amorphous condition when released from stress. In resistance to aliphatic hydrocarbons and to most chemical reagents it is definitely superior to natural rubber. It has, moreover, a greater resistance than rubber to corona and sunlight. Carothers' work laid the foundation for the development by other chemists and by chemical engineers of the du Pont Company of the commercial product which has found wide industrial use and which is marketed as neoprene.

These practical results, however, were of no greater importance than the theoretical. In the course of the investigation, many analogs and homologs of chloroprene were prepared and studied. Their behavior threw light on the relationship between the chemical structure of a diene and its suitability as a precursor of rubber. Fundamental information concerning the character and formation of the various polymers from these compounds was revealed and their structures clarified. The reactivity of

the vinylacetylenes and the mechanism by which the products formed was studied in detail. New light was thrown on 1,4 addition and on  $\alpha,\gamma$  rearrangements. His work in this field was a basic contribution to acetylene chemistry.

The most outstanding scientific accomplishment of Carothers was his work on linear polymers. In a letter written to Dr. John R. Johnson of Cornell University on February 14, 1928, Carothers made a statement which demonstrated the careful thought and study which he had given previously to polymerization and polymeric molecules. It follows—

“One of the problems which I am going to start work on has to do with substances of high molecular weight. I want to attack this problem from the synthetic side. One part would be to synthesize compounds of high molecular weight and known constitution. It would seem quite possible to beat Fischer’s record of 4200. It would be a satisfaction to do this, and facilities will soon be available here for studying such substances with the newest and most powerful tools.

“Another phase of the problem will be to study the action of substances  $xAx$  on  $yBy$  where A and B are divalent radicals and x and y are functional groups capable of reacting with each other. Where A and B are quite short, such reactions lead to simple rings of which many have been synthesized by this method. Where they are long, formation of small rings is not possible. Hence reaction must result either in large rings or endless chains. It may be possible to find out which reaction occurs. In any event the reactions will lead to the formation of substances of high molecular weight and containing known linkages. For starting materials will be needed as many dibasic fatty acids as can be got, glycols, diamines, etc. If you know of any new sources of compounds of these types I should be glad to hear about them.”

These initial ideas culminated in the publication of a series of thirty-one papers in the field of polymerization. In these he proposed a general theory of condensation-polymerization and a logical and systematic terminology suitable for use in this previously disorganized field. The implications of his theory were illustrated by a series of experimental studies dealing with polyesters, hydrocarbons, polyamides, and polyanhydrides. These studies provided experimental material for correlating chemical structure and physical properties of materials of high molecular weight, and furnished evidence favoring a view now generally accepted for the structure of such natural high poly-

mers as cellulose. In these investigations a new technic—molecular distillation—was applied to the propagation of chemical reactions.

In this study a method new in principle was developed for the synthesis of many-membered cyclic compounds. A large number of many-membered cyclic compounds was synthesized, including several of entirely new types. Some of these compounds had musk-like odors and are otherwise similar in their properties to the genuine musks. One of these new many-membered ring compounds has found industrial application. The large amount of experimental material made possible important deductions bearing on the relationship between chemical structure and ease of ring formation. His contribution was a major one to the field of many-membered ring compounds, which is one of growing significance in organic chemistry.

He investigated the means by which polymers structurally analogous to cellulose and silk could be prepared, and synthesized a large number. These materials constituted the first completely synthetic fibres with a degree of strength, orientation, and pliability comparable with natural fibres. Their study made possible the development of a theory for the relation between structure, fibrous properties, and other physical properties. The work was brilliant and the most important aid in recent years to the understanding of such polymers. This information, and the modification of the physical and chemical properties of polymers by slight changes in the mode of preparation, has made possible the exploration of a wide variety of substances of most promising industrial application.

Based on this work, a commercial development by the chemists and chemical engineers of the du Pont Company has already resulted. An announcement has just been made (October 28, 1938) that the du Pont Company will erect a plant in Seaford, Delaware, which will cost upwards of eight million dollars, for producing a new textile yarn to be known as nylon. This consists of a synthetic fibre-forming polymeric amide with a protein-like chemical structure, characterized by extreme toughness, strength and peculiar ability to be formed into fibres and into various shapes such as bristles and sheets. Filaments of extreme

fineness can be spun, much finer than the filaments of either silk or rayon. One of the more important uses to which nylon will be put is the manufacture of fine hosiery from high-twist nylon yarn. Hosiery made of the new product possesses extreme sheerness, high elasticity, high strength, and improved resistance to runs. Other uses are sewing thread, knit goods, brush bristles, racquet strings, fishing lines and leaders, narrow fabrics, woven dress goods, velvets, plastic compositions, textile finishing agents, and coated fabrics. Exton bristles, the name given to those made from nylon, have already reached the commercial market in the form of "miracle tuft" tooth brushes.

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(With G. J. Berchet)

*Number*

- 1967860 Rubber-like polymerization products of 2-chloro-1,3-butadiene.  
(With A. M. Collins and J. E. Kirby)
- 1967862 Cyclic compounds prepared from  $\beta$ -substituted- $\alpha$ ,  $\gamma$ -dienes, etc.  
(With A. M. Collins)
- 1995291 Trimethylene carbonate, etc.
- 1998442 Dichlorobutadiene.  
(With G. J. Berchet)
- 2008003 Alkylated lead phenolates.
- 2012267 Esters of dibasic acids.
- 2013725 Alcohol addition products of unsaturated compounds such as mono- or divinyl acetylene.  
(With R. A. Jacobson)
- 2019118 Laminated glass ("safety glass").  
(With G. J. Berchet and R. A. Jacobson)
- 2020298 Formation of cyclic esters by depolymerizing the corresponding linear polyester.  
(With J. W. Hill)
- 2029410 Polymerization products suitable for molded articles, coatings, etc.  
(With A. M. Collins and J. E. Kirby)
- 2038538 2-Chloro-1, 3-butadiene, etc.
- 2061018 Hydrogen polysulfide addition products of unsaturated aliphatic hydrocarbons (resinous products suitable for use in film-forming compositions).
- 2066329 Polymerizing compounds such as 2-chloro-1,3-butadiene.  
(With A. M. Collins and J. E. Kirby)
- 2066330 Polymerizing 2-chloro-1, 3-butadiene in the presence of vinyl compounds to form rubber-like polymers.  
(With A. M. Collins and J. E. Kirby)
- 2066331 Polymerizing 2-chloro-1, 3-butadiene in the presence of  $\alpha$ ,  $\beta$ -unsaturated aldehydes, ketones, esters, anhydrides, nitriles, etc.  
(With A. M. Collins and J. E. Kirby)
- 2067172 Chlorination products of polymerized 2-chloro-1, 3-butadiene, etc.
- 2068265 Vapor-phase production of aliphatic organic acids.  
(With G. B. Carpenter)
- 2071250 Linear condensation "superpolymers" suitable for production of pliable, strong elastic fibers.
- 2071251 Artificial synthetic fibers from synthetic linear condensation superpolymers.
- 2071252 Synthetic linear polyacetals by condensation between a glycol and an acetal of a monohydric alcohol.
- 2071253 Polyamides from amino acids.
- 2072867 Synthetic rubber and initial materials for its production.
- 2073363 Butadienyl compounds.  
(With G. J. Berchet)

*Number*

- 2080558 Dispersing and polymerizing a 2-halo-1, 3-butadiene.  
 2082568 Vinylacetylene derivatives.  
 (With G. J. Berchet)  
 2082569 Production of alkyl-vinyl-acetylenes.  
 (With R. A. Jacobson)  
 2102611 Dichlorobutene and its preparation.  
 (With A. M. Collins)  
 2104789 Isomerization of isohaloprenes.  
 2110199 Vinylethynylmethylamines.  
 2110499 Cyclic acetals.  
 2124686 Trialkoxybutanes.  
 (With H. B. Dykstra)  
 2130523 Linear polyamides.  
 2130947 Diamine-dibasic acid salts.  
 2130948 Polyamide fibers and methods of making.  
 2136177 Reaction of chloro-4-butadiene-1, 2 with amines.  
 (With G. J. Berchet)  
 2136178 Reaction of chloro-4-butadiene-1, 2 with alkaline reacting metal  
 inorganic compounds.  
 (With G. J. Berchet)  
 2137235 Shaped articles from polymeric materials.

Several other patents will be issued to Doctor Carothers during the next two years.