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# **RECOGNITION PROGRAM**

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# WINFRED F. COOVER, THE MAN

#### ANSON HAYES

Research Laboratories, The American Rolling Mill Company, Middletown, Ohio

Professor Coover was born May 29, 1875, at the Beardshear home near Vandalia, Ohio. His father, John Quincy Adams Coover, and mother, Marcella, became recognized as leaders in farming on a farm which was devoted largely to the breeding of fine horses, cattle, and sheep. Professor Coover completed the public school education and high school while living on this farm. He obtained his college education at Otterbein University, majoring in chemistry. After graduating from Otterbein, he took graduate work at Ohio State University, where he continued his specialized training in chemistry, and obtained the master of science degree.

He was employed as assistant professor in the Chemistry Department at Iowa State College in 1904. He was made professor of chemistry in 1907, and head of the department in 1913.

Soon after Coover came to Iowa State in 1904, his unusual ability, tremendous energy, and broad interest in the college activities were recognized. For many years he served on the Athletic Council and on many committees of the college. He has always been active in the Sigma Alpha Epsilon fraternity, of which he is a member.

President Friley, Dean Buchanan, and Dean Gaskill already have told you of the service which he has given in these fields. Dr. R. E. Kirk has told you of his service to chemistry. Now I find myself in somewhat of a dilemma in discussing COOVER, THE MAN, because it is difficult to talk about Coover without also talking about the services he has rendered to the college and to chemistry—all of which during my acquaintance with him have been so important a part of the Man.

The demand on chemistry in a school whose job it is to train men and women in agriculture, in engineering, in home economics, in industrial science, and in veterinary medicine is one of broad scope. Especially so when the requirements for undergraduate, graduate, and research training are considered. Vision and faith were essential in planning to meet the situation. Wisdom, courage, persistence, and patience were needed in carrying them out. Elements of endurance and an unusual degree of unselfishness also were required.

In the summer of 1914, which was the year I met Professor Coover, his office and laboratory were in the old agricultural extension building. In addition to teaching a full schedule, he was in the final struggle of getting enough of the new Chemistry Building in shape so that work could be moved into it for the fall quarter. I well remember how greatly I was impressed with the size and arrangement of the structure, for in its planning it was well abreast of facilities of the most advanced major

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schools in the country. It was not completed at this time for we used ship-lap tables supported on sawhorses for most of the laboratory work. In fact, it was not completed to a major degree so far as equipment of rooms is concerned until well toward 1928, when I left the college. All this, however, fitted into a plan which took into consideration many factors existing at that time. Though many of us were impatient at times, yet we learned in due time that the plans which were being followed made for the best progress at the moment and gave time to study more soundly the detailed features of requirements over the long pull in a laboratory which was intended to serve not only the present but the future of a rapidly changing field of science.

In addition to the vision evidenced in the new Chemistry Building and other physical facilities which were provided, there was equal foresight in the plan and the selection of a faculty. Dr. J. A. Wilkinson already was on the scene with his stimulating presentation of work in analytical and physical chemistry. Dr. F. E. Brown came in 1917. During this early formative period of the department as it is now known, Drs. E. I. Fulmer, N. M. Naylor, V. E. Nelson, Ruth O'Brien and Henry Gilman were employed as members of the major faculty of the department. At this time Dr. R. M. Hixon was an undergraduate student but he had attracted the attention of members of the faculty with whom he took work and returned to the department after extensive graduate work was completed. Dr. Rachel Edgar was employed at the time Ruth O'Brien went to the Department of Agriculture, and Dr. N. A. Clark came to organize the work in soils chemistry.

These people were mostly untried but, as has now been well proved, the insight and understanding on Coover's part of the potential ability and growth of these young people have fully justified the judgment and the faith which he placed in them at that early date. The wise selection of this faculty group has resulted in Iowa State College being known for the leading authorities in the Chemistry Department in many lines of research which have been conducted here, and for the high quality of instruction given both in graduate and undergraduate subjects. Many scientific publications in the form of reference books, scientific articles, and textbooks, and the success of the undergraduate and graduate students in the field fully support these statements.

During the last ten years there has appeared a somewhat younger group including Drs. I. B. Johns, F. H. Spedding, H. C. Diehl, H. A. Wilhelm, R. E. Rundle, Sidney Fox, L. A. Underkofler, and W. B. King, who already have amply demonstrated their leadership in their respective fields.

The provision of a basic set of physical facilities and the selection of a faculty of potential growth and leadership in the many lines of work which chemistry dominates or influences, are only the beginnings of the accomplishments of the chairman of the Chemistry Department. It does, however, demonstrate the vision on his part.

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There are various features, such as fostering, guiding, and encouraging this faculty, and an understanding of the individual members of it, the recognition of potentially important lines of work, and the provision for space and equipment for carrying them out—all of these also are essential. Then there is the requirement of open-mindedness in accepting good advice from the various specialists on the staff in regard to the shaping of their own lines of work and facilities.

All of these things require faith in people, wisdom in dealing with the many problems, courage to carry out the plans, patience in dealing with interfering difficulties, both in the faculty and on the outside. Frequently in addition to these qualities, plain unadulterated endurance on the part of the chairman becomes a characteristic of merit. Coover has all of these qualities to an unusual degree.

I expect that at the time I was in the department I was as much of a problem for him as any member of his staff. I know I obtained a great deal of support from him. Many times when I entered his office with some very troublesome problem, I came walking out on light air and with all the enthusiasm in the world for the solution of the problem, which was worked out during the conference.

In short, I believe that the success of the members of the staff is due not only to their own excellent abilities, but also in a very considerable measure to the provision of a setting in the department in which their talents could develop and produce the many pieces of constructive work which have been done. Coover has not only used all of his own talents but has drawn on his staff frequently for advice and counsel in their own specialized fields and on questions of broad interest to the department as a whole.

I have criticized him for taking so much of the burden of the details of operations of the department on his own shoulders. His reply to these criticisms always was that he wished to make the money that this work would otherwise cost available for the support of the department and that he wished to conserve the time of the members of his faculty to do more work in their own special fields. At times his close friends have tried to persuade him not to use his own personal funds for various features of expense around the department, always without success.

I have played golf and have gone shooting with Coover and, although I have never had the privilege of observing his behavior when I was winning, I am sure he is a most modest and gracious winner.

The features of my experience while associated with him which so impress me and which I have tried to express in the form of his vision and faith in the future of chemistry and his staff, his wisdom, courage, patience, and endurance in meeting the many problems which are encountered in accomplishing marked leadership in a field of science, perhaps may be summarized in another and possibly a more direct manner. This is the readiness and energy with which he supported the members of his faculty who, first, had demonstrated evidences of leadership; second, who

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were willing to work very hard; and, third, who were engaged in projects which would develop interest of the public in the college, the department, and the faculty.

Prior to 1915, when I came with the Department of Chemistry at Iowa State, analytical chemistry was one of the major branches on which emphasis had been placed. Since that time whole industries have come into existence based on what is now known as "surface chemistry."

A good example of one of these companies is the Minnesota Mining and Manufacturing Company of St. Paul. This concern contributed to the industrial uses of chemical development, although one would not be led to expect it from the name of the company. This company is a major factor in the manufacture of the well-known "scotch" tape, an adhesive, It has developed highway warning signs which are lighted by the automobile which furnishes the light for the fluorescent effect to warn its driver. It has been an important factor in the development of flotation in its application to the beneficiation of industrial ores. In the steel business, this turns out to be of extreme importance in the beneficiation of iron ore. The supplies of the highest grades of this ore are rapidly approaching depletion, and it will be necessary to provide means of economically using much lower grades. The physical chemistry as largely developed in aqueous solutions has now been extended to a rather complete physical chemistry of steelmaking and steel processing. Free energy values are available to about as great an extent in this field as in the usual fields which chemistry had earlier served.

The application of fermentation and of chemical reactions promoted and controlled by specific bacterial action has resulted in the present great alcohol industry. Organic chemistry has contributed greatly to industrial processes of production of alcohol from crude oil and gas supplies.

All of these lines of chemical development have safeguarded the nation in the present loss of sources of supply of natural rubber.

Penicillin, which comes from controlled mold action, is now manufactured in many large specialized industrial plants, and sulfa drugs, which are the result of organic chemical synthesis, have appeared during this war period. Essentially all that is known in regard to the action of hormones has been developed since 1915, and the tremendous business of manufacturing vitamins has resulted from recent chemical development work.

The whole field of plastics which has without cause frightened managements of structural materials, although a large industry, is still in its infancy. Synthetic fuels which, no doubt, will lead to the industrial use of low grade coals, of which Iowa has so much, already are in sight. Even industrial power from nuclear decomposition can well be expected within the next half century.

The accelerative rates of industrial utilization of industrial research were well stated by Harry L. Derby, president of the American Cyanamid and Chemical Corporation, in the October 25, 1944, issue of Chemical and Engineering News. He points out that in 1920, about 300 industrial

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companies in this country employed 9,300 persons in research. By 1930, these numbers had grown to 1,625 establishments with personnel of 34,200. By 1940, the figures were 2,350 establishments and personnel of over 70,000. In other words, in 20 years there was more than a sevenfold growth in the number of establishments and of personnel engaged in industrial research. Expenditures by industrial firms for this purpose in 1940 have been estimated to be about \$300,000,000 a year.

I mention these things because the Chemistry Department of Iowa State has kept abreast of the demands on it during these phenomenal growths of industrial research.

A hint as to the tremendously increased demands on Iowa State College and the Chemistry Department is gained through this statement of the tremendous importance of industries which have been born within the last 25 years purely as a result of developments in chemistry. A hint of the requirements in scientifically trained personnel in chemistry comes from this same review of growth, which shows an increase in research personnel from 9,300 in 1920 to over 70,000 in 1940.

The plan of the building in 1913, the establishment of the faculty and its growth and supplementation during the succeeding years, and the recent selection of Dr. Hixon as chairman of the department, all lend support to confidence in the Chemistry Department at Iowa State continuing to be in the position of leadership which it has maintained. It has a tremendous job to do.

The final test of a man which is so rarely found is that which foresees and appreciates the necessity of having developed talent which can take over the leadership at the time when it should be relinquished in the best interests of the department. An important further step to that of selecting leadership which can carry on, is to have obtained it early enough so that it is possible to demonstrate that it can unquestionably take over and carry on with the continuing requirements of expansion and changes in facilities necessary to maintain the advanced position the department has reached. All of these things Coover has done, and it requires a degree of wisdom and unselfishness that is seldom found.

And now I wish to say that the W. F. Coover Recognition Committee is to be commended in initiating and carrying out the present ceremonies while Coover is in a position to give of his guidance and while he continues to teach the subjects in which he has had a life-long interest and experience. This he can do in the atmosphere which his life work has created. I am sure we are grateful for the kind of man he is and for the 40 years he has already served in the Department of Chemistry at Iowa State College.



# COOVER, THE TEACHER

CHARLES E. FRILEY President of the Iowa State College

In the development of her program of public higher education the State of Iowa has wisely limited the number of state-supported institutions to three. Since 1909 these institutions have been governed by a single Board. With unusual wisdom and foresight the Iowa State Board of Education has devoted its energies to the development of a unified program, assigning to each of the three schools specific lines of major educational activity. Thus, the State University of Iowa is recognized as the center for education and training in the liberal arts and the professions; the Iowa State Teachers College for the training of teachers for the elementary and secondary schools; and the Iowa State College as the center for education and training in the fields of science and technology. Within these limits the schools have advanced to high levels of standards and attainment, due primarily to the clarity of their objectives, the absence of unnecessary and unwholesome competition and duplication, and the intelligent financial support of the State.

The role of the Iowa State College in this program is distinctive. It is dedicated to the thesis that the education of young men and women in pure and applied science and in the humanities is the most effective means by which modern science can become the constructive instrument of man. It seeks to give the student a mastery of the fundamentals of the sciences in their application to the important activities and vocations of modern life; at the same time it emphasizes the necessity for an adequate background in the general studies as a basis for intelligent consideration of the shifting economic, political, social, and emotional problems of the society of which the student is a part.

I emphasize this statement of the objectives of the Iowa State College because I am convinced that the American college cannot function effectively unless its purposes are clear and its methods sound and appropriate. There is no educational problem which arouses so much discussion and dispute. The very term "education" seems to be persistently and widely misunderstood. It is too often conceived as almost entirely a process of pushing knowledge into the human mind, when in fact the word means just the opposite. To educate is not to push in, but to lead or draw out. This, of course, is elementary. The true objective is not to load the student's mind but to stimulate it. An educated man is not primarily one who merely produces facts, but one who can sort them out and think them through; and who by long training in learning, thinking, and action realizes approximately the extent of his ignorance and limitations, as well as his abilities.

It is one thing, however, to formulate a sound and acceptable state-

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ment of objectives; it is another thing—equally important but more difficult—to determine what instruments should be employed, or what road should be charted, by means of which the objectives may be approached or attained. It is on this point that educators argue endlessly, usually with more warmth than illumination.

But certain fundamental principles covering objectives and means can be clearly stated and should be generally accepted. We should face frankly the fact that great expenditures have been made for imposing physical plants, costly equipment and courses of questionable educational value and doubtful educational need. We should face frankly the fact that most colleges and universities could profit greatly by periodical inventories and self-surveys, designed to eliminate archaic courses and unnecessary activities, to provide the factual bases for revision of essential activities, and to lay the ground work for sound and desirable additions to the educational program.

The fundamental agency—and by every valid measure the most important agency—in the attainment of institutional objectives is the teacher. And the greatest single need in the program of higher education is better teaching. To make teaching most effective, scholarship should be encouraged and adequate time and facilities provided for pertinent research by those members of the staff whose talents and interests clearly lie in that direction. Scholarship, research ability, and inspirational teaching are not incompatible but complementary. The Iowa State College has a large responsibility not only for research in the fundamental problems affecting its particular fields of activity, but equally for bringing students into contact with members of the faculty who are wrestling with these problems. Such a program will definitely raise the standards of the College and will give it that creative atmosphere which is tremendously important in the education of young people.

The art of teaching, which depends for its success upon quick and understanding communication between mind and mind, has suffered greatly by the amazing amount of detailed analysis to which it has been subjected during the past few decades. I do not refer to the many excellent studies dealing sympathetically with the improvement of teaching; rather, I deplore the super-analysis and the hyperdissection of the teaching process from which there has been no appreciable gain, and to which may be attributed a direct loss of some of its effective power. The socalled science of education has received such solicitous attention in the past three decades that we have grossly neglected the more important philosophy of education, which deals with values, appreciations, insights, and powers.

So much emphasis has been placed upon training and particularly upon highly specialized training that we have failed to place adequate emphasis upon the kind of man the college teacher should be. We have been so concerned with his competence in the field of his specialty that we have failed to give proper attention to his personal appearance, his manner of speech, his grammar, his cultural and community interests,

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his attitude toward students, and many other things of highest importance in a teacher. Successful teaching is to a large degree a matter of personality; a man's teaching ability and power increase only as he enriches his own life, as he broadens his tastes, and as he enlarges his own horizon. In short, the first duty of the teacher is not to do something with or for the student but with himself.

It seems fair to say, then, that one of the important aspects of good teaching is the extension of the teacher's personality through the medium of subject matter. Most of us can recall, with gratitude, certain teachers whose influence, whose personality, and whose outlook on life have made an impression far more permanent than the information they imparted. I do not mean by this statement to detract in any way from the importance of what is taught. The subject matter of a course must be well organized and thoroughly authentic, and must form an adequate vehicle; it must have definite significance and merit; and it must be of such character and such pertinence that the teacher feels fully justified in dedicating all his talents and energies to its development, its interpretation, and its transmission. But the thoughtful student will not dissociate what the teacher knows from what he is.

The problem of the teacher is not new. In 1832, Alfred Tennyson, speaking of Cambridge, said:

"Therefore, your halls, your ancient colleges, Your portals statued with old kings and queens Your gardens, myriad-volumed libraries, Wax-lighted chapels and rich carven screens, Your doctors, and your proctors and your deans, Shall not avail you when the day-beam sports New-risen o'er awakened Albion—No! Nor yet your solemn organ pipes that blow Melodious thunders thro' your vacant courts At noon and eve: because your manner sorts Not with this age, wherefrom ye stand apart; Because the lips of little children preach Against you, you that do profess to teach And teach us nothing, feeding not the heart."

Nearly one hundred years later President Wilkins of Oberlin portrayed the good teacher in these words:

"The good teacher knows his subject and believes profoundly in its significance, immediate or ultimate, for the enrichment of human life. He cares about his students, as thinking, feeling and growing individuals, and is glad to listen to them, in the classroom or outside the classroom. For their sakes, and because of the nature of his own mind, he selects his material rigorously and orders it effectively. His presentation has always some measure of informality, of give and take. He is courteous and helpful to all; but his chief concern is for the stimulation and guidance of his ablest students. He is a born teacher, but he is a made teacher as well—

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made through friendly contacts with colleagues in his own college and elsewhere, through deliberate study of the art of teaching in his own field, and through the resolute development of all his powers."

Those who have had the good fortune through the years to study Chemistry under his direction will recognize in W. F. Coover the embodiment of all those enduring qualities, tangible and intangible, which make up the great teacher. His broad knowledge of the field, his deep sympathy for and understanding of students, their problems and relationships, his high sense of honor and integrity, his loyalty to his associates, mark him as a man whose influence will abide long and warmly in the hearts of his students.

Mr. Coover, you have been an honored member of this staff for forty years; you guided the destinies of the department for more than thirty of those years. You saw the program in Chemistry grow in size, scope, and influence to the point where it now receives world-wide recognition. Your friends here tonight realize full well that this remarkable progress is largely due to your foresight, your singleness of purpose, your courage in the face of difficulties, and your constant and high faith in the destiny of the institution to which you have devoted your life. And we, your friends, know also that through all the years you have been not only Coover, the chemist and administrator, but even more important and in the best sense of the terms, you have been and are—Coover, the man and the teacher.

We are grateful to you—more grateful than words can express—and we look forward with a deep sense of gratification to our continued close fellowship and association in the challenging years ahead.

# PROFESSOR W. F. COOVER AND THE DIVISION OF SCIENCE

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# HAROLD V. GASKILL

#### Dean, Division of Science, Iowa State College

My assessment of Dr. Coover's contributions and worth to the Division of Science is to be limited to five minutes—imagine the plight of an organic chemist told to cover his field in five minutes!

No index to Dr. Coover's wisdom and foresight in the thirty-one years he has spent building a department of chemistry is better than the department's character today. He has insisted upon a well-rounded department integrated with the purposes and objectives of The Iowa State College. The staff which Dr. Coover has brought together includes distinguished men and women in many fields of chemistry. The range of courses developed under his guidance and leadership is broad, without a dissipating of strength. The only limitation he has placed, either on fields of chemistry and courses or on personnel, is that the area represented be consistent with the purposes of the College and the Division.

The curricula in Chemistry and in Chemical Technology have had all of their development—from inception to the present—under his guidance. So often course offerings and curricula stemming from a complex department can develop an inflexibility of structure and purpose, can confuse means and ends, and fail to meet new needs. From the beginning, Coover has prevented these errors. The undergraduate outline for Food Technology of some six years ago recognized new needs and evidenced flexibility. Our department's requirement of three fields of chemistry in graduate programs manifests the insistence upon integration. His demands for quality of performance for both undergraduate and graduate are well known to us all. Degrees in Chemistry since 1913 are, roughly, B.S. 330, M.S. 175, Ph.D. 260.

He has been uniquely successful in providing in his department an environment designed to enhance the spirit of enthusiastic teachers and ardent research workers. As a department head he has mastered the ability to develop initiative and a feeling of responsibility on the part of men and women of his staff.

A list of his other general services to the Division is long indeed. Many years of valuable aid were given our Curriculum Committee, the Athletic Council, the Division's Science Day, Divisional Personnel Committee, and many, many others.

Parents, employers, and society at large demand a great deal more of chemistry graduates than education in chemistry and intellectual training. They must be fine people and worthy citizens. Teaching the value of consummate honesty and indomitable character by precept has been

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Professor W. F. Coover's forte to a degree which, in my opinion, has not been excelled anywhere.

I count myself fortunate for having been associated with him as Head of the Department of Chemistry and look forward to his continued service as Professor of Chemistry.

# THE ORGANIZATION OF A COLLEGE CHEMISTRY DEPARTMENT

# RAYMOND E. KIRK

# Polytechnic Institute of Brooklyn

Mrs. Kirk and I are indeed very happy to return to Iowa State College to share in this occasion. We pay tribute to the college and to Professor Coover for their influence on our lives and our careers. I came to the campus in 1915 as a graduate student and returned to it after the last war to serve briefly as an instructor. Those were formative years; and the ideas gained then have been potent in giving direction to the following years.

It is a pleasure to speak on the topic assigned to me both because it is one in which I have a vigorous interest and because it is one that has been so well exemplified in the distinguished career of our honored guest. I shall talk in general terms. He has thought in general terms and then he has reduced these ideas to practice. The success of this endeavor is attested to by our meeting tonight, a meeting to celebrate the continuing success of a strong department of chemistry.

The first general principle in the organization of a college chemistry department is that the department of chemistry must stand on its own feet. It must have an identity of its own. It must have a characteristic flavor and a distinctive personality. In order that a college chemistry department may perform its function as a servant, it must first of all be a master in developing its own point of view, its own pattern of thinking, and its own contribution to science.

Reflecting upon the place of chemistry in the land grant college system, one realizes that to a very large extent the land grant colleges were built around chemistry and around chemists. Read the names of the early directors of agricultural experiment stations! Note the names of the early presidents of the land grant colleges! Leaf through the faded pages of the old catalogues! The names of chemists are at once to be seen in the majority! Chemistry was the key subject! There was indeed, a reason for this. The science of chemistry was a well organized body of knowledge. It had in its ranks many competent and well trained persons available to apply the experimental method to the problems of agriculture. The traditions of Liebig and of the famous Rothamsted Station were well known to chemists of that day. The profession of chemistry had enlisted many of the most vigorous minds of the time. Many of them had obtained European training and had then returned to the United States to use that training. They found little outlet in industrial fields but ample opportunity in the rapidly developing experiment stations of the land grant colleges. Each of the early experiment stations had a coterie of famous chemists. Each land grant college was tremendously influenced by its vigorous chemists and by their enthusiasm for the profession of chemistry.

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Then there came a time when chemists and chemistry became somewhat submerged in the work of the land grant college. Other and equally important disciplines had been developed. Vigorous and enthusiastic investigations were going forward in borderline fields between chemistry and the various biological sciences. The emphasis in biological science was shifting from form to function; from morphology to physiology. Along with this, unfortunately, there had developed some serious defects in the work of chemistry and of chemists in the land grant colleges. There had come to be an undue formalization in the chemical instruction. The courses in chemistry offered to students placed emphasis upon descriptive chemistry rather than upon fundamental principles, thus repelling vigorous young minds. Chemistry was "just analysis". "Dry rot" was making its appearance in chemistry departments and in chemical sections. Inbreeding was prevalent largely because of salary schedules.

Then too the land grant colleges were faced with the necessity for the training of a large number of extension workers, of demonstration workers, and of vocational teachers for the high schools. The laboratory scientists, especially in chemistry, became submerged in all of this. Departments of chemistry became merely service departments for the training of such workers without simultaneously pushing vigorous investigational problems of their own. Worst of all, the chemical industry was, by that time, drawing off a great many of the young men coming out of graduate schools of chemistry. This occasioned the shift of many of the ablest minds in chemistry away from academic institutions, especially those not closely affiliated with vigorous research in the fundamentals of chemistry. Physical chemistry and modern organic chemistry were not represented in the programs or on the staffs of many land grant colleges. This was the era of "hyphenated chemistry."

Now we are coming to a period closely related to my topic and to the career of our honored guest. This is the period of the rebirth of departments of chemistry in the land grant college. Dr. S. W. Johnson, of the famous Connecticut Experiment Station, once put it this way, "If one wishes the respect of others, he must first earn his own respect." This leads us back to our first general principle. The college chemistry department cannot occupy its proper place in an institution unless it has an entity of its own. It must not only train men who are to use the knowledge developed in chemical laboratories; it must also train men to develop knowledge through chemical investigation.

The college chemistry department cannot have on its staff good teachers unless it does major work in chemistry at all educational levels. It cannot earn the respect of its sister departments in the college unless it first of all earns its own respect. This is the fundamental premise on which the college chemistry department must be organized.

The second general principle in the organization of a college chemistry department is that the whole is greater than the sum of its parts. We are not discussing geometry. We are discussing something far more complex. Our experience justifies noneuclidean statements. Each general subject

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matter division of chemistry will, in the well planned college chemistry department, be organized vertically from undergraduate years, on through to graduate years, including research at all possible levels. This will be done, and must be done despite the usual and desirable horizontal organization of student registration, student direction, student guidance, and student regulations. It will be done and must be done despite the conflicting details of budgets and research assignments. It must be done this way if chemists are to be well trained and chemistry is to be well served.

Along with the vertical organization of subject matter the training of students and the organization of research must be completely integrated. This is important for the best interests of minor students and of major students. The chemist is first and foremost an investigator! He must be! Investigational problems demand the use of all subject matter developments and of any and of all possible experimental techniques. There are no subject matter divisions in research.

The fundamental principle of vertical organization of subject matter with horizontal integration of the science extends to all of the applications of chemistry to the far flung interests of the investigational programs of the land grant college. If an investigator in a related field needs help from chemistry and from the chemist he should first of all decide where he wishes help, at the technician level, or at the scientific level. No chemist can give his best to an investigational problem if he is to be considered only as a machine for analysis. Routine tests should be made by technicians, not by scientists. Scientists are too precious a commodity to be wasted in this fashion. When routine tests are needed they should be made under the direction of a responsible investigator by a technician. When scientific help in chemistry is needed it should come from a well organized, thoroughly integrated department of chemistry. The liaison chemist can then marshall all the resources, methods, and disciplines of the science back of the project. A college chemistry department of this sort will very soon establish that the whole is greater than the sum of its parts.

Such a department will contribute to the educational program of the college. It will contribute to the research program of the college. It will add prestige to the college and to the state.

The third principle in the organization of a college chemistry department is that a scientific organization consists of men. It is not created by a neat outline of administrative responsibilities carefully framed and placed in an executive office. Organization means men. Direction of that organization involves vigorous leadership. I scarcely need elaborate on this aspect of the college chemistry department to this audience. You have seen it work! Able men must be chosen. They must be selected from diverse backgrounds and with very different preparations. They must be brought together, indoctrinated and encouraged to work out together the real problem of organization, which is "what each man can do."

One of my former students employed at the time in a large research laboratory operated by one of the major chemical companies was once

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asked by an administrative superior, "Are you the section leader?" My friend and former student replied, "I do not know, am I?" The question came back, "Don't the men in certain groups always talk to you about their work?" "Yes, they are my friends." The pay-off is that this young man had been carried on the budget as a section leader for two years before he found it out. He had not bothered to find out, he had just gone ahead with his chemistry. He now holds a very high position of administrative responsibility with the company. The way to be a leader is to be one. The way to do chemical work opens up before the worker.

It is easy to write the prescription for the college chemistry department that good young men should be obtained for its staff. That is not enough. They must be kept enthusiastic both about their teaching and about investigation. Their needs must be supplied with respect to equipment, with respect to supplies, perhaps even with respect to stenographic assistance. Graduate students must be turned in their direction. Special research assistance must be obtained, vital as it often is to the development of special interests and abilities. Finally the men must be *pushed*. I need not elaborate on this topic before this audience. Too many of us have keen memories of how the push got clear down to the level of the graduate student.

The fourth general principle is that the work of the department must be integrated with the needs and interests of the state. The best crop in Iowa has always been the young men and women who crowd the laboratories, libraries and classrooms of its colleges. Their vigor must be given adequate outlet, their enthusiasm must be given proper direction. The Department of Chemistry at Iowa State College has long stood for "science with practice." In it thousands of men and women have trained for vigorous leadership in the profession of chemistry. Additional thousands have been given guidance in the use of chemistry in related professions. All of these men and women meet with us in spirit tonight in tribute to Professor Coover.

The scientific work of the college department of chemistry must also be integrated with the industrial and agricultural possibilities of the state. Need I review here the achievements of the department in such endeavors?

We meet here tonight to review the past and to predict the future. But the permanent record of the achievements of our honored guest is written on the minds and hearts of thousands of his former students now scattered round the world. Eyes front! Heads up! Coats off for the future of science!

# FORTY YEARS OF PROGRESS

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# INTRODUCTION

#### JULIAN HARRISON TOULOUSE

# Chief Engineer, Quality and Specifications Division, General Manufacturing Department, Owens-Illinois Glass Co., Toledo, Ohio

Perhaps we are opening our meeting a little formally, but this is no ordinary meeting. To plan to honor Professor Coover by a scientific program is very nice; to be able to honor him by bringing together five of his students who have made names for themselves in so many diverse fields, is something for all of us to be proud of.

One of these students is a leader in the field of chemical engineering, particularly in high-pressure metallurgy. Another leads in food chemistry, particularly in the development of baby-foods. A third is engaged in that intensive research drive in synthetic rubber. Another has gained national recognition in the control of insect-borne diseases and infestations, particularly in the war-time use of the fumigation bomb. The fifth is a leader in the farm chemurgic move, a program of interest both to the farmer and the chemist.

We speak of these people as Professor Coover's students, but I am not sure that any of them actually took class work under him. They are his students in a much broader sense; it was his organizational work that made their studies here both possible and profitable. That is the phase that I want to touch upon before opening the real part of the program.

The organizational aspect of teaching is not usually given the credit it should receive. We take too much for granted; we begin to think that all you have to do is to give a teacher a classroom and some students and the rest comes as a matter of course. Since I happen to be employed in an establishment which because of its large size is highly integrated, I have learned at first hand the value of this thing called organization.

If we are skeptical about the importance of organizational work, we can learn something by comparison with the present emergency. Generals Eisenhower, Somervell and Marshall are said to be the leaders they are, not because of any particular ability in combat, but because of their ability to organize.

There is no real secret about the leadership in chemistry teaching this department has taken. When, for an altogether too brief a time, I served Professor Coover as an assistant in his office, he told me one of the reasons why the Chemistry Department of Iowa State College is so outstanding in teaching. That reason is: he has never allowed the department to become inbred, or to follow too closely any one school of thought.

That means that his teaching staff was developed, and enlarged as time demanded, with the utmost care. Every important school of chemistry has been represented, and with outstanding people. No one-sidedness has been allowed to develop. This has not meant the exclusion of our own

# JULIAN HARRISON TOULOUSE

outstanding students—many are to be found on the staff, but balance has been carefully maintained. That such efforts have borne fruit is shown by the leadership his students have reached in their respective fields.

Another monument to Professor Coover's organization is this building. As chemical laboratories go, it is getting along in years. It was one of the first of its kind, designed for extreme flexibility in arrangement and alterations. It is possible to make a large number of changes simply by removing curtain walls. It was built for the future and has kept pace with the expanding demands. No doubt improvements could be made now, which were not known some thirty years ago. Perhaps some of the facilities are being outgrown, but the planning job done by Professor Coover over thirty years ago, and the efficiency of the building that was the object of his planning were the results of real organizational ability. The arrangement of the main lecture room, its availability to the principal entrance, the organization of the laboratories in relation to the store rooms, all are on a plan I have not seen equalled. It is a perfect example of how mass-teaching and research can be carried on together without mutual interference.

Because of this organization, the Chemistry Department has been of utmost assistance to all the divisions of the college that needed its centralized service. In other words, it was not only designed to serve chemists, but chemistry. Without it our agricultural students, our engineering students, our home economists, and our science students might have been studying chemistry in isolated groups which, even though they might have been efficient and well led, would not have had the strength, or the facilities, or the technical completeness of this single unit.

Yet each of these groups has had its own thoroughly organized staff. None was thrown into a melting pot (or should I have said crucible) with a mixture of other divisions and other divisions' needs, until the finished product in students was an alloy of no particular specialization, yet released to a specialized field. I can speak of the thoroughness of this in mentioning that my wife and I, (we entered together as freshmen two years after our marriage), one taking work in agricultural chemistry, the other in chemical engineering, did not once cross paths in relation to either courses or teachers. Our one hardship was in not being able to caution each other on the foibles of our instructors.

I have taken advantage of the position of presiding officer to pay this personal tribute to Professor Coover. It is in the nature of paying a debt to his teachings and counsels. Since all of us on this program use the letters D and R in our titles, might it be equally applicable today as the initials of the word "debtor"?

With this thought in mind, it is now my privilege to introduce the first paper of this program of scientific papers by students of Professor Coover.

# TWENTY-FIVE YEARS OF RESEARCH ON FERMENTATION PROCESSES IN PROFESSOR COOVER'S DEPARTMENT

# LEO M. CHRISTENSEN

# University of Nebraska, Lincoln, Nebraska

# INTRODUCTION

Those of us who have had parts in this research program on fermentation processes have a feeling it has occupied a special place in Professor Coover's plans, and have justified that opinion on the basis that fermentation processes are so closely related to agriculture and so important to it. All of us know that in building the Chemistry Department, Professor Coover aimed at service to Iowa and the Midwest above all else, and he built his staff around that ideal. Graduates who have had the privilege of doing research on fermentation processes in this department have known of the care with which Professor Coover selected the man to direct this program, and have seen his good judgment fully confirmed. Today I am honored with this opportunity to tell you about the research that Dr. E. I. Fulmer has directed as his part of the program of service that Professor Coover set up here more than twenty-five years ago.

At the outset the term "fermentation process" should be defined, but that is not easy to do. The expression developed by Dr. Fulmer, "microbiological dissimilation products of the carbohydrates" is, to say the least, intriguing. But in the end we have usually considered a fermentation process one in which chemicals are produced from farm crops by the action of yeasts, molds, and bacteria, and let the matter rest there.

From the research standpoint it is pertinent to use another of Dr. Fulmer's characterizations, "autocatalysis in a heterogeneous system," because it so aptly describes a general basic problem which the zymologist must constantly keep in mind. In studying the influence of any one factor upon the operation of a fermentation process, he is concerned with the influence upon the catalyst formation as well as its action. It is a rare case when one can be entirely separated from the other. Add to that the difficulty that the chemical nature of the materials entering the process is still not well established and it can be appreciated that the operation of a fermentation process on laboratory or plant scale is both an art and a science.

# EARLY RESEARCH WAS CONCERNED WITH DEVELOPMENT OF THE CATALYST

Man has used yeasts almost since he quit living in a cave, to make his wine, brew his beer, and to raise his bread. One of the classic debates of science was that of Liebig and Pasteur concerning the function of yeasts in these old processes. But in spite of the long association with yeasts, man's knowledge of them is still quite meager.

#### LEO M. CHRISTENSEN

A new approach to a better knowledge of yeasts was early developed at Ames. It was based upon a simple theorem—if you want to know something about a biological form, ask it. The questions asked must be of the type that get a yes or no answer, and must be carefully planned. First, a certain strain of *Saccharomyces cerevisiae* was selected as the test organism, and it was cultured in a standard manner. Then it was put into media in which one single component was varied, in a series selected to extend above and below an optimum. Yeast population was the measure used in these studies. A systematic application of this method developed a great deal of new information about yeasts, and some principles that seem to be widely applicable to biological systems.

Thus it was found that the ammonium ion is only a little less active than are hydrogen and hydroxyl ions in their effect upon yeast growth. Furthermore, for each temperature there are two definite optimum ammonium ion concentrations, not affected by other components of the substrate. Both are linear functions of the temperature and this relation is described by the following equations, where t<sup>o</sup> is in <sup>o</sup>C.

(1) Optimum normality  $= 0.00179 + 0.00057 t^{\circ}$ 

(2) Optimum normality = 0.111 + 0.0042 t<sup>o</sup>

These formulae were found to be more fundamental in character than was at first anticipated. Thus in the production of citric acid by Aspergillus niger in a synthetic medium, at  $30^{\circ}$ C., the optimum ammonium ion concentration is exactly that forecast by the formula derived from the studies on yeast. And in the thermophilic fermentation of cellulose to yield ethanol, at 55°C., the actual optimum and that forecast by the formula are the same. Furthermore, it was found that over a wide range of temperature, both in synthetic media and in beer wort, the ammonium ion concentration optima calculated for yeast growth are the same as those at which wheat gluten is least hydrated.

A study was made of the influence upon yeast population of many so-called growth stimulants, and the multiple nature of bios was clearly established long before this was reported from other laboratories. Another fundamental principle in biological studies was uncovered in this work. It was very clearly demonstrated that when substances are compared as sources of growth stimulants, they must be compared when each is used at its optimum concentration, and at an optimum temperature, not at arbitrarily selected equal concentrations and temperatures.

During these studies it was noted that yeast would grow in synthetic media containing so little of nitrogen sources that there was a question whether any but elemental nitrogen was available. Still the yeast contained the usual amount of protein. An intensive research program showed that under certain conditions yeast is able to build its protein from atmospheric nitrogen, in amounts and at rates like those found for Azotobacter species.

The importance of available phosphorus received its proper attention. Up to an amount required to supply the phosphorus needed to form cell

# TWENTY-FIVE YEARS OF RESEARCH ON FERMENTATION PROCESSES 251

protoplasm, there is a linear relation between phosphorus content of the medium and yeast population, but beyond that point the phosphorus content of the medium is without effect, other conditions being equal. It was a source of astonishment how efficient yeast is in transferring phosphorus from the substrate into its own cell substance. Even with highly purified ingredients, with no added phosphorus, yeast is able to grow, getting its small phosphorus requirements from a substrate containing only an infinitesimal amount of it.

The influence of calcium, magnesium, sodium, potassium, iron, and other ions, antagonistic actions among these ions, and other factors in yeast growth were systematically studied, and fundamentally important information developed. Here is a method that deserves much more attention among biologists than it has received. Systematic questioning of the biological form, using this prosecuting attorney technique, can reveal much that is only a mystery today.

# DEVELOPMENT OF THE AGRICULTURAL DEPRESSION SHIFTED THE EMPHASIS

A service institution is sensitive to the needs of its constituency, and with the development of the serious agricultural depression in the early 1930's, the fermentation research program was tailored to the needs of the day. Making fermentation chemicals from farm crops was the new keynote, but the systematic question and answer technique still prevailed.

Investigation revealed that industrial alcohol manufacture was one possible constructive use for the great national starch surplus. True, grains had not been able, in normal times, to compete with blackstrap molasses as raw material for this industry, but might not this situation be changed by research? Although almost no modern research had been done in this old chemical industry, it seemed likely there might be something of interest.

An excellent opportunity to evaluate the orthodox processes for making grain alcohol was furnished by the investigation set up by the late Francis P. Garvan, of the Chemical Foundation, in 1936. At Iowa State and elsewhere, research had been directed toward an exact evaluation of alcohol as an automotive engine fuel, and as a result some rather pointed arguments had developed concerning the cost of making alcohol from grains. Mr. Garvan said he was tired of listening to such idle debate and set out to get a definite answer. At the same time, he said, it could be ascertained whether there were opportunities to improve the economy of making alcohol from the starch of grains.

One man from the University of Idaho and five from Professor Coover's fermentation research program were assigned the job of getting this information for Mr. Garvan. A closed small distillery at Atchison, Kansas, was borrowed and was remodeled and enlarged, to make it an orthodox but modern grain alcohol plant. For two years various orthodox procedures were applied, to get Mr. Garvan the data he had requested. The following conclusions were then announced:

- 1. Whereas statements from various sources had placed the cost of alcohol from corn costing 50 cents per bushel at from 10 cents to \$1.00 per gallon, the actual cost was 25 cents per gallon, using strictly orthodox processing and including all reasonable capital charges.
- 2. Whereas it had been said that there were no opportunities for research to improve the economy of making industrial alcohol from starchy substrates, actually there were two very large processing costs, and many small ones, that research could certainly eliminate.

These two major inefficiencies were described in several reports, both technical and general, as follows:

- 1. For every 90 pounds of grain, 10 pounds of malt were required, malt costing 2 cents per pound more than grain and therefore contributing 4 cents per gallon to the cost of the alcohol.
- 2. The alcohol, carbon dioxide and total residual solids obtained failed by 15 to 20 per cent to account for the grain put into process, a loss equal to around 6 cents per gallon of alcohol processed.

The first problem was intensively investigated in Dr. Fulmer's laboratory, and a series of reports by him and by Dr. Underkofler tell the story of the development of simple and inexpensive methods for the manufacture, at the alcohol plant and under exact control, of fungal amylases that almost completely eliminate the cost of saccharifying starch, and at the same time improve alcohol yield and reduce contamination hazards. If mold bran were used in place of malt in the present grain alcohol program, it would save the government \$20,000,000 per year.

The second problem was undertaken in a cooperating research project at the University of Idaho, where it was ascertained that the loss was in the carbohydrate fraction of the raw material, resulting from a hitherto unsuspected chemical change in cooling starch gels. Several means for avoiding this undesirable starch reaction were developed and as a result the products were stoichiometrically equivalent to the reactants. If these improved mashing procedures were used in the present program, they would save the government \$30,000,000 per year.

Between 1932 and 1939, Professor Coover's fermentation research group tried to tell the public that there would shortly be a vast increase in the need for industrial alcohol, one that could not be supplied from blackstrap molasses and other accustomed sources. Apathy, skepticism and opposition were the answer. Beginning in 1940, that national need has arisen. Whereas in 1940 only about 5 million gallons of industrial alcohol were made from grain starches, the 1944 production from this raw material will reach 500 million gallons, an increase of 100 fold in four years. And so acute is the shortage that all industrial alcohol produced is taken by the government.

# TWENTY-FIVE YEARS OF RESEARCH ON FERMENTATION PROCESSES 253

But still apathy, skepticism and opposition have prevented full commercial application of the research results described above. In one Midwestern plant, however, there is an unprejudiced and enterprising management that is, as rapidly as possible, putting this research to work, with the help of several of the technical pioneers. It is only a matter of weeks now until commercial demonstration of the research accomplishments will be at hand. In the meantime, you may be sure, this plant management has fully satisfied itself of the utility of these research accomplishments.

Professor Coover, we think you will be pleased with the results of this research project. We believe it is the kind of job you have wanted your department to do.

# AGRICULTURAL WASTES MAY FIND USE IN FERMENTATION INDUSTRY

It has long been known that from such agricultural wastes as corn cobs, plant stalks, grain hulls and bran, mixtures of pentose and hexose sugars can be obtained in yields of from 20 to 40 per cent by weight using a simple and inexpensive hydrolysis with dilute acids. Quite naturally the fermentation research workers have been interested in these raw materials.

Methods for improving the ability of *Cl. acetobutylicum* to utilize the sugars of these hydrolysates were developed, and good yields of nbutanol, acetone and ethanol were obtained. It is interesting to note that this organism produces from xylose the same products it makes from hexoses, in the same ratio and with the same yield in per cent by weight.

An intensive study was made to determine the best conditions of acid concentration and time and temperature of digestion for the production of these pentose and hexose sugars from several agricultural wastes.

Research in cooperating laboratories is extending this work. Thus in one it has been found that when certain oilseed crop residues are properly digested, the residue is highly satisfactory as a source of paper, alpha cellulose and plastics, and the combined value of the sugars and the residue may develop a commercial utilization of this research.

# 2,3-BUTYLENE GLYCOL AN INTERESTING FERMENTATION CHEMICAL

It has long been known that many bacterial species produce some 2,3-butylene glycol from a wide variety of carbohydrates. A systematic investigation in Dr. Fulmer's laboratory showed that when the carbohydrate concentration and other factors were correctly adjusted, the yield reached 50 per cent by weight of the carbohydrate consumed, and this aroused new interest in the process.

Research on the production of the glycol and its conversion to butadiene has recently been very active, both here and in other laboratories. Since about 1912, 2,3-butylene glycol has been recognized as a good source of butadiene for synthetic rubber. But the organic chemist sees many other good uses for this four-carbon compound with two hydroxyls so conveniently placed.

#### LEO M. CHRISTENSEN

# MICROBIOLOGICAL OXIDATIONS ARE DELICATELY BALANCED

When the chemist looks over the chemical results of microbiological activities, he is impressed with the fact that these living forms, in attaining their life objectives, have a remarkable facility for gently moving oxygen atoms from here to there.

Aerobacter suboxydans was found to be a convenient tool to study some of these microbiological oxidations. This research has been especially active under the direction of Drs. Fulmer and Underkofler during the past five years. With approximately quantitative yields, sorbose is converted to sorbitol, mannitol to levulose, glycerol to dihydroxyacetone, and 2,3-butylene glycol to acetylmethyl carbinol. From *meso*-erythritol, 90 per cent yields of 1-erythrulose are obtained. From *i*-inositol, which has six secondary alcohol groups, a diketo-*i*-inositol is produced.

This Aerobacter exhibits a high degree of specificity in its oxidation of 2,3-butylene glycol. The fermentation product using Aerobacter aerogenes is slightly dextro-rotary, and contains about 90 per cent of mesoglycol. Aerobacter suboxydans converts the meso-glycol to acetylmethyl carbinol, leaving the dextro-glycol behind.

There is certainly no need for me to point out here how useful a tool has been forged.

# FERMENTATION INDUSTRIES SHOULD BE AN IMPORTANT FEATURE OF POSTWAR ECONOMY

American agriculture has increased its productivity 23 per cent since the war started, using nearly 10 per cent less land and working under serious handicaps of machinery and manpower shortages. At a rate never before witnessed, the splendid research accomplishments of the Agricultural Experiment Stations are being put to use. Better crops, better land use practices, and many other developments from agricultural research are paying big dividends in this war period.

For comparison, look at the agricultural program of World War I. A 5 per cent increase in productivity was obtained, almost wholly the result of plowing new land, land that since has had to be returned to grass.

What about postwar markets for this increasingly productive and efficient farm factory? Fermentation industries can help a great deal in providing a market at a profitable level. The industrial alcohol expansion of this war period has amply demonstrated that fact. And please bear in mind that these fermentation processes use only the starches and sugars of the farm crop, products of photosynthesis; all the nitrogen and other elements of soil fertility are recoverable and can be returned to the land from which they came.

And so, Professor Coover, this research program on fermentation processes which you established here at Iowa State more than twentyfive years ago is not only doing its share in the war effort, but it should be even more important in the years to come, helping to make profitable use of the production of an ever more efficient agriculture, creating opportunities for new productive employment in industry, and establishing a higher standard of living for all.

# NEW DEVELOPMENTS IN INSECTICIDES

#### L. D. GOODHUE

# Bureau of Entomology and Plant Quarantine, Agricultural Research Administration, United States Department of Agriculture

The tremendous scope of this war has greatly increased the insect problems of our armed forces over those heretofore encountered. This fact was recognized very early, and steps were taken to provide adequate facilities for the Bureau of Entomology and Plant Quarantine to develop and test new insecticides. A laboratory for this purpose was first set up at Orlando, Florida, with funds from the Office of Scientific Research and Development; later this program was extended to other laboratories in this bureau and to some universities. Preventing the spread of malaria, yellow fever, dengue, and filariasis by the mosquito, of typhus by the louse, and of dysentery by the fly were serious problems that were given to the chemists and entomologists for solution.

Before the war research on insecticides proceeded slowly. There was no acute need to spur this study in peacetime. When the war broke out, the fly spray used twenty-five years ago was almost the only weapon available for fighting adult mosquitoes and houseflies. No good louse control was known, and repellents had not attracted much attention. The war has not only given an impetus to the development of better insecticides, but has made it necessary to find substitutes for those made scarce by the cutting off of supplies from abroad. Some of the accomplishments in this field have recently been pointed out by Roark (24).

The recent developments in insect control include DDT, various repellents, improved louse powders, improved mosquito larvicides, organic thiocyanates, synergists for insecticides, new methods of making pyrethrum extracts, new fumigants, and the aerosol method of applying insecticides.

# DDT

The most outstanding new insecticide to come into use during the present war period is the synthetic compound 2,2-bis (*p*-chlorophenyl)-1,1,1-trichloroethane. For convenience it is called DDT, from the initials of the generic name, dichloro-diphenyl-trichloroethane. It was first prepared by Zeidler (33) in 1874 by condensing anhydrous chloral and chlorobenzene in the presence of sulfuric acid. It is a colorless, almost odorless, crystalline solid, melting at 109°C. It is insoluble in water but soluble in most organic solvents. Cyclohexanone, the best solvent, will dissolve more than its own weight of DDT.

DDT was found to be a good insectcide about five years ago by Müller (23) in Switzerland, who reported its effect on flies, moths, and aphids. Its contact and stomach-poison action and the lasting effect of the residue on flies were reported in Switzerland (32). Its toxicity to the body louse on man was also noted there (8); a formula containing it was later developed in this country for use as an Army louse powder (2). The insecticidal use of DDT is now covered by a number of patents in Switzerland, England, and the United States.

DDT is approximately as toxic to flies as the pyrethrins, but it has a very slow paralytic effect. Where a rapid paralytic action is desirable, either a thiocyanate or pyrethrum must be added. It is much less toxic to adult mosquitoes than the pyrethrins.

DDT is effective against a wider variety of insects than any other synthetic organic insecticide so far tested. It fills several gaps where there has been no effective control. For example, it can be considered the almost perfect answer to the bedbug menace (20), and it is an excellent chemical control for the Japanese beetle. Against many insects it promises to give better control than the insecticides previously recommended. One part in 100 million parts of water or 0.1 pound in oil per acre of surface is stated by Stage (29) to give excellent control of mosquito larvae. The effect of DDT on many different insects was reported in the February, 1944, issue of the Journal of Economic Entomology.

The excellence of DDT has naturally aroused interest in its chemical isomers and analogs. The compounds containing methyl, methoxyl, bromine, and other substituents in the place of chlorine have been made and tested for toxicity to insects, but preliminary tests show that DDT is the most toxic member of the group so far prepared. Little is known of the isomers of DDT formed by changes in the position of the chlorine on the benzene rings.

Among other synthetic insecticides, phenothiazine (28) xanthone (27), phthalonitrile (25), and certain thiocyanates have given control of some insects, but in most cases they have been much less effective than DDT. Phenothiazine has proved to be a very effective anthelmintic (16).

# REPELLENTS

The repellent method of combating insects is very old. Probably smokes were the first repellents. Later certain essential oils, such as citronella, were commonly used, but not much organized research was done to find better repellents. Shortly before the war interest in repellents was beginning to pick up, and several proprietary preparations appeared on the market. In 1937 Kilgore described a method of measuring the repellent action of chemical compounds on houseflies (18) and he was granted a patent for Indalone (alpha, alpha-dimethyl-alpha'-carbobutoxygamma-dehydropyrone) (17). At the outbreak of hostilities great emphasis was placed on this method of protection as a means of preventing the spread of malaria. Research was undertaken by the Bureau to prepare chemicals and test their repellent effect on insects. Those showing promise were then tested for toxicity to warm-blooded animals. One proprietary product already on the market, a mixture of butyl carbitol and its acetate, was eliminated because of its toxicity to man by absorption

### NEW DEVELOPMENTS IN INSECTICIDES

through the skin, but a substitute was soon found in 2-ethyl-1,3-hexanediol, known as Rutgers 612 (21). This compound, Indalone, and dimethyl phthalate, patented by Moore (22), are three good repellents. A mixture of these, patented by Travis and Jones (31), will give protection against bites for several hours.

No repellent has yet been found that gives perfect protection. There is considerable specificity, and what repels one species of insect may not repel another. Moreover, a chemical effective on one man may fail utterly on another. The conditions under which they are used also influence the repellent action and the time of protection.

#### SYNERGISTS FOR INSECTICIDES

One of the most fascinating subjects included in the studies on insect poisons is synergism. A synergist is a material which, when present with an insecticide, gives a mixture whose toxic effect is greater than the sum of the effects of the two materials acting independently. It may or it may not have any toxic action of its own. Since pyrethrum is relatively expensive, most of the synergists have been developed for use with it. The first commercial synergist was N-isobutylundecyleneamide, IN-930 (24). This compound increases the action of pyrethrum on flies considerably, and on lice attacking man the increase is more than 50 times. This combination was used in the Army louse powder (3) before DDT was introduced. Among other substituted amides (9) that have been tested, benzamide and piperonylamide show considerable synergistic action with pyrethrum in fly sprays.

Sesame oil (5), containing sesamin (14), is one of the best synergists for pyrethrum. It has found extensive use in the insecticidal aerosols.

The action of synergists is usually highly specific. A chemical that is a synergist for pyrethrum is not necessarily a synergist for rotenone or other insecticides. Also, the synergistic action varies greatly with the insect species and may be entirely absent with some. The search for synergists must be made for the most part by the trial-and-error method, since very little is known about their physiological action.

# BETTER PYRETHRUM EXTRACTS

For use in sprays no attempt was made to refine pyrethrum extracts, because most of the inert materials extracted along with the pyrethrins were soluble in the oil used for extraction. With the advent of aerosols containing Freon-12, which will be described later, refined pyrethrum extracts became necessary in order to insure better solubility in Freon. All the companies extracting pyrethrum have greatly reduced the amount of materials insoluble in Freon-12. Specifications now require this amount to be less than 4 per cent. They have also improved the color and removed most of the substances irritating to the nose and throat.

Barthel and Haller (1) have perfected a new process of making mixtures of pure pyrethrins. They have found that nitromethane, which is immiscible with kerosene, will extract practically nothing but pyrethrins

#### L. D. GOODHUE

from a kerosene extract of pyrethrum flowers in a two-phase liquid extraction. Upon further clarification with activated carbon 100 per cent total pyrethrins can be obtained.

# FUMIGANTS

Of the fumigants, methyl bromide has had the greatest expansion in use in recent years. It is now employed to fumigate many kinds of vegetables, especially in refrigerator cars, against Japanese beetles and other insects. It is also coming into use on grain and mill products because of its unequaled penetrating ability.

The war has brought methyl bromide into use as a fumigant for delousing clothing (19). It is more readily applied, quicker in action, and less injurious to clothing than the steam-sterilization process used in World War I. This fumigant is also 100 per cent effective against bedbugs and their eggs, even acting through a woolen blanket. It is applied to clothing in bags or other closed spaces by breaking a glass ampule containing 20 ml. of the liquefied gas, a technique developed by Latta (19). Millions of these ampules have been filled for the armed forces.

A new soil fumigant known as DD mixture has aroused much interest lately. It consists primarily of 1,2-dichloropropane and 1,3-dichloropropylene obtained as a byproduct in the manufacture of allyl chloride. It has been used most successfully in Hawaii for killing nematodes in the soil (4) where pineapples are grown. It has given promise in California against wireworms (30). Both these pests are destructive enemies of growing crops, and a good material for their control will be of great value.

# INSECTICIDAL AEROSOLS

Even before the war, work was in progress at the Beltsville Research Center to find better methods of applying the spray type of insecticide. Goodhue and Sullivan (10, 13) suggested eliminating the liquid carrier and applying the insecticide in the form of a smoke, or aerosol. In this form the insecticide stays suspended and active much longer than when applied as a spray. Tests have shown (6) the aerosol to be more effective after 20 minutes than a spray is after 5 minutes.

There are numerous ways of producing aerosols, but the most convenient is the one employing a liquefied gas (10). It is only necessary to dissolve the insecticide in the liquid under pressure and release it through a small orifice into the atmosphere. The aerosol is produced by the rapid boiling of the liquefied gas, which merely furnishes the energy for the dispersion of the insecticide and plays no further part.

Many insecticides and liquefied gases have been used in this method, but the most popular combination has been pyrethrum and sesame oil dissolved in dichlorodifluoromethane, a refrigerant known to the trade as Freon-12. This aerosol is now extensively used by our armed forces for the control of mosquitoes. It is well adapted for use on airplanes, since it is nontoxic to man, noninflammable, light, convenient to use, and very effective. Only 5 mg. of pyrethrins per 1,000 cubic feet in aerosol form is required to kill all yellow fever mosquitoes with an exposure of only 1 minute.

The experimental work required to develop the aerosol method was easily done with commercially available equipment. Before the Army could use it, however, small, light containers had to be devised. A large electric company using Freon in household refrigerators developed the first practical dispenser. It consists of a sealed container holding 1 pound of the solution, which is dispensed through a capillary running from the bottom on the inside and out the top. To open the container the protruding capillary is broken off while the container is held in an inverted position. A temporary cap is provided to retain the contents between sprayings. This company has made and shipped several million of these 1-pound dispensers. Other companies entered the field later and have produced large quantities of the aerosol solution in various types of containers.

DDT in combination with pyrethrum in the aerosol has been found to be very effective, especially on flies (11). With this combination it is possible to produce aerosols equally toxic to flies and mosquitoes. With some of these solutions only 3 seconds' spraying (2.5 grams of solution) will produce enough aerosol to kill all the flies, mosquitoes, and many other species of insects in 1,000 cubic feet. Considerably more is required for crawling insects, such as roaches, bedbugs, and ants, because less insecticide collects on them than on flying insects.

The aerosol method can also be used to apply insecticides to field and gardens crops.<sup>1</sup> Experiments with DDT aerosols produced with methyl chloride have been very successful against the pea aphid. As little as 10 pounds of a 5-per cent DDT solution per acre has given very good control. This is in contrast to 150 gallons of the recommended derris spray (3 pounds of derris [4 per cent rotenone] per 100 gallons). The aerosol method appears very promising for the control of several other agricultural pests, such as the potato aphid, the onion thrips, the peanut thrips, and the Mexican bean beetle.

Plant hormones (15) have also been applied successfully in aerosol form. This method is especially useful to induce the setting of fruit under greenhouse conditions.

Germicides (12), fungicides, or in fact any substances soluble in a liquefied gas can be dispersed in aerosol form by this method.

With the commercial production of aerosols some chemical and physical problems arose. The purification of pyrethrum extract mentioned above was the first to require attention. The water content of the constituents must be kept low to insure against corrosion of the containers. A high grade of material must be used throughout.

The physical behavior of solutions in liquefied gases was also studied. A relationship has been developed to show the increase in concentration

<sup>&</sup>lt;sup>3</sup> In this work the author is cooperating with F. F. Smith, of the Bureau of Entomology and Plant Quarantine, and L. P. Ditman, of the University of Maryland.

of a liquefied gas solution as the solution is withdrawn from the container (26). The equation is:

$$\mathbf{c} = \mathbf{C} \left(1 - \frac{\mathbf{Q}}{\mathbf{M} - \mathbf{V} \mathbf{D}_{g}}\right)^{-\mathbf{r}}$$

where c = concentration of insecticide after withdrawing Q

C = original concentrationQ = weight of liquid withdrawn M = weight of initial total contents V = volume of container  $D_r = density of saturated vapor$  $\mathbf{r} = \mathbf{r}$ atio of density of gas to density of solution

A differential manometer method of determining the vapor pressure over a solution in a liquefied gas has been developed, and measurements on several concentrations of oil in Freon have been made. As much as 15 per cent of sesame oil reduced the vapor pressure only 35 mm. from a total pressure of about 5,000 mm.

Densities were also studied with the aid of a small hydrometer bob in a closed system. The bob is calibrated by varying the temperature of pure Freon (26).

Although much progress has been made in the development and practical utilization of aerosols, there is still much research to be done. This method of dispersing insecticides is still very new and considerable research is still necessary. A concerted program is under way to study all angles of this method, especially to provide an inexpensive dispensing unit which will be adaptable for civilian use after the war. The results look very promising.

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# CHEMISTRY AT WORK

# HAROLD L. MAXWELL

# Head of Metallurgical Section, E. I. du Pont de Nemours and Company, Wilmington, Del.

The subject of today's paper is "Chemistry at Work." And what is meant by that subject is not a theoretical and involved treatment of the fundamentals of chemical reactions, about which we sometimes write and talk so much and actually know so little; instead let us dwell a little while on chemistry as it fits into the work of every-day life.

New commercial chemical products, such as synthetic ammonia, synthetic alcohols, urea, synthetic rubber, and nylon, are not born in adult maturity into a strange world. Rather they are conceived in abstract form first, as a research laboratory specimen, and they are nurtured through the period of semiworks growth and development until finally a use is found. This is when yesterday's laboratory curiosity becomes a new commercial product for today requiring plant sites, building materials, engineers, chemists, laboratories, and machines.

The beginning is therefore in the research laboratory where trained men and women maintain a relentless quest for truth. How important proper laboratories can be! This building we are in this afternoon, designed and erected through the vision and energy of the man we are honoring today, has provided the physical facilities for training several hundred research men and women in addition to many thousands of undergraduates. The importance of laboratories was concisely summarized by Louis Pasteur in the following words:

"Take interest, I implore you, in those sacred dwellings which one designates by the expressive term: 'Laboratories.' Demand that they be multiplied, that they be adorned. These are the temples of the future temples of well-being and of happiness. There it is that humanity grows greater, stronger, better."

It is possible that Louis Pasteur wrote better than he realized that day in France, when he called attention to benefits brought to humanity through laboratories. Since that time laboratories have been the birthplace of scores of drugs, health-giving vitamins, and new articles of clothing, food, and shelter that add materially to the beauty and comforts of living. However, twice in a lifetime all of those laboratories, yours and ours, have been turned into instruments for destructive processes rather than constructive. Twice they have been groomed into sinister perfection. In order to prevent its happening again, it is time that men and women throughout the world give thought to better ways of settling international differences before the tools we are forging now destroy us.

The research laboratories so deftly described by Louis Pasteur have played a vital part in developing new materials and processes that lend themselves to large scale commercial development, thereby providing employment for many more technically trained men and women. The course to be pursued from test tube to tank-car lots is long, but often must be traversed in a few weeks or months. The few crystals, or whatever the new product may be, are first produced in a sufficient quantity, on a semi-works scale, to permit evaluation of such factors as temperature and pressure characteristics, impurity limitations, reaction rates, corrosive effects and thermodynamic data. If the period of semi-works or experimental development can be extended, that is usually helpful in collecting data of direct assistance in design matters. The corrosion data determined by further tests is always helpful in choosing materials with a high degree of selectivity as to permanence in service and tolerance of corrosion products or impurities.

In so restricted a subject as corrosion testing, there are right and wrong ways of proceeding. It is known that in most instances a stressed material will corrode more rapidly than an unstressed material in the same service. It is only reasonable then that in certain corrosive conditions, the test pieces themselves should be stressed, before exposure, to the same degree as calculated for the projected plant equipment. This stressing of metal samples may best be done by the use of electrical strain gauges. These gauges are constructed of thin wires and cemented onto a thin sheet which in turn is attached to the metal part by an adhesive. The wire in the gauges is highly responsive, electrically resistance-wise, to slight increases in length. By standardization, the changes in electrical reaction of the gauge wires, as they undergo slight elongation in conforming to the change in shape of the underlying metal, may be converted directly to strain values. From these strain values, and through knowledge of the elastic modulus of the material used, the stress values are readily calculated.

An even more valuable application of electrical strain gauges has been found in determining the stresses throughout heavily loaded chemical equipment. We might take as an illustration a large smokeless powder press that extends from the basement of the factory building up into the second story. Another example might be a high pressure converter for synthesizing crystal urea by highly compressing two gases, carbon dioxide and ammonia. It is of vital concern to the plant whether the stresses are within a safe operating range or whether some parts of the equipment are bearing an abnormal load that could lead to rupture and possible accident. Fortunately, largely as a result of research in materials of construction and electrical instruments, the newly-developed electrical strain gauges can be depended upon to give reliable information. These tests are made by cementing the gauge units containing the fine wire at points of the equipment to be examined. As many as forty-eight points may be located in one series of resistance circuits, each balanced separately, and recorded on a chart serially for each stress condition as increments of load are applied externally. By this direct means, and at relatively small cost, one is able to construct a complete stress-strain diagram for each

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part of the plant equipment where a gauge was attached. These researches in stress distribution in high pressure equipment are expected to have wide application in chemical process post-war developments.

It may be of interest, before leaving the subject of stresses in heavily loaded chemical equipment, to mention a rather simple means of locating, qualitatively, areas of stress concentration. This is done by the use of brittle lacquer, known as "Stresscoat." The lacquer is sprayed on and if dried under controlled conditions will result in a film that will crack at a predetermined degree of strain in the underlying metal. The clarity of the cracks can be improved by the use of dyes. A number of different lacquer compositions, all of high brittleness, provide a range of materials that might justify the term of semi-quantitative in describing the obtainable accuracy.

The problem of corrosion also enters the development of a new commercial chemical product such as nylon.

As you may know, nylon is a long-chain body produced by the reaction between two chemicals such as hexamethylenediamine and adipic acid. These two chemical compounds each have six carbon atoms, so, for convenience and the lack of a better name, the filaments and yarn were called "66" until the name nylon was coined in October of 1938. Actually, quite a number of different nylons are possible. Many already have been made.

In the manufacture of the intermediates in the production of nylon, the reactions are such that corrosion is active, prohibitively so, on many metals. Fortunately, one of the molybdenum-modified stainless steels, if water quenched from 2,000°F., pickled and passivated, is resistant to a remarkable degree. Many tons of this material, valued at \$1.00 to \$1.50 a pound depending upon size and shape, were used in building the intermediates plant.

Throughout the nylon process development innumerable problems of filtering, heating, agitating, and pumping of liquids, slurries, and viscous polymers were encountered and successfully solved by chemical engineers, several of whom were research specialists on temporary loan.

The selection of construction materials for the nylon plants was the responsibility of a group of engineers with experience and training in one or more such fields as physical chemistry, chemical and metallurgical engineering. One of the more troublesome problems in the nylon development was the selection of material for and the building of metering pumps of high accuracy to operate on molten polymer at 285°C. with no lubricant except the molten polymer itself. In this, there were several problems superimposed on one another, i. e., problems of wear, thermal expansion, heat transfer, fluid flow, and quality of surface finish.

From the first, it was recognized that the smallest variations in process conditions and even traces of any contamination in the nylon polymer were reflected in adverse physical properties in the finished yarn as well as in color characteristics. Each step in manufacture, in semi-works as well as in the commercial plant, had to be scrutinized and standardized

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in every detail of design and materials of construction in order that no undesirable side reaction or contaminants would find their way into the material being processed. In this one respect there is a parallel with mankind where undesirable traits of character and temperaments may be transmitted from one generation to another across the narrow biological bridge of a single microscopic cell.

It was a long way between two important events, one the extrusion of the first few inches of a nylon fiber in a physician's hypodermic needle. and the other, the production on a tonnage basis. Yet the steps between these events, although taken at a double-quick pace, were nevertheless orderly and well thought out. For example, a semi-works pilot plant was authorized in January, 1938. On October 27 of the same year, nylon was announced to the world. The first commercial nylon plant, built at Seaford. Delaware, was designed to produce 3,000,000 pounds a year and promptly increased to 4,000,000 pounds a year. Before it turned a wheel, before a pound of material was made, funds were appropriated and the plant was doubled in size to produce a total of 8,000,000 pounds of nylon varn a vear. Now 8.000.000 pounds is a lot of anything, but 8.000.000 pounds a year of nylon is enough to protect a lot of ankles, large and small. Incidentally, this enlarged plant at Seaford has since been duplicated at Martinsville, Virginia, and for the duration of the war the total production of nylon from both sources is pledged to the government for military uses in parachutes, tents, glider tow-ropes, raincoats, and other products.

The story of nylon is a story of invention and initiative, of fundamental research followed by bold development applications based on the premise that a thing or material to be good must be made good for something and produced in quantity and at a cost that will add to the comforts and pleasures of living of the largest possible number of persons. Nylon, like neoprene, synthetic rubber, synthetic camphor, and penicillin, is the result of the system of free enterprise where men can study and work together as they choose, invest their savings, and use their combined capital to initiate larger undertakings, for only in the accumulation of working capital is there assurance of employment. We must not lose sight of the tremendous influence of chemical research which creates new products and new demands and, through that means, employment and general prosperity.

The Development Department of the du Pont Company has made a study of organized industrial research in relation to economic progress as reflected in sales of old and newly developed products. The results from that study indicated that the new projects and products that the du Pont Company will be ready to launch when the war is over, together with outlets for existing products, are expected to bring an all-time high in the Company's peace-time employment. Certainly we are not alone in this prospect.

We thought in 1928 that the products we were selling were modern. We were selling still more in 1942. But note this important fact—in 1942, 46 per cent of du Pont's gross sales consisted of products that either

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did not exist in 1928, or were not then manufactured in large commercial quantities. You may safely conclude from these figures, we believe, that industrial concerns are relying upon their research programs to create new products and new jobs, both of which are among the essentials if we are to insure employment and prosperity. What is to be brought out during the coming years in the way of new chemical products is, for the most part, left to speculation. But already products of the research laboratories, possibly only microscopic in quantity, are finding engineering expression in lines of definite length and direction on the drafting boards.

The reason for success of a new chemical venture sometimes is obscure. In the main, it appears to be a combination of factors of supervision, experimental equipment, and the element of time, but perhaps the most important single factor is that of the spirit of cooperation and persistence of the men working on the development. And in speaking of persistence, I'd like to inject at this point a quotation credited to Calvin Coolidge. He said:

"Nothing in the world can take the place of persistence. Talent will not; nothing is more common than unsuccessful men with talent. Genius will not; unrewarded genius is almost a proverb. Education will not; the world is full of educated derelicts. Persistence and determination alone are omnipotent. The slogan, 'Press On,' has solved and always will solve the problems of the human race."

Nothing will bring better results in solving a particularly hard development problem than intelligent and systematic planning fortified with a determination to keep everlastingly at it. Goethe, the very human German poet, states in summary in his "Faust":

> "He only earns his freedom and existence Who daily conquers them anew." (Faust, Act V, Scene VI)

Nowhere, we believe, is Goethe's thought more true than in research developments and in application of the results in providing for commercial scale of production.

And now, before closing, it might be worthwhile to say that industry looks to the colleges and universities for men and women of high caliber for their research organizations.

Sometimes while I was teaching at Purdue University, I felt that there might not be quite the community of interest beween the graduate students and faculty on the one hand and the industrial research worker on the other. Once each year this gap appeared to be closed in an exchange of pleasantries when industrial men came to the University to interview candidates for positions. My own feeling is, and I believe it is shared

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by many men in industry, that it might be to our mutual benefit to maintain at more frequent intervals, a medium for exchange of ideas and points of view.

It is not uncommon for graduate students or even young faculty candidates in considering industrial positions to express considerable doubt or even a degree of fear at the prospect of leaving—what is called— Academic freedom. From my own experience of having had a professorship for four years at Purdue University followed by approximately fifteen years with the du Pont Company, I definitely recommend considering a career in the chemical industry. The Commencement orators sometimes tell you to get ready to fight the battle of life. Don't you believe it. The life you are preparing for is not a battle; it is simply a succession of rapidly changing situations and if you are smart you will prepare yourself so well that you can adapt to the changing conditions that are bound to come to you in the years ahead. Marie Curie, the daughter of Madame Curie, put a wealth of thought on this subject in two sentences. She said: "There is nothing in life to be feared. It is only to be understood."

You students and particularly the graduate students in chemistry of Iowa State College have been the life concern of Dr. Coover. It will be your responsibility to help to carry forward the standards of quality and accomplishment he has prescribed for you.

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# FORTY YEARS OF PROGRESS IN FOOD CHEMISTRY

# LILLIAN B. STORMS

Director of Research, Department of Nutrition and Service, Gerber Products Company, Fremont, Mich.

Since the beginning of the present century food chemistry has not only made great progress but the emphasis has changed. Harvey W. Wiley directed the publication, beginning in 1887, of a series of monographs on "Foods and Food Adulterants." The Food and Drug Act of 1906 was largely a result of his efforts. Without in any way belittling his achievements in the policing of food production and with appreciation of the need at that time for protection of the public from the adulteration, the lack of sanitation and of impurities in foods, the emphasis was negative. The present interest of the food chemist is largely positive. He looks upon his function not so much as protection against unscrupulous or ignorant producers, not so much as protection against hazards, but he thinks of food as a source of positive health.

The food chemist is trained in the related sciences, especially in bacteriology and nutrition, as food cannot be divorced from its use, i. e., nutrition.

Harvey W. Wiley was instrumental in the early development of methods of food analysis which have resulted in a compendium of official methods which have been adopted by the Association of Official Agricultural Chemists.

Forty years ago food chemists were concerned mainly with the determination of the percentages of carbohydrate, protein, fat, and ash of food, that is, its proximate composition. Atwater believed that the chemical composition, showing him the fuel values of all feeds and foods, with a knowledge of the digestibility factors and the energy requirements of man, would make it possible to place the nutrition of man and animals on a sound economic basis. He regarded fruits and vegetables, both high in water, and also eggs and milk, as extravagant food purchases. At that time \$0.25 would buy but 645 calories of eggs, but the same \$0.25 would provide 8,000 calories from dried beans and 10,000 calories from wheat flour. That was simple nutrition arithmetic. How vast has been the change from this conception of the value of food solely from its yield of energy!

Bulletin 28, first published in 1899 and revised in 1906, was the standard reference until quite recently. Present day tables of food values include more than the percentages of moisture, carbohydrate, protein, fat, and ash, which were given in Bulletin 28. The first considerable division of these general food constituents was made on the ash. Sherman's "Chemistry of Food and Nutrition" was published in 1911. He compiled all available data on food composition and one table of the ash constituents included calcium, magnesium, potassium, sodium, phosphorus, chlorine,

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sulfur, and iron. Perhaps it is well that these figures were obtained before the food chemist got so busy on vitamins and amino acids.

Calcium, phosphorus, iron, and iodine are the mineral elements for which care needs to be taken to meet body requirements. The other minerals are easily obtained in even a poorly chosen diet, so that we do not usually consider them in dietary calculations.

**PROTEIN:** The emphasis on caloric values gave place to interest in protein and it became evident that the quality as well as the quantity of protein was of significance.

Proteins have been of primary interest both at the beginning and at the end of the period covered since 1900. The word "protein" was coined about a century ago from the Greek verb "to take the first place" and was given to what was considered to be the fundamental substance of body tissues.

For two decades overlapping the beginning of the century, T. B. Osborne of the Connecticut Agricultural Experiment Station was analyzing proteins. In 1907 he published a report on the proteins of the wheat kernel and pointed out that these proteins differed so much in the proportions of the then known 16 amino acids they contained that he challenged the prevalent assumption that all proteins were of the same nutritive value.

The question, "How much protein is required?" caused a lively controversy, stimulating observations and experimental study. Voit's standard of 125 grams of protein intake for a man doing moderate work was being challenged. In 1901 Chittenden showed that much less was necessary for maintenance of nitrogen equilibrium and health. He found that from 36 to 55 grams were sufficient for a period of several weeks.

In 1909 Sir James Crighton-Browne asserted that a definite relationship existed between protein intake and racial success, that those on higher protein diets were the more vigorous. This belief is still prevalent and is possibly true, but definite proof, other than surveys, has been lacking. A paper from the Harvard Fatigue Laboratory has just appeared. A diet high in first class protein of 160 grams daily intake and one low in protein, containing little of animal origin and of 50 to 55 grams, demonstrated no effect on muscular efficiency. The experimental period was of only two months duration and on but eight men. Doubtless this question will soon receive further attention.

Studies on animals showed that rations of similar chemical composition were extraordinarily different in nutritive value. A new method of experimentation was developing, the feeding of experimental animals with simple food stuffs and with equivalent chemical substances. In 1906 Hopkins wrote, "No animal can live on pure protein, fat and carbohydrate and, even when the necessary inorganic material is carefully supplied, the animal still cannot flourish." He postulated that many unknown substances were essential, the first guess of the existence of what have since been called vitamins.

At about the same time it became generally recognized that the

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values of proteins could not be assessed without consideration and knowledge of the amino acid content. Over the period of the intervening years a vast amount of information has been gained about the amino acid content of foods and some knowledge of the function of amino acids in the bodies of animals. Recently spectacular results based on human studies have been reported by W. C. Rose at the University of Illinois. It has been determined that only eight of the amino acids are required for nitrogen equilibrium and they are called the essential amino acids. It is believed that species of animals differ in these requirements and at least two additional amino acids not necessary for adult life appear to be required for growth.

As recently as 1942 the statement was published in the British Scientific Journal, "Nature," that the classification of amino acids into essential and non-essential is based on studies on the experimental rat and it is doubtful whether there is evidence that any of the known twenty amino acids may be considered to be unessential for man. Thus in less than two years we have reduced the number of amino acids required to be present in the food of man, from 20 to 8. Again we have learned that the rat is not a human being.

A rather startling finding has been the rapidity with which a deficiency of certain amino acids becomes evident. Nine days deficiency of valine resulted in loss of appetite and in fatigue and restoration produced an almost immediate effect. Vitamin deficiencies are not as dramatic.

Amino acids have been tagged with heavy nitrogen to trace their route and deposition in body tissues, showing an astounding rapidity of change in the amino acid and protein structure of the body.

Proteins are vitally important nutritionally but also economically. The cheaper vegetable proteins are being examined as possible substitutes for the more expensive animal proteins. Processing of vegetable proteins through a bovine or poultry factory is expensive and inefficient.

The rat is being displaced by the "despised" microbe as a means for measurement of amino acids. Only within the last year has it been possible to separately determine the three acids, valine, leucine, and isoleucine, and this has been done by means of microbial methods.

All enzymes so far studied and many hormones are proteins. A virus causing a disease of the tobacco plant, known as tobacco mosaic, has been identified as a protein. Dr. Paul Cannon of the University of Chicago states that all bacteria causing infections are foreign proteins. He maintains that, since amino acids are essential in the development of antibodies, reduced protein intake may seriously impair ability to resist infections. This is of especial interest in control of plagues in war areas and in depletion of body tissue from disease or surgery. The ability to form antibodies is impaired and the diagnosis of an infection as the cause of death is really giving first place to a secondary factor.

Protein is as necessary in the formation of hemoglobin as is iron.

Proteins broken down by enzymatic action to form "protein hydrolysates" are being used parentally, instead of the more expensive and diffi-

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cult to obtain amino acids, post-operatively, for war wounds, and after severe burns, as in the cases from the much publicized Cocoanut Grove disaster.

The knowledge gained in the last two years about amino acids is making possible more intelligent supplementation of inadequate proteins, especially the more efficient use of vegetable proteins. However, we do not yet know much about the amino acid content of vegetable proteins.

IRON: Another illustration of a changed concept is that of iron. In Sherman's first edition of "The Chemistry of Food and Nutrition," 1911, fifteen pages were devoted to the controversy of organic vs. inorganic iron and the biological utilization of iron.

In 1902 Bunge, in Germany, published a series of experiments on rats, rabbits, and dogs in which he showed that a diet of milk and rice alone, or milk, rice, and ferric chloride, resulted in highly anemic animals. Contamination of the iron salt with copper would have changed the result. This study led to the belief that even though inorganic iron and organic iron followed the same route in the body, hemoglobin was derived essentially from organic iron. Now we know that inorganic iron salts, with small amounts of copper, are effective sources of available iron. We need much more information about the availability of the various forms and sources of iron.

INTERRELATIONSHIPS: The influence of copper on the availability of iron illustrates the biological effect of catalysts. It is not surprising that catalysts operate in the field of biological chemistry. Only within the last few years have we learned much about the subjects of biological catalysts, trace elements in foods and in the animal body, about vitamins and enzymes and about their interrelationships and interdependence.

Now the interrelationships and effects of various nutrients upon each other are filling the literature. To mention only a few, cobalt deficiency on the anemia of cattle, carbohydrates on the requirements for thiamin, influence of choline on the utilization of vitamin D, of copper in food processing equipment on ascorbic acid, mineral oil on availability of vitamin A, the relationship of ascorbic acid and of protein to infections, of protein on calcium absorption, of temperature of environment on the thiamin, pyridoxine and choline requirements of man, and of intense sunlight which increases the need for vitamin A, riboflavin, and niacin. These few examples illustrate a variety of types of interrelationships and many of them are similar to reactions in other fields of chemistry. To mention one more example, we do not yet know the effects of imbalance caused by deficiencies or of excesses of certain nutrients.

The early food chemist visualized the substitution of pills for food. The druggist now has that idea, but the modern nutritional chemist, as he learns more about the complexity of the apparently simple matter of eating, believes ever more firmly that food is essential.

COLLOID CHEMISTRY: A new development is in the field of the applications of colloid chemistry to food chemistry. A few examples will serve to illustrate the applications of the principles of colloids to cookery processes and procedures.

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The gluten of flour has colloidal dimensions. Gluten particles of cake and pastry flours are of smaller size and more dispersed than those in bread flours, a quality of use in obtaining the desired texture in cakes. The same principles in the control of time, temperature, concentration, and various manipulations are effective in the making of a cake as in reproduction of other colloids. A paper at the last meeting of the Cereal Chemists was on the effect of varying mixing speeds and dry milk solids in the making of bread.

Heating and homogenization of milk in the manufacture of evaporated milk result in greater dispersion of the fat. But heating of protein sufficiently to produce coagulation decreases the dispersion.

The addition of acids or alkalies in strengths insufficient to cause true chemical change may either increase or decrease the dispersion of particles.

Mayonnaise is an emulsion of the oil-in-water type composed of salad oil, eggs, vinegar, and spices. In the manufacture of margarine, while the margarine oil and the milk are being churned together, the emulsion is of the reverse to that of mayonnaise, water-in-oil.

Some Contributions of the Food Chemist: Much of our present common knowledge, many carefully controlled commercial procedures resulting in foods widely and generally available, have been developments since 1900.

The study of the bacteriology of canning started in 1895, when Prof. H. L. Russell applied bacteriology to trouble with swells encountered by Wisconsin pea canners. By about 1924 adequate processing procedures, based on extensive bacteriological studies, had been established, resulting in the safe canned foods industry as we know it. Methods were devised for measuring the heat penetration in sealed cans, to obtain data on the heat transfer in different foods with varying media and in different sized cans. The recommended processes are sufficient to assure in the center of the can the thermal death point of *Clostridium botulinum*, a widespread, dangerous, and resistant organism. Since 1925 no case of poisoning from the toxin produced by this organism has occurred in any commercially canned food packed in this country. This has been a notable industry achievement. Other industries can point with pride to similar accomplishments.

Just before 1900 Dr. Samuel Prescott determined that spoilage in canned foods was microbial in origin. It is surprising that this fact was not established until ninety years after Appert, during the Napoleonic Wars, had first succeeded in preserving food by means of heat in a sealed container. It was fifty years after Appert that Pasteur introduced the principle of pasteurization. The advancements made in the last forty years have been truly astounding.

A few examples of the contribution of the chemist to new developments in foods are the following: cereals of the rolled, flaked, granulated, and pre-cooked, ready-to-eat types; good milk produced under sanitary conditions either as raw, pasteurized, evaporated, or dried milk; the application of bacteriology to all foods with reference to control of spoilage and food poisoning; the modern meat industry; a new industry of edible

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fats and oils from cotton and other seeds; spray drying of eggs; development of sanitary unit packaging, which in some cases involves methods and packaging which will delay the development of rancidity; quick freezing of a wide variety of foods; commercial dehydration of foods where an old home industry was commercialized during the Boer War and subjected to scientific study during World War I, greatly improved during World War II. We now have a food industry, largely developed since the beginning of the century, with a wide variety of foods from soup, both in cans and dried, to shelled nuts in air tight paper containers.

Electronics is just now being applied to sterilization of foods in packages.

FLAVOR IN FOOD: We have learned much about the action of enzymes in foods on their qualities after processing and storage. Both canned foods and frozen foods are subjected to a blanch before canning or freezing. This inhibits enzyme activity, preserving color and in the case of frozen foods, prevents a hay-like off-flavor which develops in frozen vegetables if not adequately blanched.

Flavor in food is one of the newer interests of the food chemist. Flavor is still quite largely an "unknown" in food chemistry.

There are not yet objective tests for variations in flavor. Some chemical tests parallel loss in flavor. Ascorbic acid loss usually coincides with loss of quality, which in turn is closely akin to loss of flavor.

Flavor is a mixture or combination of sense reactions, emotional rather than chemical. The sight or appearance of food, odors, texture, and memory are all of influence in determining individual flavor preferences. People vary in all of these responses, as anyone who has used a taste panel can testify.

A recent paper carries the title, Relative Taste Potency of Some Basic Food Constituents and Their Competitive and Compensatory Action.

At the meeting of the American Chemical Society this fall, one session was devoted to the subject, Food Flavor and Quality. A few of the titles of papers at that meeting were the following: Some Visual Aspects of Quality Control and Quality Research; Physico-chemical Research and Its Relationship to Flavor Development and Control; Volatility in Food Flavor; Flavor in Food Fats (i. e., enhancement of flavor is desired in some fats and its elimination in others); The Problem of Prevention of the Development of Oxidative Changes.

To quote from one paper: "Preservation of the hidden qualities of foods is in a very primitive state of development. Finer hidden qualities, not readily apparent to the consumer, can be bred into fruits and vegetables and improved methods of agriculture and transportation and food processing will eventually preserve most of the nutritive properties for the ultimate consumer." The as yet undeveloped hidden qualities are of great interest to the food chemist because of the possibilities of improvement of foods, especially the processed foods.

The term "processed foods" should include certain raw foods. Some

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so-called "raw foods," as fresh fruits for example, have passed through six or eight-unit operations requiring elaborate equipment and technological skill.

Some of the procedures which have been developed to enhance appearance or flavor are now being subjected to assay for the effects on nutritive values.

EFFECTS OF WAR ON THE WORK OF THE FOOD CHEMIST: As previous wars have stimulated the production of foods suitable for the use of armed forces, so have the two wars within this century. New foods have been devised to meet specific requirements, as butter which will withstand the high temperature of the tropics by the addition of a cotton seed oil preparation. Heat does not cause the development of rancidity in this product, as it does with butter, although the flavor is adversely affected. The dehydrated food industry received a great impetus because of the needs of transportation in a world-wide war. We have been learning which foods can be more successfully dried and we have found out considerable about the packaging and storage problems of that industry.

Concentrated rations supplying the minimum nutritive requirements and suitable for combat troops have been developed and are being improved. Knowledge about human food requirements, practically unknown during World War I, has made these concentrated rations possible.

The army and navy had need for more information about the nutritive values of foods, especially the vitamin content of foods as eaten. Until recently, most of the tables giving nutritive values included few data except on raw foods. One result of this demand, because of the large amounts of canned foods used, was the initiation of a long-time extensive study by the canning industry on the nutritive value of canned foods. The first series of papers has just appeared in the *Journal of Nutrition*.

Certain procedures used in modern canning practice are favorable to retention of some of the nutrients. The virtual "exhaustion" of air, by heating the food before sealing the can, has a favorable effect on the retention of vitamin C. While losses of soluble vitamins and minerals take place during blanching, those dissolved in the liquid in the can combined with what is in the vegetable or fruit, furnish more than in the usual methods of home cooking of raw foods. Methods of preparation of canned foods for serving will be a phase of this study. If the general public can be educated to use the information which is being made available, the effects on the nutrients obtained will be stupendous. Discarding the liquid in the can, or for that matter the water in home cooking of vegetables, sends nearly half of some of the food values down the kitchen drain.

Studies are in progress on the effects of environmental temperatures of canned foods during storage. In temperate climates it has been found that storage does not cause serious losses of the essential dietary constituents in canned foods. Until more information is available the army believes that in hot and humid climates, the fortification of certain foods is desirable if not necessary. Requirements have been imposed for stability of both natural and fortified foods at 100°F. for one year, far more severe than domestic requirements.

This canning industry study is an extensive piece of work and already has supplied a considerable amount of information, especially on the ranges of vitamin and mineral content which reasonably may be expected to occur. It will show the proportions of the available canned foods giving close to average values and the procedures which result in extremely high or low content.

Of practical value to all of us as consumers will be the improvements which may be anticipated in the procedures used in canning, the growing of crops not only for good yields per acre but higher nutritive values, and also in the education of people in the preparation of canned foods for serving.

We are so familiar with the present tin can that it may be surprising to realize that the first open top sanitary style can appeared in 1900, to replace the former solder sealed can. It was not universally used until about 1918. The needs of global warfare and the shortage of tin for food containers has resulted in improved packaging of foods in paper containers. The shipping carton of today is a vast improvement over that used during the first few months of the war. Plastics and aluminum alloy cans are already familiar to you. However, no one has yet been able to put a zipper on the can.

The Quartermaster Corps has stimulated work on anti-oxidants. The anti-oxidants being used have shown variability at different temperatures. Certain ones which have proved to be fairly satisfactory at the boiling point of water are of little use at room temperature; others which are effective at room temperature are inactivated by heat. Some of these reactions show sharp changes at certain temperatures.

FORTIFICATION OF FOODS: The enrichment and the fortification of foods is another phase of the work of the food chemist. Aside from the question of the justification or the desirability of the practice, there have been practical problems. The stability of white flour, over long periods of storage, has been the principal reason for its general use and acceptance. The enrichment of flour has not restored the values removed in milling, and doubtless improvements will be made both in nutrients added to flour and in stabilizing these substances.

One of the substances added to enriched flour is iron. Not only the stability of the various forms of iron used in the fortification of foods, but the availability of the iron to the body and the stability of the food itself in the presence of ionizable iron are problems still under investigation.

Both food chemistry and nutrition have been builded upon a scientific foundation. This fact has probably had at least some effect in safeguarding us as a people from fortification of almost everything we eat as a result of overenthusiasm. White flour and cereals have been generally accepted as justifiably proper mediums for fortification at least back to pre-processing levels or natural levels of dietary essentials. At present

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the enrichment or fortification of the following foods is favored: flour and bread, possibly cornneal, the vitamin D fortification of milk, vitamin A to fats, and iodine to salt. The Foods Committees of the American Medical Association and of the National Research Council oppose the fortification of carbonated beverages and confections or the fabrication of foods or beverages containing multiple fortification to the extreme point of provision of all nutrients necessary for the day in one or two servings of a single food.

The education of the public on methods of preparation of natural or commercially prepared foods and on the desirability of the use of foods instead of super-fortified foods or concentrates certainly is more desirable than uneconomical fortification. Dr. Elvehjem has commented that the public seems determined to spend about so many millions at the drug store. Perhaps less harm and just possibly some good may result if it is spent on vitamin pills instead of the old fashioned patent medicines.

THE NUTRITION FOUNDATION: A recent, entirely new development is that of food manufacturers cooperatively providing for fundamental and basic research. The Nutrition Foundation is financed by forty-two commercial food companies for the purpose of allotting grants to laboratories in educational institutions. The research is largely fundamental in character, although a few grants have been made in response to requests from the army for information of immediate interest. Individual firms are visualizing something beyond the confines of their immediate interests, their obligations to develop fundamental research in food and nutrition. This recognition does not ignore much fundamental research which has been conducted by many firms and industries, but it is a new approach. It is a union of industry and research, something which would not have been possible only a few years ago.

COMMENTS ON FUTURE TRENDS: Perhaps it is unwise to speculate on the future, because time eventually catches up with prophesy like it does with politicians, but it is interesting. It is especially so in a field where the progress made since the beginning of the century has been as rapid and as great as it has in the realm of food chemistry.

It would seem inevitable and desirable that the science of food chemistry will become increasingly allied with and interdependent on nutrition as it has been in the studies on proteins, on bacteriology as it has in the canning industry, on engineering in the development of equipment, and with other phases of chemistry such as physiological chemistry and enzyme chemistry.

The fundamental scientific research in these interrelated sciences will stimulate and will give a sound foundation for an increasing amount of technical and applied research.

Economic phases will also enter into the development of industrial applied food chemistry. As George A. Sloan recently said at the Institute of Food Technologists, "Only by the development of products acceptable to the public, can companies expand to make employment and thus make a powerful contribution to prosperity and a higher standard of living." This development must be economically sound, by improvement of existing products, fabrication of new products, and, through mechanical means, reduction of production costs.

We do not yet know many things we should about constituents of the foods we eat, their nutritive values under various conditions, the interrelationships of the various nutrients, the conservation of essential nutrients by better processes of production and preservation. Much needs to be learned about packaging from the angles of food chemistry, nutrition and protection of food flavors.

Food chemists will discover uses for food stuffs other than as nutrients for men and beasts, especially in an era of surpluses. Foods may be sources of hormones, substitutes for gasoline and other fuels, in ways somewhat similar to the manufacture of plastics and the casein-base materials, as medicinals, and for many other possibilities as yet unthought of.

The food chemist is interested in supplies of foods, therefore in the problems of farm production and the transportation of foods. A very large proportion of our population is directly concerned with the production of food, its manufacture, processing, packaging, distribution, and ultimate uses, and more and more will the problems of these groups be presented to the food chemist and technologist.

And finally, the food chemist in the phases of food research bordering on nutrition is concerned with the public health aspects of food, in what food is needed as well as in what will sell. Since 1900 the emphasis has changed from the negative to the positive, to the production of better foods of higher nutritional values and in all probability this trend will be further accentuated.

CONCLUDING COMMENTS: There has been no attempt to make this in any way a complete or even a partial survey of the progress of food chemistry during the past forty-four years, but merely to give a few developments which might be of interest to this group.

The more narrow confines of the chemistry of foods have been enlarged to include or cooperate with other phases of chemistry and of bacteriology and particularly is there evidence of the union of food chemistry and nutrition.

Illustrative of the extended influence and interest in the field of food chemistry is the fact that in 1900 there were only a mere handful of persons engaged in this work. Now, literally hundreds gather at the meetings of the groups and associations including food chemists among their members. The development of food chemistry as a science and its applications in the food industry are due to many factors, among others the growth of the related sciences and to wider interest in nutrition.

Food chemistry is no longer a "closed corporation" or exclusive fraternity. This is fortunate, for our interests are food and human-wide.

# SYNTHETIC RUBBER

# JOSEPH F. NELSON

Group Head, Research and Development of Synthetic Rubber, Esso Laboratories, Chemical Division, Standard Oil Development Company, Elizabeth, N. J.

The development of synthetic rubber is based upon the wealth of information which has been accumulated on the structure and properties of natural rubber. According to the present concept, natural rubber is a linear polymer of extremely high molecular weight, in which isoprene is the recurring unit. Isoprene was shown to be present in the products resulting from the pyrolysis of rubber by Williams in 1860. In 1875 Bouchardat succeeded in reconverting isoprene to a solid rubber-like material by polymerizing it with the aid of concentrated hydrochloric acid. However, the study of a means of preparing synthetic rubber from isoprene never reached appreciable proportions. In fact, no known polymer of isoprene has been synthesized to date which has properties that can compare with those of natural rubber, although the Russians, shortly before the start of their present war with Germany, were reported to have developed a new method for making isoprene rubber (1). From a commercial standpoint, no known economical source of isoprene has been made available. The Germans in the period following the first world war turned their attention to butadiene in preference to other diolefins.

The first synthetic rubber of note was prepared from dimethylbutadiene, which had been found to polymerize to a rubber-like mass in 1900. During World War I, the Germans developed this type of rubber on a commercial scale. It is reported that they operated a plant with a capacity of 150 tons per month for a considerable period. Methyl rubber, as the product was called, was an inferior grade of rubber, and as a result its manufacture was discontinued at the close of the war. It was prepared from acetone by the following series of reactions:

$$2(CH_3)_2CO + 2H \rightarrow (CH_3)_2COH \cdot COH(CH_3)_2$$

The polymerization of the monomeric diolefin was effected by using sodium as a catalyst or by heating at about 70°C. In an alternate method, the polymerization was allowed to proceed at room temperature, after the monomer had been seeded with polymer.

During the late 1920's and the early 1930's, the Germans developed a

group of products known as the Buna rubbers. The first ones of the series were prepared by polymerizing butadiene with sodium. The name Buna is derived from the first two letters of Butadiene in combination with the symbol Na for sodium. It is postulated that the sodium adds 1,4 to the diene and that the resulting organometallic compound adds 1,4 to another molecule of diene. There is evidence that some 1,2-addition also occurs. The addition process is thought to continue until a long chain molecule is built up. Two types, Buna-85 and Buna-115, were developed. The numbers designating the types refer to the molecular weight in thousands.

In 1931, du Pont announced a new synthetic rubber which was called Duprene. This name was later changed to Neoprene. Neoprene, a polymer of chloroprene, was developed by Carothers as an outgrowth of the work by Nieuwland on the polymers of acetylene.

Thiokol was introduced commercially in 1932. This class of rubbers consists of a series of organic polysulfides developed by Patrick.

In 1935 the commercial production of the Buna rubbers was announced by Germany. Emulsion polymerization replaced the older method involving the use of sodium; and copolymers, known as Buna S and Buna N, replaced the polymers previously prepared from butadiene alone. Synthetic rubbers of the copolymer type are generally prepared from a diolefin and an unsaturated compound of the vinyl type. Thus, Buna S is a copolymer of butadiene and styrene, and Buna N is a copolymer of butadiene and acrylonitrile. The product is a true copolymer only if both species of monomer enter into the formation of the individual molecules which make up the polymerizate.

Butyl rubber was discovered in 1937 and announced to the public by Standard Oil Company (N.J.) in 1940. A pilot plant was in operation at the time of the announcement. In June, 1941, the construction of a Butyl rubber plant with a capacity of ten tons per day was authorized. In October of the same year, this capacity was doubled. Goodrich and Goodyear also announced in 1940 synthetic rubbers under the names of Ameripol and Chemigum, respectively. By April of 1941, the Standard Oil Company of Louisiana had completed construction of a Buna N plant with a capacity of five tons per day.

Thus, at the time of Pearl Harbor, the foundations of the synthetic rubber industry in the United States had already been developed. Without the wealth of information available at that time, it is doubtful that the amount of synthetic rubber recommended by the Baruch Committee could have been made available in time to meet the requirements of the national emergency. It should be noted, however, that in spite of the information available at the time of Pearl Harbor, a tremendous amount of effort had to be expended on research and development of raw materials, manufacturing processes, and on the fabrication of synthetic rubber into finished articles. Research is still in progress on a very large scale in these fields. At the present date, the rate of production of synthetic rubber has reached a figure in excess of our imports of natural rubber prior to the war. Production figures for Buna S, Butyl, and Neoprene GN are given in Table 1.

#### SYNTHETIC RUBBER

۶	Rated Annual Capacities			Estimated Ultimate Annual Capacity	Estimated Appual Rate
Type Rubber	Baruch Recommen- dation U. S. Only	Present U. S. Only	Present U. S. and Canada	with Present Plants U. S. and Canada	4th Quarter 1944 U. S. and Canada
Buna S Butyl. Neoprene GN Thiokol N	845,000 132,000 69,000 60,000	705,000 68,000 6,3,000 * (Pros	735,000 75,000 63,000 * gram Suspende	1,000,000 75,000 70,000 d)	780,000 38,000 57,000
Total	1,106,000	836,000	873,000	1,145,000	875,000

# TABLE 1 PRODUCTION OF SYNTHETIC RUBBER (2) (LONG TONS)

\* Includes 14,000 tons plant capacity scheduled for completion during 1944.

Thiokol N was at one time included in the synthetic rubber program for retreading and for passenger tire production. However, it was later found that conservation methods and availability of reclaimed rubber were sufficient to meet the situation without the production of the 60,000 tons per year recommended by the Baruch Committee (2). Buna N is not included in the above table. The best unofficial estimates place plant capacity in the United States at 29,000 to 30,000 long tons per year (3).

Real progress in the development of synthetic rubber was not realized until the idea of synthesizing natural rubber was abandoned.<sup>1</sup> As soon as the emphasis was placed on making synthetic rubber by the polymerization of the many types of available unsaturated compounds, polymers were produced which began to excel natural rubber in one or more respects. Recently, phenomenal progress has been made and is still being made in the construction of tires from synthetic rubber. For many other uses, synthetic rubbers have properties that excel those of natural rubber. However, it must be admitted that so far no synthetic has been developed that is equivalent to natural rubber in all respects. Most types tend to build up more heat under flexing conditions than does natural rubber. For this reason and as a result of problems in adhesion, it has been difficult to produce a synthetic fully the equal of natural rubber in the fabrication of tires.

The preparation and properties of the more important types of synthetic rubber are discussed below.

# Buna S

Buna S constitutes the bulk of our synthetic rubber program, since it appeared to be the most promising type that could be made available in quantities sufficient to meet the emergency requirements of the tire

<sup>&</sup>lt;sup>5</sup> The writer, however, is of the opinion that the incorporation of more isoprene into synthetic rubbers or the synthesis of an all-isoprene rubber may lead to improved products which more closely approach natural rubber in their properties,

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industry. The butadiene and styrene required to produce it are prepared or can be prepared by the following methods:

Butadiene	
1. $C_{2}H_{0}OH$ 2. $n - C_{4}H_{10}$ 3. $n - C_{4}H_{8}$ 4. Naphtha	$-\rightarrow CH_2 = CH - CH = CH_2$ $-\rightarrow CH_2 = CH - CH = CH_2$ $-\rightarrow CH_2 = CH - CH = CH_2$ $-\rightarrow CH_2 = CH - CH = CH_2$
5. $HC = CH + H_2O$ $2CH_3CHO$ $CH_3CH(OH)CH_2CHO + 2H$ $CH_3CH(OH)CH_2CHO + 2H$	$ \begin{array}{l} -\rightarrow CH_{1}CHO \\ \rightarrow CH_{4}CH(OH)CH_{2}CHO \\ \rightarrow CH_{4}CH(OH)CH_{2}CH_{2}OH \\ \rightarrow CH_{2}CH_{2}OH - CH = CH_{2}+2H_{2}O \\ \end{array} $
6. $C_2H_3OH$ CH <sub>3</sub> CHO as in (5)	$ \xrightarrow{\rightarrow} CH_3 CHO + H_2  \rightarrow CH_2 = CH - CH = CH_2 $
Styrene	
1. $C_6H_6 + C_2H_4$ 2. $C_6H_8C_2H_4$	

TABLE 2				
PREPARATION	OF	BUTADIENE	AND	STYRENE

Butadiene can also be prepared from butylene glycol-2,3 obtained by fermentation.

In the manufacture of Buna S, styrene and butadiene are emulsified in water with the aid of an emulsifying agent, and the polymerization is effected with a peroxide type of catalyst. Approximately 25 per cent of styrene is used. Modifiers for the polymerization, such as thiuram disulfides, mercaptans, zanthogen disulfides, etc., have been used (4). These modifiers favor the formation of linear polymers in preference to the undesirable branched and cross-linked types of polymer.

TABLE 3	
PREPARATION OF BUNA	S-



Buna S is compounded and fabricated in a manner similar to natural rubber, although variations in the formulae are used in order to bring out

### SYNTHETIC RUBBER

its optimum properties. Buna S possesses good abrasion resistance, good age resistance, and wears well in tire treads. It is deficient under conditions of hot service, wherein a change takes place known as "heat embrittlement."

# Perbunan

Acr

Buta

Poly

Perbunan, formerly called Buna N, is a copolymer of acrylonitrile and butadiene. It is synthesized by the emulsion process in a manner analogous to Buna S.

TABLE 4

PREPARATIO	N OF PERBUNAN AND RAW MATERIALS
vlonitrile	
1. HOC <sub>2</sub> H <sub>4</sub> Cl+NaCN	
adiene	
(See Table 2)	
merization	г
xC <sub>4</sub> H <sub>6</sub> +CH <sub>2</sub> =CHCN	$\longrightarrow \left( -CH_{2}-CH=CH-CH_{2}-\right) x -CH_{2}-CH - \left  \begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$

About 25 per cent of acrylonitrile and 75 per cent of butadiene are used in the polymerization process. Higher amounts of the nitrile increase oil resistance, but brittleness at low temperature is adversely affected. The polymer during the early stages of the polymerization is oil-like in nature, and the polymerization as in the case of Buna S must be stopped at an optimum conversion in order to prevent the product from becoming too hard and tough, which it will, if the conversion is allowed to proceed too far. Polymerization modifiers are used as in the Buna S synthesis. It is indicated in Table 4 that the butadiene polymerizes by 1,4-addition. How-

Perbunan is a highly oil-resistant type of rubber. It has good to excellent resistance to abrasion, tear, cold and hot flow, aging, and gas diffusion; but its resistance to checking in sunlight is only fair. Like all synthetics it generates appreciable heat through hysteresis. However, it can be used at higher temperature levels than natural rubber. Due to its oil resistance, it is used in hose for transferring hydrocarbons, in self sealing so-called bullet-proof gasoline tanks, and in many other applications where rubber comes in contact with oil.

ever, there is evidence that some 1,2-addition also occurs.

The copolymers of butadiene with acrylonitrile or with styrene are superior to the straight polybutadiene type of polymer. They are far more rubber-like, and possess better processability and tensile strength than their straight butadiene analog.

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# Neoprene

Neoprene is a polymer of chloroprene. It also is prepared by the emulsion technique.

TABLE 5 Preparation of Neoprene and Raw Materials			
Chloroprene	Des 7. In a paper of 1	Seller Die Algeragion-F	
1. 2HC=CH	H Cu <sub>2</sub> Cl <sub>2</sub> NH <sub>4</sub> Cl	-→CH₂=CHC=CH d c 20030600	
$CH_2 = CH$	IC=CH+HCI	$\rightarrow$ CICH <sub>2</sub> - CH = CH <sub>2</sub>	
ClCH <sub>2</sub> -0	$CH = C = CH_2$ Isomerization	$\rightarrow$ CH <sub>2</sub> = CH $-$ CCl = CH <sub>2</sub>	
Polymerization $xCH_2 = C$	$Cl - CH = CH_2$	$\rightarrow \left[ \begin{array}{c} -CH_{a} - C = CH - QH_{a} \\ Cl \end{array} \right]_{x}$	

Chloroprene is stated to polymerize 700 times as fast as isoprene. Since the polymer does not keep well in the raw state, it must be vulcanized within a reasonable time after preparation. The method of vulcanizing polychloroprene is quite different from that used with natural rubber and other synthetics discussed so far. Metallic oxides such as magnesium oxide are used in place of sulfur, although sulfur is stated to act as an accelerator for the vulcanization.

Neoprene is comparable to natural rubber in many respects and is superior in its resistance to the solvent action of petroleum products and natural oils. It possesses good to excellent resistance to abrasion, sunlight, aging, heat, and flames. Because of these properties, neoprene has found extensive use in hose for handling hydrocarbons, gasoline tank linings. cable coverings, water-resistant clothing, and oil-resistant electrical insuoptimum conversion in order to prevent the product from become noise

# Butyl Rubber bewalls at noisersynon out it fliw it doubt on bush

الدرر هدار

Butyl rubber as produced commercially today is a copolymer of iso-butylene and isoprene.

PREPARATION OF BUTYL RUBBER AND RAW MATERIALS

ant its resistance to checking

Isobutylene

 $Cracking of Petroleum Fractions \rightarrow (CH_a)_2 C = CH_2$ Isoprene anodesonit le used in alle for transferring hydrocarbons, service lin

Cracking of Petroleum Fractions

CH, Lie strive tions where rubber comes in the transfer of the solution of th Polymerization HCHCH2 -CH1-C=CH-CH4+  $x(CH_3)_2C = CH_2 + CH_2 = C - CH = CH_2 - CH_3 - CH_3$ ubber-like and massar her CH. INCOL SITAPPOL DEGREERC ADALOS

Which end of the isoprene unit is joined to the methylene group in the isobutylene unit is not known, but it is known that the isoprene polymerizes by 1,4-addition. No products of ozonolysis corresponding to an unsaturated side chain have been detected (5).

Butyl rubber is made by a continuous polymerization process which leads to the formation of a polymer of rather uniform molecular weight. The polymerization is effected below -100°F. This low temperature is necessary since higher temperatures lead to low molecular weight polymers, which lose their rubbery properties and eventually become oily in nature as the temperature is increased. The reaction, which is catalyzed by metallic halides of the Friedel-Crafts type, is extremely rapid.

Other diolefins such as butadiene, piperylene, dimethylbutadiene-2,3, etc., can be used in place of isoprene. Since a minor proportion of diolefin is used, the resulting polymer has only about 1 to 3 per cent of the unsaturation of natural rubber. In spite of this low unsaturation, the uncured polymer is susceptible to oxidation and must be protected with a stabilizer.

At any given reaction temperature the quantity of diolefin in the polymerization mixture affects the properties of the polymer. Unsaturation increases and molecular weight decreases as the diolefin content is increased.



FIGURE 1 EFFECT OF DIOLEFIN CONCENTRATION

Diolefin Concentration, Weight %

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The quantity of diolefin also affects the modulus, i.e., the "tightness," of the cured rubber. The greater the amount of diolefin in the polymer, the higher the modulus.



FIGURE 2 Modulus of Butyl Rubber (Tread Stock)

Butyl rubber is compounded and cured in much the same way as natural rubber, except that ultra-accelerators are required due to the low unsaturation. Butyl, Neoprene, and natural rubber are the only rubbers that possess a high pure gum tensile strength. All other well known synthetics have low gum tensiles and must be compounded with carbon black in order to realize useful properties. Both Butyl and Neoprene may be used either in pure gum or carbon black formulations.

Since Butyl is an all hydrocarbon polymer, it is not oil-resistant, being similar to the natural rubber in this respect. As a result of its low unsaturation, Butyl is quite resistant to chemicals such as mustard gas. Some modifications are resistant to strong inorganic acids and even to ozone.

An outstanding characteristic of Butyl is its impermeability to gases. Inner tubes made of Butyl are reported to retain their air pressure six to ten times as long as natural rubber. In a recent road test, natural rubber inner tubes lost air eight times as fast as Butyl inner tubes that were run in the same test. During the eleven weeks period covered by the test, the

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Cure in Minutes at 287° F. \* Per cent of Diolefin in the feed.

### SYNTHETIC RUBBER

former had to be reinflated approximately every two weeks, whereas the Butyl tubes did not require reinflation.

To date the major uses of Butyl rubber have been in inner tubes and in proof goods, i.e., impregnated fabrics. Part of the inner tube production of the United States is being rapidly converted to Butyl rubber, and total conversion is a possibility as soon as sufficient Butyl is available. Although Butyl does not fit into the present tire program, tires have been built of Butyl that have run up to 25,000 miles at speeds not in excess of 40 miles per hour. No natural rubber was used in the construction of these tires.

# Thiokol

Thiokol is the reaction product of sodium tetrosulfide and adihalide such as ethylene dichloride or B,B'-dichlorodiethyl ether. The polymer, although it contains no olefinic linkages, can be cured with metallic oxides such as zinc oxide. This type of synthetic rubber possesses excellent oil resistance. As a result, it is used in hose for handling petroleum products and in gaskets.

# Norepol

A new type of synthetic rubber called Norepol has recently been developed. Commercial varieties under the trade names of Agripol (6) and Vulprene (7) have been introduced on a limited scale. Oils of the non-mineral type, such as soybean oil, furnish the basic material used in the synthesis of this type of rubber. By special methods, the unsaturated fatty acids can be isolated from these oils. They are converted to polymers which have the properties of dibasic acids. These dibasic acids freed essentially of monomeric acids (6) are esterified with dihydric alcohols to form high molecular weight products which are capable of being vulcanized (7).

The commercial varieties have tensile strengths of the order of 400 to 1200 pounds per square inch. Norepol itself, when prepared from purified fatty acids, possesses tensile strengths in the range of 1000 to 2000 pounds. The future commercial possibilities of this type of rubber are as yet unknown. It has been reported that the biggest single use for Agripol is in gaskets for food closures (6).

No attempt has been made in this paper to list all the uses of any given type of synthetic rubber. In fact, in most cases, only a few typical uses have been indicated. Since there are modifications of each type of synthetic rubber and since properties can be further modified by compounding, it should be realized that the properties listed are not all-inclusive. Other types of vulcanizable polymers also are known, and many more varieties probably will be made.

It has been estimated that the world's production of synthetic rubber at the end of the war will be 1,200,000 tons per annum (3). This is probably a conservative figure, since it is estimated that the United States and Canadian production will reach a figure of 1,145,000 tons. The Russian and German productions are unknown. What the future of synthetic rubber will be after the war, as far as volume of production is concerned, is unknown at the present time. However, present trends indicate that synthetic rubber is here to stay and that selected types excel natural rubber for specific uses.

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