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REPORT OF THE AD HOC COMMITTEE ON PRINCIPLES OF RESEARCH-ENGINEERING INTERACTION

MATERIALS ADVISORY BOARD

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Under a contract between the Office of the Secretary of Defense and the National Academy of Sciences, the Board's present assignment is

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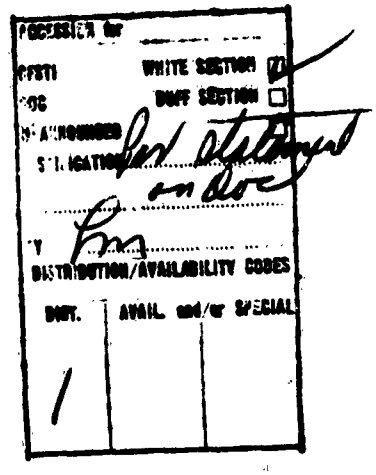
Report of the

AD HOC COMMITTEE ON PRINCIPLES OF RESEARCH-ENGINEERING INTERACTION



Prepared By The

MATERIALS ADVISORY BOARD

Division of Engineering

National Research Council

as a service of

The National Academy of Sciences

to the

Office of Defense Research and Engineering

Department of Defense

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This report completes a study undertaken by the Materials Advisory Board for the National Academy of Sciences in execution of work under ARPA Contract No. SD-118 between the Department of Defense and the National Academy of Sciences.

No portion of this report may be published without prior approval of the contracting agency.

MAB-222-M

REPORT OF THE AD HOC COMMITTEE ON PRINCIPLES OF RESEARCH-ENGINEERING INTERACTION

ERRATA

Page following p. 38 should have been numbered "A-1"

Page following p. A-14 should have been numbered "B-1"

Page B-18 is blank. No text has been omitted.

Page C-1. "Frequency of Factors Considered in REIs" appears on Page C-15.

Page G-11 should read as follows: "6. Motivation and Morale"

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FOREWORD

This is not a technical report in the usual sense. It is instead a study of the events which lead up to and surround technical accomplishment. In this respect it represents a first effort of this type by the Materials Advisory Board. As in most first efforts the reader will discover many weaknesses. However, also, as in the case of some first efforts, there may be the germ of some new realization. It was in this hope that the effort was first conceived and subsequently pursued.

The report consists of two principal parts. Part I is a summary of the background, chronology, findings, and recommendation of our study. These are based on the content of Part II which consists of the case histories prepared by the Committee members. In the authors' minds, however, the case histories themselves may well be the most valuable contribution of the Committee's efforts.

The case histories record a number of selected events in the development of materials. Each history has been written as an individual effort of a member of the Committee. The subject of the history was also selected by the individual author. Frequently the events described involve the author in some peripheral way. Thus, the histories are sometimes highly personalized. For that reason, in spite of the efforts to be objective and complete, the histories undoubtedly contain weaknesses that reflect the position and imperfections of the authors.

Similarly, the findings in Part I of the report must be suspect to the same degree. Nevertheless, the Committee supports the findings and recommends their consideration. The single fact that certain elements stand out in spite of the wide variety of histories which we have explored encourages us to believe that the historical approach has value. Although we must deny that we have determined <u>sufficient</u> conditions for assuring optimum research-engineering interactions, we believe that the cases do suggest <u>necessary</u> conditions that must be considered.

ABSTRACT

The evolution of ten separate material developments were investigated and case histories are presented.

A technique of analysis was developed and applied to the case histories to identify common elements and patterns which might be used as guides by the Department of Defense to stimulate research-engineering interactions in the solution of materials problems. The analysis identified several elements which were prominent in many of the cases. Among these are:

1. Flexibility for the individual investigators to make major changes in direction and goals was frequently required.
2. Close and frequent communications between organizationally independent groups were often essential.
3. Key individuals played essential roles in bridging the geographical, organizational, and functional barriers between groups.
4. The recognition of an important need was most frequently the principal factor in stimulating research-engineering interactions.
5. Often technical approaches were available and lay dormant for some time before their pertinence to a specific need was recognized.

It is recommended that these findings be considered in future materials research and engineering efforts of the Department of Defense. In addition, the value of the case history approach as an educational tool is emphasized and suggested for further consideration. A series of questions is developed to aid further self study by research and development organizations. Finally, the need for more effective tools of case history analysis is identified.

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PART II

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By J. J. Harwood B-1

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PART I

Background, Chronology, Findings, and Recommendations

BACKGROUND

Introduction

Man's progress, social as well as technological, is highlighted by certain signal occurrences that mark milestones and occasionally turning points in his development. Generally, these are not spontaneous but mark the culmination of forces and directions whose roots can be traced back to periods long before the actual occurrence. Nevertheless, in historical retrospect, the occurrences themselves appear as pinnacles and valleys which rise and fall abruptly from the more gradually ascending slope of man's advance.

This report is a study of a number of selected accomplishments in the recent history of materials science and technology. At the request of the Department of Defense we have tried to trace the historical forces and directions that surrounded the events leading to these accomplishments. Our objective was to define the circumstances which encourage the application of scientific knowledge to materials development and utilization. This is an exceedingly ambitious objective. A principal motivation for most historical studies is to define the causes of past events to permit a more rational control of future events. Our success in the social and political sphere should temper our expectations of the present study.

In his letter of January 5, 1965, the Assistant Director (Materials) of Defense Research and Engineering asked the Materials Advisory Board to undertake a study of research-engineering interactions that would be addressed to three tasks. These were:

1. Study of representative examples of research-engineering interaction, both in industry and the Department of Defense with a view to extracting common denominators, or clues, resulting in success or failure.

2. Selection from among those principles or techniques that have usually led to success, those most appropriate for adoption by the Department of Defense.

3. Recommendations to the Department of Defense regarding appropriate action leading to the enhancement of the transfer of research to hardware.

In responding to this request, the Committee on Research-Engineering Interaction agreed to study and document the history of several developments where new material possibilities depended upon the interaction of fundamental knowledge with the recognition of a practical need.

The Committee also commented upon some expected limitations of this study. First, as the Committee was comprised principally of scientists and engineers, it was expected that the histories might well be incomplete in detail and somewhat lacking in thorough documentation. However, we did begin with the sanguine hope that our studies would at least provide a basis for evaluation of this approach to the clarification of the problems of research-engineering interactions.

Second, it was not clear at the beginning whether our studies would indeed lead to a coherent pattern that would permit the analysis required by parts two and three of the original charge. Indeed we have discovered that our cases are very heterogeneous. This heterogeneity undoubtedly results from many factors including the method of selection of subject and the approaches of the Committee members as "amateur historians."

However, we also suspect that this heterogeneity may be characteristic of the process which we are studying--that research-engineering interactions are in the final analysis human-human interactions and will therefore show the inherent heterogeneity of human personality.

Nevertheless, we have made an attempt to develop, if not a pattern, at least a form which circumscribes the most critical events in our cases. This form and its possible pertinence to the research and development

efforts of the Department of Defense are presented in the "General Findings" part of this section. However, in order to understand the basis upon which this form rests, we believe it essential that the reader appreciate the method in which the study was organized and pursued. This is described below.

Organization of the Study

The study was organized on the following assumptions:

1. The cases should sample broadly the various areas of materials activity including metals, organic materials, inorganic nonmetallics, structural materials, electronic materials, etc. They should also cover work originally stimulated by both commercial and defense needs and performed in a wide variety of institutions. In this way we might hope to avoid any monolithic bias.

2. It was decided that the case writers should be technical specialists. Thus, the form, structure, and rigor of the cases are quite different from what they would be if the writers had been professional historians or professional case writers. It was felt that the technical approach was much more natural as a first effort by the Materials Advisory Board. Furthermore, many of the items selected involved proprietary areas which we suspected could be best probed by an "insider." This generally restricted the choice to a technical specialist. Finally, the time and funds that would be required for a truly professional historical case viewpoint did not seem justified for this first effort.

3. There was no attempt to set a rigid framework for style and attack. A first meeting of the panel addressed itself to that subject. It was concluded that the only feasible approach was to leave the style and method of approach to each individual author, having once agreed upon our general objectives.

4. A more rigid framework was adopted for the analysis of the cases. This is discussed later. Even here it was necessary to relax this rigor somewhat as the analysis proceeded because of semantic difficulties. However, the framework that remained was worthwhile in that it directed further refinements of the case histories.

The final results reflect these assumptions. The cases are heterogeneous in style, in depth of detail, in form, and even somewhat in semantic criteria. They are uniform principally in method of approach. They began with a known materials achievement that the author believed was the result of a research-engineering interaction. Then, by personal interview of the principals involved, each author attempted to document the events which occurred in order to define the circumstances and the environment in which the critical interactions took place. The final result in some cases is a relatively impersonal recounting of events and apparent motivations. In other cases, a much more personalized and individualistic description of events, frustrations, and accomplishments is presented. In every case we have attempted to be as accurate as possible in documentation of the people involved and the location of the events so that if further study is desired this report can serve as a starting point. However, the future scholar must be warned that, although the data that are presented are accurate to the best of the ability of the authors, they are by no means exhaustive. There are undoubtedly many significant events and individuals involved that were omitted by accident or by the necessary limitations of the study.

CHRONOLOGY

Chronology of the Study

The membership of the Committee was assembled in the following way. The Chairman in consultation with the Materials Advisory Board concluded that the Committee would try to investigate five segments of the broad field of materials. These were:

1. Metallic materials (structural and mechanical properties)

2. Organic materials (structural and mechanical properties)

3. Inorganic nonmetallic materials (structural and mechanical properties)

4. Electronic materials

5. Nuclear materials (It was necessary to delete this subject area before the study was well under way.)

The Chairman then selected a Committee member for each area and requested that each of them select one colleague to work with him in the assigned subject area. In addition, liaison members from the Department of Defense were asked to distribute themselves voluntarily among the subject areas. Then each of the Committee members (including the liaison members) was asked to define and choose a subject for a case history in his respective area which he believed would be suitable as a basis for studying research-engineering interactions. It would then be the responsibility for this individual member to investigate and develop a complete case history of the subject which he had selected.

In addition to the technical "historians," the Committee was fortunate in obtaining the participation of two experts in the case history approach. Professors Charles D. Orth, 3rd, and James R. Bright of the Harvard Graduate School of Business Administration provided invaluable guidance to us with regard to our individual approaches and problems. However, in the final analysis, the individual authors of the enclosed case histories take full responsibility for the limitations of their work, which arose in spite of the best efforts of our consultants.

The first meeting of the Committee was held on March 19, 1965. The entire day was devoted to a discussion of our broad objectives, a broad outline of the general method of approach, and a group discussion and comment

on the specific subjects which individual members of the Committee suggested for study.

Following this meeting the case work began on an individual basis. However, a second meeting was held on May 13, 1965. At this time, some of the Committee members presented a trial run of the cases in their initial crude form. This discussion of actual cases helped the Committee anticipate problems that would be encountered. Following this, first drafts of all the cases were prepared and circulated to all Committee members just prior to the major working meeting of the Committee which was held July 19-22, 1965. This meeting was one of the most important events of the study. During the meeting the first draft of each case was discussed in depth and an attempt was made to develop a general format which could serve as a basis to analyze each case defining its critical aspects and developing a pattern which would characterize the bulk of the critical interactions.

We soon discovered that each case was much more complex than the author had originally thought. In several instances it was necessary to divide a case into several sub-cases, each with its distinct chronology of events. Furthermore, it became clear that each sub-case involved a number of "critical events" and that as the case proceeded from original conception through to final accomplishment a whole series of important research-engineering interactions could be identified. The principal result of these discussions was the generation of a format into which the bulk of the cases could be fitted. This provided both a method for final analysis and comparison of the cases, as well as a means for identifying where essential information was missing from each case in order to aid the author to continue and complete his study.

The remainder of 1965 was spent by the individual authors in the completion of their case histories and their analyses. In the course of doing

this, further weaknesses of the pattern which had been developed during the summer meeting were discovered and discussed by correspondence. The final working meeting of the Committee was held on April 26-27, 1966. By this time each of the Committee members had had an opportunity to read the final case drafts and the individual case analyses. During this final working meeting the analyses were summarized in terms of general findings and these findings were examined with regard to their significance to the Department of Defense.

Form of the Case Analysis

As indicated above, it was discovered that several of the cases which were originally selected on inspection turned out to consist of several sub-cases. It rapidly became clear that a single research-engineering interaction (REI) might soon lead to the development of a number of somewhat diverging explorations, each of which exploited a particular result of the original interaction. Thus, in most cases, the starting point of our study corresponds to the sprouting of a family tree of material developments and the sub-cases represent branches of important results from the original primary trunk.

As each of these principal branches or sub-cases was documented, it was discovered that the events occurred at various stages of the research and development process. These stages were defined as follows:

0. Scientific findings.
1. Recognition of new material (or process) possibility.
2. Creation of new useful material (or process) form.
3. Demonstration of the feasibility of using the material (or process) in a specific equipment (or product).
4. Demonstration of a possibility of using the equipment (or product) in a system (or second product).
5. Production of the system (or product).
6. Operation (or use) of the system (or product).

The chronology of a sub-case through these stages is often tortuous. For example, it was discovered that in order to proceed from stage three to stage four it might be necessary to retreat all the way back to stage zero and proceed along another path. On the other hand, in some instances havin arduously reached a particular stage of development the succeeding few stages might follow almost automatically.

Finally, in the progression through these stages many important events occurred which did not involve research-engineering interactions in the author's definition. They might, for example, simply require the application of a well-developed engineering technique to a particular material without the necessity for any significant alteration in the technique. In the analysis of each case the author has attempted to identify only those events which qualify in his own individual definition of a research-engineering interaction.

We emphasize the phrase "individual definition of a research-engineerir interaction." Definitions of the words "research" and "engineering" have served as the subject of many treatises. In general, we have attempted to use the National Science Foundation's official definition of basic research, namely:

> "Basic research is directed toward increase of knowledge in science. It is research in which the primary aim of the investigator is a fuller knowledge and understanding of the subject under study rather than a practical application thereof."

As a definition of the word "engineering" we have considered the National Science Foundation's definitions for applied research and development.

> "Applied research is research which is directed toward practical application of science.
>
> "Development builds on the findings of basic and applied research and leads to specific achievements in diverse areas such as industrial

production, medical care, military defense and public safety."

We have interpreted these definitions to include the kind of engineering work that is often involved in the initial stages of operation of a final system or general distribution and use of a finished product. However, even within the scope of these definitions there is still considerable room for individual judgment. Although we have discussed these individual judgments in our collective meetings, the final operational definitions of "research" and of "engineering" reflect the judgment of the individual authors. Similarly, the definition of a "research-engineering interaction" often provides a compound problem in semantics and here again in final analysis the definitions are the responsibilities of the individual authors.

The final step of the analysis was to try to define the factors which characterized each of the research-engineering interactions. A list of some of the factors which were considered is contained in Appendix II. This list is reproduced not because it represents any consensus of the Committee on significant factors but rather to illustrate the range of factors that was discussed and considered.

It was here that our semantic problems became most apparent. It was our original hope that we could arrive at a set of principal factors and then determine at least semi-quantitatively the frequency with which these factors appeared to be of importance in all of the identified research-engineering interactions. Our several attempts to accomplish this resulted in a clear appreciation that we were not able to arrive at uniform standards which would permit us to have any confidence in such a semi-quantitative analysis. Instead we again settled for an individualistic appraisal of essential factors. Each author was asked to summarize each REI in his own words and to identify those factors which seemed most important to him in the research-engineering interactions which he identified. From this we were able to discover a limited number of important characteristics which seemed to be

present in a majority of the events. We were also able to agree upon a number of circumstances which appeared not to have any true statistical relevance, at least in the selected number of cases which we had studied. These considerations form the major part of our findings and also the basis upon which we have attempted to respond to the second and third charges in the letter from the Department of Defense.

FINDINGS

General Findings

The factors that are most commonly identified in the discussion of the cases can be classified into three main groups.

1. Characteristics of the environment in which the events took place, such as type of institution, its organisation and communication patterns, management involvement, nature of the support, organisational traditions, etc.

2. Characteristics of the individuals involved in the events, such as educational level, basic or applied training and interests, etc.

3. Characteristics of the problem itself, such as technical difficulties, the visible need for a solution, etc.

These findings are presented below and underlined for emphasis.

Characteristics of the Environment

Two of the three most commonly identified factors in the cases concerned the environment in which the events took place. One of these was related to the support of the activity. The second was related to the role of communications during the events.

In eight of the ten cases (A, B, C, D, G, H, I, J)* the authors observed that the flexibility of support was critical to the final success. In these cases the majority of the REI events required the ability to shift direction and explore unanticipated paths. This was readily done because the support was on a broad enough base to permit adequate discretion on the part of the investigators. In the remaining two cases (E, F) the flexibility of support was important in at least one of the critical events, though it was not identified in the majority of the events. In these cases it was most frequently identified as important in the REI events which occurred in the first three stages (0, 1, 2).

There were two kinds of flexibility which were identified. Most frequently an unanticipated change in direction of attack was required without any significant change in the over-all objectives of the work. However, in two of the cases (G, C) a fundamental change in the over-all objectives of the work occurred and the final result was strinkingly different from the original goals.

It is, however, necessary to qualify this finding in view of its relation to other findings of the study that are discussed below. Indeed, each of our separate findings must be considered in the context of all of the findings. Thus it is noted below that the recognition of a need characterized most of our cases. Therefore, the flexibility to which we refer above generally operated in an environment that was structured by the recognition of a need. This, of course, moderates the degree of flexibility which was exercised.

In nine of the ten cases (A, B, C, D, E, G, H, I, J) the majority of the identified events required close and frequent communications between organizationally independent groups. In many cases these groups were geographically separated and had different functional responsibilities (e.g., basic

* The key to the letter identification of the cases will be found at the beginning of Part II. It is also indicated in the Table of Contents.

research vs. development). In eight of the cases (B, C, D, E, F, G, H, I) geography was very infrequently cited as a significant factor. This latter finding at first seems at variance with the identified importance of communications. On the other hand, close examination of these latter cases showed that in every instance there were one or two key individuals who, through their efforts, bridged the geographical, organizational, and functional gaps; actively stimulated communications; and sometimes performed the technical work which was a vital part of the REI. These key individuals are the people whom we will refer to as "couplers."

Other environmental factors such as the role of management, the type of organization (government, commercial, university, nonprofit, etc.), organizational structure, research and development traditions, etc. are variously cited as important in about half of the total REI events. Thus one might conclude that in these cases these factors played important but not crucial roles. This observation is, of course, based upon an assumption that applies to the entire analysis; namely, that each of the events had the same significance to the over-all achievement. Indeed, it may well be that these factors played a crucial role in the most critical event in a given case. The present method of analysis would not identify that situation. Indeed in retrospect, the Committee has recognised that our study did not probe deeply into these other environmental factors. We recognize this as a major weakness in our efforts and we will refer to this later.

Characteristics of the Individual

Many of the cases include biographical sketches of, or comments about, the principal individuals who were involved in the critical events. In every case an individual with postgraduate (often doctoral) education was involved in at least one of the events. In about half of the cases (A, B, D, E, I, J) most of the events revolved about individuals with formal postgraduate academic training.

In only three of the cases (D, I, J) did the majority of events involve in any way some individual whose principal interests were in basic research as defined on page 10. However, if attention is restricted only to REIs in stages 0, 1, and 2 then in more than half of the events an interaction with basic research findings or a basic researcher was discovered to be important. This is not surprising since stages 3, 4, 5, and 6 are rather far down the development and engineering paths. In some cases a basic researcher was involved in the solution of problems in these later development stages, but this did not occur frequently.

In several cases an individual emerged whom we will define as a "champion." This is an individual who becomes intensely interested and involved with the over-all objectives and goals and who plays a dominant role in many of the REI events through some of the stages, overcoming technical and organizational obstacles and pulling the effort through to its final achievement by the sheer force of his will and energy. We have selected the word "champion" to indicate an individual whose extensive energies were focused upon a single goal with single-minded purpose. We do not intend any value judgment in the use of this term and leave such judgments to the reader in each individual case.

There are many other aspects of individual characteristics that might have been considered such as formal education in science vs. engineering, domestic vs. foreign background, age, professional experience, etc. No specific attempt was made to correlate these factors and they may provide a field for further study.

Characteristics of the Problem

One of the most enlightening aspects of the analyses was the manner in which the character of the problem itself appeared to affect the frequency and intensity of research-engineering interactions. In all but one (C) of the cases studied, the recognition of an important need was identified in a

majority of the events as an important factor in bringing about the research-engineering interaction. It was very rare that basic research by itself produced a new and unexpected opportunity which then stimulated a search for engineering application. By far the most dominant mode was the case where an urgent need stimulated a search for solution through prior basic knowledge This seems to substantiate the simile of research as a well of knowledge from which engineering can drink to satisfy defined needs rather than as a geyser which floods the engineer with solutions to present problems and with clear opportunities for exploitation.

This observation also qualifies the type of communication exchange which was discussed in the section on environment. In almost all of the cases under consideration, it was an individual with a well-defined need who was the initiator of the communications. It was most frequently he who began the dialogue with the basic researchers and determined its continuation until the need was satisfied. If this generalization is valid, then it is perhaps most important for the individual on the applications side to be able to look across the interface to basic research and know when to initiate the dialogue.

Of course, it is equally important for the individual on the basic research side to be able to hold up his end of the discussion. Furthermore, as evidenced in at least one of the cases (D), basic research often has implicit in it large new opportunities for exploitation, and if these can be recognized on the basic research side great advantage, particularly in timing, can be obtained. However, the specific cases which were studied do suggest that the initiative for research-engineering interactions is most likely to spring from the engineering side under the stimulus of a strong need.

Finally, although in all cases technical problems were enountered and overcome, in only four of the cases (B, E, I, J) did a majority of events

require the development of a new solution to a major technical problem. In many instances, it appeared that technical approaches were available but had not been pursued, and it was the act of timely recognition, bringing available knowledge tc bear on the problem, that resulted in the final solution. This leads to the suggestion that there is much knowledge in the well of research which has yet to be tested, tried, and applied in the solution of current critical problems.

The factors cited above have been emphasized because their presence or absence was particularly striking to the Committee in reviewing the case histories. It must be repeated that some of the cases emphasized additonal factors and that there are many factors which might have been of critical importance but which the limitations of our study did not permit us to investigate. We stress again that it is particularly dangerous to draw broad generalizations based upon these very imperfect analyses. We must repeat that a principal characteristic of this study has been the large heterogeneity of the environments, personalities and problems which fill our case histories. We believe that the greatest benefits are to be derived by a study of the individual cases themselves and by the individual analysis of this report by each reader.

We believe that perhaps the most important factor which we have documented is that research-engineering interactions take place within varying structures of organization and involve complex human events which require deeper and more thorough study than the present one before generalisations can be established.

RECOMMENDATIONS

The Committee found great difficulty in addressing itself to charges two and three of the letter from the Department of Defense. Although we believe that we can support the general findings of the preceding section, we feel unqualified to select those findings "most appropriate for adoption by the Department of Defense." We also feel unqualified to make specific "recommendations to the Department of Defense regarding appropriate action leading to the enhancement of the transfer of research to hardware." Even within the somewhat limited knowledge of the Committee members, we are keenly aware of the broad spectrum of organizations, missions, practices, and problems that exist within the DOD. We believe that formulation of recommendations addressed to specific situations would require individual analysis, for each situation, within the framework of our general findings. Broad, general recommendations would have little operational value. Such a detailed and special analysis, organization by organization, would be a major undertaking outside the scope of our present Committee. At the same time, we have developed a strong belief that there is information in our cases and in our findings which could be of great value. Thus, we have considered how we could most effectively aid the Department of Defense in using the results of our study. We have arrived at three suggestions.

First, the Committee discovered during the generation of our case histories and our discussions and analysis of them that there was a pattern of questions which formed and was exceedingly valuable to us in attempting to define and understand the circumstances which surround our cases. As our data accumulated and the general findings emerged, we were able to formulate additional questions which provided more useful insight. These questions applied both to the technical events and to the environments in which they took place. We have formulated a list of the questions which

seemed most pertinent and helpful to us. This list is in Appendix I. We recommend this list to the reader. We suggest that he experiment by asking himself these questions and by encouraging others around him to the same exercise. We have found this to be an enlightening experience. We are certain that the reader will identify other questions which should be asked and which will strengthen this exercise. We believe that this approach can provide a valuable tool to aid each of the DOD organizations in evaluating the factors that influence research-engineering interactions in their areas of responsibility and to highlight obstacles to these interactions if they exist.

Second, the Committee is convinced that we, as individuals, have been by far the greatest beneficiaries of the studies which have led to this report. The generation and discussion of these cases was an intensive learning experience. We recommend this experience to managers and participants in research and engineering in the Department of Defense and their contractors. The tools of analysis which we developed are imperfect but useful. The questions which we have suggested may serve as other useful tools. Case histories have been used classically as a medium for discussion and as a tool for self-enlightenment and self-examination. Our experiences in this study reinforce their value for this purpose.

Third, as we have emphasized several times, our ability to accumulate all the pertinent facts relevant to our cases and to analyse them in the depth which they might merit has been greatly limited by our inexperience, by our lack of training in case writing, and by the inevitable restrictions of time. We have mentioned many factors which we suspect may be important, but which we were unable to probe. We believe that there is more value in the case history approach than we have been able to capture. For example, the development of more useful tools of analysis would be extremely important in implementing the second suggestion. Therefore, the Committee believes that a broader and more professional attack on this problem should

be considered. We would suggest particular emphasis on cases which involve areas of special interest to DOD. Our cases are monolithic in that they treat only subjects which were eventually crowned with success. Much might be learned by studying other selected subject areas involving research and engineering programs which never reached practical fruition. The Committee recommends that these possibilities be considered.

APPENDIX I

The following list of questions has been generated as a tool to stimulate discussion and examination of how research-engineering interactions occur in an organization. They have been derived through the experience of the Committee in analyzing the case histories and relate to the general findings of the report.

It is suggested that these questions be asked by managers, of themselves, at all levels in research, development, and engineering organizations. The Committee suggests that the answers offered by nonsupervisory scientists and engineers would also be enlightening.

QUESTIONS

1. HOW MUCH FLEXIBILITY IS AVAILABLE IN LEVEL AND ALLOCATION OF FUNDING AND SUPPORT TO THE MEMBERS OF THE TECHNICAL STAFF REPORTING TO YOU? HOW MUCH FLEXIBILITY DO YOU HAVE? HOW MUCH FLEXIBILITY DO YOUR CONTRACTORS HAVE?

a) What approvals are needed to change the level and allocation of funding?

b) What are the mechanisms to change the level and allocation? How complex are the mechanisms? What time interval is usually required?

c) What is the effect of your organization's structure and controls on these mechanisms? Do they inhibit or stimulate change?

d) What is the balance in your organization between flexibility and the need for control?

e) What are the penalties and rewards involved for those who make the sometimes risky decisions to change the levels of funding and support? List some examples.

2. HOW MUCH FLEXIBILITY IS AVAILABLE TO THOSE REPORTING TO YOU WITH RESPECT TO CHANGING DIRECTIONS AND GOALS? HOW MUCH FLEXIBILITY DO YOU HAVE? HOW MUCH FLEXIBILITY DO YOUR CONTRACTORS HAVE?

a) What approvals are needed to change directions and goals?

b) What are the mechanisms for changing directions and goals? How complex are the mechanisms? What time intervals are usually required?

c) What is the effect of your organization's structure and controls on these mechanisms? Do they inhibit or stimulate change?

d) What is the balance between flexibility in this area and the need for control?

e) What are the penalties and rewards involved for those who make the sometimes risky decisions to change direction and goals. List some examples.

3. HOW MUCH FLEXIBILITY IS AVAILABLE TO THOSE REPORTING TO YOU IN STARTING (INITIATING, FUNDING, AND ACTUALLY BEGINNING WORK ON) NEW PROJECTS OR TERMINATING EXISTING PROJECTS? HOW MUCH FLEXIBILITY DO YOU HAVE? HOW MUCH FLEXIBILITY DO YOUR CONTRACTORS HAVE?

a) What approvals are needed to start new projects or terminate existing ones?

b) What are the mechanisms? How complex are the mechanisms? What time intervals are usually required?

c) What is the effect of your organization's structure and controls on these mechanisms? Do they inhibit or stimulate initiation or terminating actions?

d) What is the balance between flexibility in this area and the need for control?

e) What are the penalties and rewards involved for those who make the sometimes risky decisions to initiate or terminate projects? Give some examples.

4. DOES EACH INDIVIDUAL IN YOUR ORGANIZATION CLEARLY UNDERSTAND THE FLEXIBILITIES AND LIMITS DESCRIBED ABOVE WHICH ARE AVAILABLE TO HIM AND THE MECHANISMS, BALANCES, PENALTIES, AND REWARDS THAT ARE INVOLVED?

5. HOW DOES THE DISTRIBUTION OF TECHNICAL EFFORT (i.e., IN-HOUSE, CONTRACT, SUBCONTRACT) AFFECT YOUR FLEXIBILITY? HOW CAN THE BALANCE OF DISTRIBUTION BE CHANGED?

a) What approvals are needed to change the balance?

b) What are the mechanisms for changing the balance. How complex are the mechanisms? What time intervals are usually required?

c) What is the effect of your organization's structure and controls on these mechanisms? Do they inhibit or stimulate change?

d) What is the balance between flexibility in changing distribution and the need for control?

e) What are the penalties and rewards involved for those who make the sometimes risky decision to change the distribution of effort? Give some examples.

6. HOW FAR CAN THOSE REPORTING TO YOU CARRY THEIR WORK THROUGH THE RESEARCH-DEVELOPMENT STAGES? (SEE PAGE 9) WHAT ARE THE RESTRICTIONS ON THE DIRECTIONS IN WHICH THEY CAN WORK? WHAT RESTRICTIONS DO YOU HAVE? WHAT RESTRICTIONS DO YOUR CONTRACTORS HAVE?

a) To what degree does the formal mission of your organization affect the stages and directions in which you can work?

b) What are the mechanisms by which you can overcome the limitations? How time consuming are the mechanisms? How complex are they?

c) How can you influence other groups to carry your work forward? To support your work? How time consuming are these mechanisms? How complex are they?

7. ARE FREQUENT COMMUNICATIONS BETWEEN YOUR GROUP AND OTHER GROUPS NEEDED? WHAT ARE THE SPECIFIC GROUPS WITH WHICH SUCH COMMUNICATIONS ARE NEEDED? IN WHICH OF THE RESEARCH-DEVELOPMENT STAGES (SEE PAGE 9) DO THEY WORK?

8. WHAT FORMAL MECHANISMS EXIST TO ASSURE ADEQUATE COMMUNICATIONS BETWEEN YOUR GROUP AND OTHERS?

9. CAN YOU IDENTIFY THE "INFORMAL" OR "UNOFFICIAL" STRUCTURES OR MECHANISMS WHICH SERVE TO COMMUNICATE BETWEEN YOUR GROUP AND OTHERS? WHAT ARE THEY?

10. WHAT BARRIERS (ORGANIZATIONAL: SUCH SOCIAL ASPECTS AS STATUS DIFFERENCES, CLIQUES, MILITARY-CIVILIAN, FUNDING, ETC.) EXIST WHICH MAY INHIBIT COMMUNICATIONS BETWEEN YOUR GROUP AND OTHERS?

11. WHAT HAS BEEN DONE IN YOUR ORGANIZATION TO ENHANCE COMMUNICATIONS

12. WHO ARE THE INDIVIDUALS IN YOUR ORGANIZATION WHO HAVE ACTED AS COUPLERS? (SEE DEFINITION ON PAGE 14.)

a) *How do organizational factors affect the way these people function as couplers?*

b) *Do you give specific recognition to the coupling function?*

c) *Do you have special programs to develop coupling skills?*

13. WHERE AND WHO ARE THE PEOPLE IN YOUR ORGANIZATION UPON WHOM YOU RELY TO ACCOMPLISH THE TRANSITION BETWEEN RESEARCH FINDINGS AND ENGINEERING PRACTICE?

a) *How do your applied research people communicate with people working in relevant areas of fundamental research and with people who have end-item responsibilities?*

b) *How do your basic research people stay abreast of relevant applied research and with DOD needs?*

c) *How do those with end-item responsibilities stay abreast of relevant applied and fundamental research?*

d) How do each of these kinds of people remain current in their own specialties?

14. WHO ARE THE PEOPLE WHO HAVE BEEN "CHAMPIONS" (SEE PAGE 15) IN YOUR ORGANIZATION?

a) What kinds of barriers did they have to overcome? Do the barriers still exist? How were they overcome?

b) How was the "champion" rewarded? What is his role today?

c) What effect did he have on the organization?

15. ARE THE MISSION, GOALS, AND LONG-RANGE OBJECTIVES OF YCUR ORGANIZATION CLEARLY DEFINED?

a) Are they defined by a technical or administrative part of the organization?

b) What specific role do you play in defining the mission, goals, and long range objectives? What role do the people who work for you play?

c) Do the people who report to you have a full understanding and perspective of the mission, goals, and long-range objectives? How is this achieved? Upon whom do you depend for this understanding and perspective? Do your contractors have this understanding and perspective? How is this achieved?

d) How much of the work performed by your organization clearly conforms to the defined mission, goals, and long-range objectives? How much deviation, if any, is permitted? Who decides?

16. DOES YOUR ORGANIZATION HAVE A COMMITMENT TO THE DESIRABILITY OR NECESSITY FOR RESEARCH-ENGINEERING INTERACTION? IF THIS COMMITMENT EXISTS, WHAT DO YOU DO TO MAKE IT VISIBLE?

17. WITH WHAT FREQUENCY DO INDIVIDUALS TRANSFER BETWEEN BASIC RESEARCH GROUPS, APPLIED RESEARCH GROUPS, AND ENGINEERING GROUPS?

a) Do transfers occur in both directions?

b) Do transfers occur between line and staff organizations?

c) Who are some of the people who have transferred?

d) Is there any correlation between individuals who transfer and individuals who participated in events which you would define as research-engineering interactions?

18. WHAT IS THE DISTRIBUTION OF FORMAL EDUCATION IN THE VARIOUS PARTS OF YOUR ORGANIZATION?

a) What formal educational background is required for the assigned responsibilities of the various parts of your organization? How closely does your present staff match these requirements?

b) How does it match between groups whom you expect to communicate and interact with each other?

c) Does the distribution foster or impede communication?

19. WHO DEFINES THE SPECIFIC NEEDS TO WHICH YOUR ORGANIZATION IS EXPECTED TO RESPOND?

a) Are the needs defined by a technical or administrative part of the organization?

b) What specific role do you play in defining the needs? What role do the people who work for you play? What role do your contractors play?

c) *Are there formal mechanisms by which the various parts of your organization contribute to the definition of these needs?*

20. HOW WELL SPECIFIED ARE THE NEEDS TO WHICH YOUR ORGANIZATION IS EXPECTED TO RESPOND?

a) *Are they specified in detail or only broadly?*

b) *What is the usual time interval between the definition of a need and its expected satisfaction?*

c) *When needs are specified, are approaches usually suggested?*

d) *Are the needs always within your understanding of your mission? Can you identify needs which were not?*

e) *In the past, how reliable has been the definition of the needs with which you have been presented?*

21. HOW ARE NEEDS COMMUNICATED TO YOU?

a) *Are there formal mechanisms for presenting needs?*

b) *Are there formal mechanisms by which you can react and comment on the needs as originally defined?*

c) *What is the usual time interval between the identification of a need and the actual start of the required work?*

22. ARE NEEDS OFTEN PRESENTED TO YOU FOR WHICH YOU HAVE AN IMMEDIATE ANSWER?

a) *In such specific cases did the answer come from broad general programs in your area or from specific programs originated to satisfy other needs?*

b) Have you had difficulties in selling answers once they have been obtained? If such difficulties exist, can you recognize any common causes?

23. ARE THE PRINCIPAL NEEDS FOR WHICH YOUR ORGANIZATION IS RESPONSIBLE CLEARLY UNDERSTOOD BY ALL THE PEOPLE IN THE ORGANIZATION?

a) What are the mechanisms by which the members of your organization learn about new needs?

b) What is the usual time interval between the definition of a new need and each member's awareness of it?

24. IN THOSE INSTANCES WHERE YOU HAVE USED THE FINDINGS OF BASIC RESEARCH TO HELP SATISFY A CURRENT NEED, WHEN WAS THE PERTINENT BASIC RESEARCH PERFORMED?

a) If the research was relatively old, why do you think it had not been applied earlier?

b) What was the mechanism by which it was now applied?

APPENDIX II

FACTORS CONSIDERED IN ANALYZING EVENTS OF RESEARCH-ENGINEERING INTERACTION

1. High educational level (advanced degree) of principal investigator
2. Importance of management
3. Importance of Government-sponsored research
4. Importance of recognized need
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources)
6. Industrial laboratory involved
7. Basic research in the laboratory (or institution or organization)
8. Communications across organizations was important
9. Technical problem was the principal obstacle
10. Importance of a "champion"
11. Freedom for individuals
12. Broad spectrum of types of laboratories
13. Geographic proximity
14. Prior experience with innovation
15. Organisational structure (barriers and bonds)

PART II

Case Histories

KEY TO LETTER DESIGNATIONS FOR CASE HISTORIES

Metallic Materials

A.	Cemented Titanium Carbide	R. S. Davis
B.	Lockalloy	J. J. Harwood

Organic Materials

C.	Polysulfide Polymers	E. M. Fettes
D.	Polysilicones	T. G. Fox
E.	Polybenzimidazoles	W. E. Gibbs
F.	Antiozonants for SBR Rubber	M. P. Marks

Inorganic Non-Metallic Materials

G.	Pyroceram® Brand Glass-Ceramics	M. G. Britton
H.	Missile-Grade Graphite	E. M. Glass

Electronic Materials

I.	Lodex® Magnets	R. H. Pry
J.	Superconductors for High Magnetic Field Solenoids	M. Tanenbaum

A CASE HISTORY
OF
THE DEVELOPMENT OF CEMENTED TITANIUM CARBIDE CUTTING TOOLS
AT THE FORD MOTOR COMPANY

Prepared by

R. S. Davis

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A CASE STUDY

THE DEVELOPMENT OF CEMENTED TITANIUM CARBIDE CUTTING TOOLS AT THE FORD MOTOR COMPANY

The cermet system tungsten carbide-cobalt has developed wide application in industry, principally as cutting tools. The significant contribution of this material to the modern machine tool industry may be traced to its high hardness, strength and toughness, particularly at elevated temperatures. Advances in this field of technology have been confined to the evolutionary development of a range of compositions and microstructure within this system for a variety of applications. Recently, however, a competitive cermet system, titanium carbide-nickel-molybdenum has been developed which demonstrates a significant improvement as a cutting tool material for many applications; a better than four-fold improvement in life limited by wear in semifinish and finish machine cutting of steel, for example. This case centers on the events leading to the discovery, development and commercial realization of this cermet system.

The major reorganization of the Ford Motor Company undertaken after the second World War included the formation of a corporate research and development activity as an adjunct to corporate engineering. An organization structure based on field-oriented departments in physics, chemistry, engineering mechanics, metallurgy, etc., plus a department that was devoted to the development of gas turbine engines was adopted. This latter, project oriented, department represented a major activity in this laboratory during the early 1950's.

At the early period of the development of the laboratory the metallurgy group was small, including only one professional metallurgical engineer with previous Ford experience. Others in the group were new to Ford Motor Company. Dr. M. Humenik was the first member of the group to be trained in the field of ceramics. In this early period, the laboratory was in the process of developing and purchasing facilities and equipment required to carry out the research programs. The following factors contributed to Humenik's decision to undertake an extensive long range

research program in the field of ceramics.

1. The laboratory had considerable interest in gas turbines during the early 1950's. Materials impose a principal limitation on the development of an efficient gas turbine. This is particularly true for the case of a relatively low first cost turbine intended for use in motor transport. During this period there was an extensive interest in the potential of cermets for this application and a considerable investment of government Research and Development funds in this area.

2. When Humenik had started his thesis work at MIT during 1949, that Institution was heavily involved in the Oak Ridge NEPA (Nuclear Engine for the Propulsion of Aircraft) project. A sub-project was the development of cermets. Within this program Humenik selected as a thesis topic the wetting behavior of liquid metal-ceramic systems under the direction of Professor W. D. Kingery. He had developed a sessile drop technique[1] for measuring contact angles at elevated temperatures and had developed considerable insight into wetting phenomenon, as it was then understood[2]. At the same time he had been exposed to the work of Joseph Gurland and J. T. Norton on the role of the metallic phase in determining the properties of the WC-Co system[3]. A keen appreciation for the part that microstructure plays in determining the properties of these materials was therefore developed. All of this combined to suggest an approach to improving the properties of cermets designed for high temperature applications.

3. The Metallurgy Department had been assigned responsibility for a materials development program in support of the gas turbine effort.

Although the WC-Co system was obviously not suitable for gas turbine application, it was also recognized that this system did indeed embody many of the desirable properties that were strived for in cermets. The possibility of developing a cermet based on TiC, which has a relatively

low density, with a binder that would provide a significant resistance to oxidation, was attractive. The TiC-Ni system had been investigated but extensive grain growth occurred during the early stages of sintering[4]. The Gurland-Norton work had demonstrated the importance of a fine dispersion of the carbide in a thin c ntinuous metallic matrix. Humenik postulated that the grain growth in the TiC-Ni system was due to agglomeration of the carbide particles rather than solution and reprecipitation. He therefore focused on the wetting problem and set out to find a metallic binder that would completely wet TiC. To this end a sessile-drop apparatus was developed at Ford and wettability studies were started early in 1954.

The early work at MIT on the wetting of oxides with liquid metals had suggested that the addition of strong oxide formers improved wettability. Following this lead preparation of a series of binary alloys of nickel with elements ranging from the strong carbide formers like titanium to the weak carbide formers like molybdenum was undertaken. The early experiments starting at the top of the series were disappointing. However, before the experiments progressed to the bottom of the series a nickel liquid drop accidentally came in contact with a molybdenum radiation shield and completely wet the TiC, thus moving ahead by a few weeks the discovery that Mo added to Ni forms a liquid alloy that exhibits a zero contact angle with respect to TiC. The fine dispersion and insignificant grain growth characteristic of the WC-Co system were subsequently shown for the TiC-Ni-Mo system.

During the winter of 1954-55 Humenik and his co-workers undertook an intensive cermet development program concentrating on the TiC-Ni-Mo system. They measured impact resistance, bend strength and hardness. They solved a variety of problems in preparing specimens. Experiments to optimize composition and particle size with regard to final microstructure and properties were initiated. At about this time, the gas turbine project had progressed to a state of development where the possibility of introducing a cermet material was minimal. On the other hand the cemented

TiC material was showing hardnesses greater than those obtained in the WC-Co system, suggesting that it might be worthwhile to evaluate it for other applications such as a cutting material.

The Ford Motor Company has a development group in manufacturing staff that is organizationally separate from corporate engineering and, therefore, the laboratory. This group provides certain testing services as part of their function including machinability tests. During 1955, specimens of the newly developed TiC-Ni-Mo material were submitted for evaluation. The results indicated that the tool showed plastic deformation but that a considerable reduction in flank wear was experienced. Within three months the composition was modified to the point where the tools now demonstrated substantial potential for improvement over the existing commercial materials.

A three-year development program followed that clearly demonstrated the value of the material. Included was evaluation in production machining operations. Significant savings in tool costs, reduced downtime, and production efficiencies were established. During this period, the Manufacturing Development Office - Manufacturing Staff continued to provide laboratory machinability test data, and another Manufacturing Staff organization, the Design and Standards Office, was instrumental in carrying out the production machining tests.

Management felt that it was now appropriate to consider the commercial exploitation of the cemented TiC. Various possible approaches were reviewed and it was concluded that the greatest economic gain could be achieved by the immediate utilization of the TiC tools in the Company's manufacturing operations. The proposed strategy involved the manufacture of tools in Ford until arrangement of licenses with outside companies could be effected. Top management approved and authorized the investment necessary to develop the production facilities. Research Staff was directed to establish this facility since it had the necessary capability as well as an intense interest in a successful outcome.

A facility for producing cemented TiC cutting tools became operative in Research Staff during 1959 and Humenik undertook the task of introducing this material into the manufacturing operations of Ford directly from the laboratory. The following factors would seem to minimize the difficulty of introducing this innovation.

1. The laboratory had complete control of production of the product.
2. Ford had its own Carbide Fabrication Department which provided a means for distributing the tools and promoting their use in the manufacturing plants.
3. In general, the substitution of cemented TiC for cemented WC did not involve a major modification of the machine tools involved or the machining processes used, and its advantages could be readily demonstrated.
4. The unit cost of producing a small number of samples of a cermet for test was not exorbitant.

At present, cemented TiC has replaced a significant fraction of the WC used at Ford. Since the patent issued during 1961, outside firms have been licensed to manufacture for sale both to Ford and to the general market. This and related activities continues to be one of the major projects in Humenik's group, however, progress has not been as rapid as they would have liked. The following factors may have contributed to the difficulties experienced:

1. The automotive industry at this time was experiencing an unprecedented period of increasing production schedules which put great demands on manufacturing personnel.
2. The automotive industry is, of course, very cost conscious. However, in the short term, production schedules take precedence and the uncertainty associated with an innovation in a manufacturing process at least threatens their capacity to meet production commitments.
3. Suppliers of the competitive cemented WC maintain an active sales organization and provide technical service to their custo-

mers. It is difficult for a corporate research laboratory to gear-up to provide similar services.

4. The value of the cemented TiC cutting tools over the existing materials can only be demonstrated unequivocally in actual production. Production tests have to be carefully monitored and an extensive evaluation covering a diversity of manufacturing plants and operations requires a major effort.

From time to time, manufacturing operations are confronted with specific production problems. Humenik and his group have had, and continue to have, an opportunity to provide solutions to a number of machining problems within Ford, based on the use of cemented TiC cutting tools. It is the success achieved in these difficult operations that has been a major factor in generating the interest and enthusiasm of manufacturing personnel to adopt TiC tools on a broad scale.

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ANALYSIS
OF
CASE HISTORY
OF
THE DEVELOPMENT OF CEMENTED TITANIUM CARBIDE CUTTING TOOLS
AT THE FORD MOTOR COMPANY

DESCRIPTION OF RESEARCH-ENGINEERING INTERACTIONS (REIs)

REI	Description
a	A high temperature materials program initiated at the Ford Scientific Laboratory in support of Ford's turbine program and Humenik's interest in this field.
b	The recognition of the potential of the NiMo-TiC cermet for machine tool applications.
c	The initiation of a testing and development program to optimize the Cemented TiC for specific metal cutting applications.
d	The development of a pilot manufacturing operation in the laboratory.
e	Troubleshooting plant machining problems as a basis for introducing this new product.

STAGES AT WHICH REIs OCCURRED

Stage* No.	REI
0	a
1	b
2 and 3	c
5	d
4 and 6	e

*Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	Definition
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From its study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs. The statistical analysis of the frequency of these factors in this case is shown below.

Factor No.		REI a	b	c	d	e	Total
1.	High educational level (advanced degree) of principal investigator	x	x	x	x	x	5/5
2.	Importance of management	x		x	x	x	4/5
3.	Importance of Government-sponsored research	x					1/5
4.	Importance of recognized need	x		x	x	x	4/5
5.	Requirement of flexibility to change direction during work and local control of funds (easily available resources)	x	x	x	x	x	5/5
6.	Industrial laboratory involved	x	x	x	x	x	5/5
7.	Basic research in the laboratory (for inst. or org.)	x					1/5
8.	Communications across organizations was important	x	x	x		x	4/5
9.	Technical problem was the principal obstacle						0/0
10.	Importance of a "champion"	x	x	x	x	x	5/5
11.	Freedom for individuals	x	x	x	x	x	5/5
12.	Broad spectrum of types of laboratories	x					1/5
13.	Geographic proximity	x	x	x	x	x	5/5
14.	Prior experience with innovation				x	x	2/5
15.	Organizational structure (barriers and bonds)						0/5

SUMMARY ANALYSIS

This case is interesting in that a single individual played a central role in all phases, from the original research through to the introduction of the product to the manufacturing operations. In the one extreme he conducted an enlightened research program that led to the basic discovery and on the other hand he provided technical service to manufacturing as a basis for accelerating the introduction of his product. In every phase he received significant support from the management of the Ford Motor Company.

A CASE HISTORY
OF
THE DEVELOPMENT OF "LOCKALLOY" -- A Be-Al COMPOSITE ALLOY

Prepared by
J. J. Harwood

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A Case History

of

The Development of "Lockalloy" -- A Be-Al Composite Alloy

Introduction

Lockalloy is the trade name for a class of beryllium rich-aluminum alloys developed by the Lockheed Missiles & Space Company, a division of Lockheed Aircraft Corporation. While not yet in extensive commercial use, its properties of low density, high elastic modulus, good strength, good ductility and good fabrication characteristics have indicated considerable potential for structural applications in aerospace vehicles. Details about its composition, preparation and processing are still proprietary (patent applications by Lockheed have been filed) but the key feature of the alloy resides in its controlled microstructure thus providing the characteristics of rollability and ductility. Although it is not yet in any volume applications, Lockalloy represents an interesting case study for a number of reasons: its roots reside almost entirely in a readily identified materials need of aerospace vehicles; its exploitation was aggressively pursued by a consumer rather than a primary metal producer; commercialization was accomplished in approximately 3 years from date of conception, indicating the speed of transition from research to engineering practice which is possible by a properly funded, corporate supported, aggressive program of materials development; it provides interesting implications about the background value of DOD and other government supported materials research programs and the problems associated with materials R and D conducted under specific military system contracts.

Background

Historically, there has always existed a long-standing DOD objective for low-density, high modulus, high strength alloys for military aircraft and aerospace systems. The design of aircraft structural members, based upon buckling and rigidity parameters rather than merely tensile strength, made it evident that significant vehicle advances could be achieved if lightweight

alloys with higher modulus than aluminum were available. Prior to and during World War II some efforts were pursued along these lines, but more serious programs were initiated after World War II to accomplish these objectives, both in this country and abroad. It was recognized that normal metallurgical practice could only affect the modulus in a minor way, and in the period of 1946-1949 the Bureau of Aeronautics (Navy Dept.) sponsored research to increase the modulus of aluminum alloys by addition of beryllium. There is little mutual solid solubility of aluminum in beryllium. These programs resulted in the laboratory development of aluminum-beryllium alloys with a modulus as high as 20×10^6 psi, but these alloys were not well received by the aeronautical industry because of the low ductility as well as the lower strength properties than the commercially available high strength aluminum alloys. As a result of the limited receptivity for such alloys and the concern that sufficient supply of beryllium would not be available for structural alloys because of AEC needs for nuclear reactors, research activity along these lines ceased.

Because of its important use as a moderator in nuclear reactors, the AEC had launched a massive R and D program in the post World War II period for the production of beryllium in massive form and for the investigation of the properties of beryllium and its alloys. By the early 1950's, beryllium had achieved a status as a commercial material with singular importance for the atomic energy program. Practically all of the beryllium produced was channeled for AEC utilization. Although Be was being produced in substantial quantity and in massive form and although Be exhibited the unusual combination of lightweight and high modulus, several important features precluded its serious consideration for major non-nuclear applications, such as a structural material: (a) the AEC requirements, (b) its extreme brittleness, (c) the question of toxicity, (d) its high cost. In 1954, the American Society for Metals in conjunction with the AEC, sponsored a conference on Beryllium, the proceedings of which were published in 1955 in a book The Metal Beryllium by White and Burke. This volume made available to the public a large amount of information on the technology of

beryllium developed under AEC contracts. By 1955 the AEC needs for beryllium had diminished and satisfactory procedures for handling beryllium had been worked out such that the toxicity problem was not a serious deterrent. In 1956 Micks and Hoffman of the Rand Corporation issued a report to the Air Force emphasizing the advantage of beryllium as an important material for advanced aircraft and missile systems, for both structural and nose cone applications. It must be recognized that at about this time, missile systems were beginning to assume prominence over aircraft and the nose cone problem for the Atlas missile was a high priority program in the Air Force.

The Rand report generated considerable discussion in DOD circles which led to the initiation of R and D programs for the investigation of Be (and Be alloys) as a structural material. The problems of ductility and fabricability of Be sheet were major targets. The Air Force undertook a comprehensive program in this field with the scope ranging from research to manufacturing methods and more limited efforts were sponsored by the Bureau of Aeronautics concentrating on the brittleness problem.

It is of interest to note that a few patents existed claiming ductility for Be alloys, one in particular teaching that an alloy including approximately 70% Be and 30% Al overcomes the inherent brittleness of the beryllium and makes possible mechanical operations such as rolling and forging. Such claims, however, apparently were not generally validated since A. R. Kaufmann and P. Corzine reported in the 1955 ASM volume on Beryllium as follows: "One can imagine that the brittleness of beryllium can be partially overcome by preparing an alloy in which small beryllium grains are completely surrounded by matrix of ductile metal. The most obvious possibility is an alloy of beryllium and aluminum since no compounds are formed in this system. Several studies of such alloys have been reported in the literature . . . . For the present purposes it seems sufficient merely to say of these results that none of the alloys between 10 and 70% beryllium appeared to be outstanding in strength and ductility . . . . . It was also difficult to obtain homogeneous, gas-free castings because of the large difference in melting points of the two metals and the fact that the liquidus and solidus temperatures

are widely separated. For these various reasons, Be-Al alloys had not become of commercial importance so far as is known to the writers. Alloys of Be containing only a few percent of aluminum (insufficient to establish a ductile network) have failed to show any improvement in physical properties over "pure" Be, although there may be some advantage in improved fabricability and castability." Here is a clean-cut example of the concept of a composite material, whose exploitation at that time was limited by technical difficulties.

By 1956, nose cone materials for ICBM's and IRBM's had achieved a high priority status. The high weight penalties associated with the use of copper heat sinks focussed attention upon other materials and other systems of heat alleviation and thermal protection. Because of its high temperature thermal properties, beryllium was an interesting contender for such applications. The AVCO R and D Laboratories under Air Force contract, were investigating the applicability of Be as an afterbody material for the copper nose cone. Joining and brazing of large sections of beryllium were problem areas which received particular attention. By 1958, J. B. Cohen of AVCO had developed a satisfactory method for brazing of Be through the use of silver as a brazing material. Quoting from Patent 3,052,521, filed January 19, 1959, and granted March 26, 1963: "Contrary to earlier reports, alloys of silver and beryllium can be made ductile if produced by the novel process to be described. Briefly, the invention comprises the production of a metastable form of the alloy in which the beryllium is present as discrete globules surrounded by a matrix of substantially pure silver. The metastable form of the alloy is made by quickly cooling it through the temperature ranges in which peritectic phases tend to form under conditions of temperature equilibrium. In other words, it has been found by actual laboratory experiments that chill casting of alloys having a high beryllium content yields a ductile material, a discovery that is diametrically opposed to the teaching of the prior art." Although the descriptive portions of the patent have obvious reference to making ductile alloys of beryllium and silver the patent claims are specifically directed toward producing temperature resistant joints from the use of a beryllium-silver alloy by controlled solidification procedures. In 1931

Patent No. 1,816,961 had been granted to H. S. Cooper on ductile two phase Be-Al alloys. J. B. Cohen reported his results at an AIME meeting (probably in early 1959) and it was published in Trans. AIME February, 1960, Vol. 218. In this paper, he showed that Be-Ag alloys containing primary Be phase embedded in matrix network of silver, possessed sufficient ductility to be cold-formable. Photomicrographs revealed that the beryllium particles underwent extensive plastic deformation during the rolling treatment. Cohen also stated that alloys with lower silver contents, which did not have a continuous silver network, were brittle.

Related work on copper impregnated tungsten and on other beryllium alloy systems was going on at AVCO and it is highly probable that they recognized the implications of the ductility achieved in the Be-Ag alloy system. A number of factors apparently coexisted at this time which precluded exploitation of this development by AVCO.

1. With the change from the Atlas vehicle to the advanced re-entry vehicle for the Titan missile, beryllium was phased out for nose cone applications and replaced by ablating materials. As a consequence of official Air Force decision, beryllium work was discontinued at AVCO.

2. No special interest was evidenced by Air Force materials organization in the Be-Ag results and no funds for continuation of this work were made available by the Air Force.

3. Much of the original work was supported by direct AVCO funds, and in view of other pressing materials problems associated with vital AVCO projects, continuation of the program did not have high priority and did not receive funding.

4. Structural materials for air frames and related application were of secondary importance to the major AVCO objective of nose cone systems.

5. The principal investigator, J. B. Cohen, left AVCO about this time and some of the technical impetus thereby was lost.

Thus, timing appears to be an important consideration in the AVCO picture. It also indicates the inhibiting circumscribing factors surrounding materials R and D conducted as a direct support to systems or end item procurement. Developments out of line with systems objectives often are relegated to a back seat because of other pressures.

During the same period of time as the AVCO work was progressing, Armour Research Foundations under Bu Aer contract was investigating the development of ductile beryllium alloys based upon particular composites -- i.e., preparation of composite materials predominantly of Be containing a continuous ductile phase, by means of liquid phase sintering. Armour Research Foundation had previously shown that such an approach could lead to promising cold rollability with such materials as tungsten and chromium. In addition, ARF had developed working principles for consideration of materials selection for such composites based upon matching of the flow stresses of the principal phase and the ductile matrix. The Bu Aer contract with ARF, beginning in late 1958, was arranged prior to the published reports of the AVCO work and apparently independently. Similar to AVCO, Armour also was successful in preparing ductile Be-Ag and Be-Al alloys, particularly through the use of ternary additions, e.g., germanium. The Final Report of ARF to the Bureau of Naval Weapons (ARF 2187-6, October 20, 1960) on "Ductile Beryllium Alloys" concludes as follows: "The feasibility of liquid phase sintering for producing beryllium alloys has been established. The development of engineering materials appears imminent." WADC issued a technical report on the AVCO Beryllium joining program in April 1960 (WADC Tech. Rept. 59-695, Part I). Both of these reports were available to Lockheed and it seems probable that the Lockheed metallurgists were well aware of this work, prior to formal issuance of the reports. The Bureau of Naval Weapons work was reported at the NASA Research Advisory meeting throughout 1960; Lockheed was represented on that group. Both the Armour work and the AVCO work are referenced in a literature survey on Be prepared by Lockheed and issued in April 1960 (LMSC 288190).

This then is the background which set the stage for the development work on Lockalloy by the Lockheed Missiles & Space Division. To this picture must be added the strong internal motivations which prompted the Lockheed group to aggressively explore the implications of the concepts and alloy developments outlined above. As a major DOD contractor for aerospace systems, the Lockheed group was highly conscious of the advantages to be gained from the use of materials exhibiting lightweight-high modulus characteristics.

Lockheed was using Mg-Th alloys for structural applications in such aerospace systems (because of its good moderate temperature creep strength and low density) but its low modulus was imposing a serious design penalty. Lockheed had also established a major facility and program for the investigation of beryllium sheet, but fabricability difficulties and brittleness, particularly under multiaxial stress conditions, still presented major problem areas. This field of materials development obviously was of prime interest to Lockheed for their space systems programs. Starting in 1957, the design and structure groups at Lockheed had analyzed the potentialities of beryllium, which led ultimately to its extensive utilization for re-entry bodies in the Polaris program. This was the (or one of the) first large scale use of Be in aerospace structures and established Lockheed in a strong position regarding utilization of the then "state of the art" Be technology.

A weight saving analysis by Lockheed of one major space system indicated that one pound of weight saved for the space vehicle was worth the investment of $20,000 R and D work on new materials development. Thus, the availability of technical information in 1960 on possible ductile Be composites coincided in time with a strong Lockheed internal need for improved high modulus materials. This point is important since it appears that in the 5-year period since 1960, the state of art of fabrication and machining of beryllium has progressed to the point such that a program on Be-Al alloys might not have been pushed in 1965 by Lockheed as it was in

1960. By 1962 Lockheed had completed a 3-year program analyzing the problems related to the utilization of Be sheet for aerospace structures (ASD Tech. Rept. 61-692, Feb. 1962, "Strength, Efficiency and Design Data for Beryllium Structures"). This program culminated in the use of Be for forward section skins in the Agena vehicle which was successfully launched in June 1964. Be is now in full production for this application.

Lockheed Chronology

The information available by the fall of 1960 on Be-Ag and Be-Al alloy developments triggered the Materials group at Lockheed Missiles & Space Company (LMSC) to explore the potentialities of the composite approach as a practical means for making ductile Be alloy sheet. The Director of the Materials Laboratory (Dr. M. Steinberg) at LMSC was particularly conscious of the implications and was a moving force in stimulating such consideration. A detailed literature review and analysis of Be alloy systems was undertaken with the conclusion that the Be-Al system represented the best system to achieve an acceptable trade-off of modulus for ductility. The projected properties of the Be-Al system were enthusiastically accepted by the structure and design people, as a compromise substitute for Be and Mg alloys for specific Lockheed applications; and corporate encouragement for initiating an accelerated program was received.

A detailed applied research and development program was formulated by the LMSC Materials group and after some preliminary experimentation a comprehensive investigation of processes for making Be-Al alloys was undertaken, both in-house and with subcontractors. Powder metallurgy, casting, liquid phase infiltration and coating of Be powder were selected for study. Because of the strong internal need for materials of this type and in view of a potential proprietary position, the decision was made to support the program through corporate funding, rather than seek DOD contract support. The crash program resulted in success within 4 months, in that technological reduction to practice on a small sample scale was achieved. One of the key contributors to the success was a subcontractor laboratory, which was one of the leading laboratories in the technology of Be. It is significant to note

at this point, that the decision making responsibility and financial support resided at the level of Director of the Lockheed Materials group. His enthusiasm and perspective appear to be important features of the operation of the program.

In early 1962, a large scale R and D program (still on a laboratory scale) was instituted for alloy optimization, metallurgical control, and reduction of process costs. Decision making responsibility to invest $150,000/yr. to pursue these objectives still resided at the laboratory level (but with corporate encouragement). By the end of 1962 process feasibility on a large-size laboratory scale was demonstrated. Recognizing that Lockheed was not a basic materials producer, decision was made by Lockheed to seek outside development sources through licensing arrangements. Since Lockheed had a pressing need itself, for about 50,000 lb./yr. of the alloy, commercial organizations with available facilities for scale-up were primarily considered. A total potential market of $50 million/year was envisaged for the Be-Al alloys over a five-year period with double the value for the long-range future. A series of discussions with a number of commercial firms occurred (on a Confidential disclosure basis) to arrive at a source of an integrated facility for metal preparation and fabrication. In September 1963, an agreement was signed with Dow Metal Products Co., and the Beryllium Corporation to scale-up a production facility. (The Dow Metal Co. is no longer in the picture and the Beryllium Corporation is now producing and selling "Lockalloy" commercially.) Material is now available in commercial sizes and shapes and is being evaluated for numerous applications. LMSC has completed a detailed design data study on Lockalloy and a market analysis and is optimistic about its large-scale use in space systems and numerous other applications where low density, high modulus, and good strength are required.

The environment in the Research Laboratory of LMSC must be considered as an instrumental factor in the Lockalloy story. The Lockheed Research Laboratories play an important role in contributing to Lockheed's key position in the aerospace field. In addition they provide a base for

diversification opportunities for LMSC. A broad spectrum of research relevant to the interest of LMSC is conducted with a large, highly professional organization. About 50% of the programs are contract funded with the balance supported by the Company's Independent Research Program. A key feature of the operation appears to be the level of responsibility vested in managers of the various research laboratories for program control. Certainly in the Lockalloy development the decision making responsibility for program initiation and funding residing in the Manager of the Materials Laboratory provided the flexibility and the push for conducting an aggressive program. The responsibility for the translation process was uniquely identified with one group -- there was no necessity to transfer money, people, ideas, or responsibilities across organizational interfaces.

Perspective

A number of factors emerge as being of significance in the Lockalloy case study:

1. Certainly the Lockalloy development has its roots in the broad field of beryllium technology, but it provides an interesting validation of the "window to science" justification for corporate support of research. The availability of a technical staff with access to channels of technical information directly led to the recognition of the implications of results reported by an external laboratory. It must be noted that the metallurgical concept upon which Lockalloy is based is not new -- it underlies numerous practical metallurgical systems. It required the laboratory demonstration of the applicability of the concept to Be to trigger off a chain of events at LMSC which led to Lockalloy.

2. The background information developed from the DOD supported R and D programs contributed to the technical origin of the Lockalloy development.

3. A well-defined materials need existed in LMSC which provided a critical stimulation for pursuing the development with an aggressive

R and D program. Recognition of the importance of the need by the Research Laboratory and an environment which enabled flexibility and funding of crash programs were important features. The existence of a captive market provided a strong basis for corporate support and capital investment.

4. The delegation of appropriate decision making responsibility on "working-level" management level -- i.e., Materials Laboratory Director. Few if any organizational interfaces were involved and the entire translation process fell under the responsibility of one group.

5. The conviction, enthusiasm, perspective, and personality of a single man (Director of the Materials Lab of LMSC) permeates the Lockalloy story. Because of his managerial position and his "coupling" role, he was the prime mover in the Lockheed development.

Status of Lockalloy as of 1966

Potential usage areas have been found in spacecraft structures; specifically in cylindrical skins supporting compression loads, solar panels, instrument mounting platforms, and substructure subjected to compression loads.

The potential usefulness of this new material is very well demonstrated in a NASA funded contract (NAS 8-11298) which shows that the instrument stage for the Saturn V vehicle presently designed as an aluminum sandwich structure weighing 250 lb. can be replaced by a Lockalloy (62% Be-38% Al) skin and stringer construction weighing only 98 lb. at a savings of $84,000 per launch.

Government support in the form of evaluation contracts (NASA: NAS 8-11448 and NAS 8-11298) was particularly valuable in characterising the material and emphasizing to structural designers the potentially useful areas for the new material.

The AFRTD Materials Laboratory is currently bidding a contract to develop shaped extrusion technology to fulfill the needs of the aerospace industry. Such financial support is essential to the development of new products having primary utility in areas predominantly governmentally controlled or defense oriented.

Appendix I
to
Case History
of
The Development of Lockalloy

THE LMSC RESEARCH LABORATORIES*

The Lockheed Missiles & Space Company is dedicated to continuing its role within the aerospace industry as a major contributor to military and civilian programs requiring outstanding performance. Research and development in the aerospace industry demands broad scientific capability and a flexible integration of engineering skills for the conception, design, and creation of spacecraft and missile systems.

The role and objectives of the Research Laboratories within the context of total company activities are set forth in the following official statement:

> The mission of Research is to provide LMSC with a broad scientific capability in the physical and life sciences relevant to missile systems, space systems, and related products which will first provide the basis for future business for LMSC and second ensure that current LMSC programs have available a maximum scientific understanding of applicable principles, phenomena, and analytical techniques.

Research includes approximately 700 people of whom about 550 are professional scientists. Roughly half of this group is engaged in the company's Independent Research Program while the remainder are supported by research study contracts or research studies which are part of major LMSC programs. With respect to Independent Research, Mr. Courtland Gross made the following statement in his open letter of January 1962, on "The Year Ahead":

> We plan to strengthen our research effort during 1962 and the years following. Research ability, essential to technical strength and future growth, is also an important factor in winning new contracts. We cannot afford to neglect it. I believe it may be desirable to increase our total research expenditures by as much as 15% a year during the next few years. This may not be easy, but we are prepared to devote a larger share of the earnings dollar to achieve this end.

*Organisation charts as of 1965

It is the policy in Research to actively encourage open publication of worthwhile results in the belief that evaluation by professional peers not only provides a sound method for appraising research but also serves as a stimulus for individual scientific accomplishments upon which the reputation of the Laboratories is collectively built.

At LMSC a central portion of the research and development capability has been placed under the Director of Research and Engineering. Reporting to him, the Director of Research manages four Research Laboratories. The study of fundamental scientific principles and their application to technology is carried out under these four Laboratory Directorates, representing the physical sciences, mechanical and mathematical sciences, materials sciences, and electronic sciences. Basic and applied research, invention, scientific innovation, and communication of this knowledge to the rest of the Company constitute basic objectives of the LMSC Research Laboratories.

The Director of Research and Engineering and the Director of Research are responsible for establishment and review of overall objectives for the laboratories, consistent with the Company's goals. The Laboratory Directors are responsible for all aspects of the management of the laboratories, including the planning of research programs: organization of the work to be performed; control of budgets, facilities, and equipment; and review of accomplishments.

Scientists in each laboratory are designated Members of the Research Laboratory. In addition, certain outstanding individuals are designated Senior Members; these are chosen on the basis of their professional standing as evidenced by publications, experience in program direction, activities in professional societies, work on scientific committees, education, and experience. Senior Members participate in selecting research projects in their fields of specialization, choosing the staff necessary to perform the work, and assuring that high standards are maintained. To the maximum extent possible, nontechnical aspects of administration are delegated to the administrative staff so as to permit Members of the Laboratories to concentrate on the technical aspects of their work. Maximum flexibility is possible, since no external controls on the size of groups or the details of working relationships are established.

The chart opposite illustrates the short channel of communication between the laboratories and LMSC management and indicates the close interrelationship between Research and Engineering direction. Senior Members in each laboratory are listed, along with a description of their principal field of interest. Although each laboratory strives to have at least one Senior Member for a scientific field in which substantial activity exists, this is not always feasible. The scope of research interests are, therefore, better understood by referring to later sections which describe the current efforts within the four laboratories.

In addition to their responsibilities for conducting research, the Senior Members of the laboratories are called upon from time to time to serve as advisors to the Director of Research and Engineering, the Director of Research, or the LMSC Planning Staff. Persons on the Director's staff whose work is closely associated with research are, in addition, designated Members of the Laboratories. All Members of the Laboratories are expected to maintain appropriate communications with the Engineering organization and with the other divisions of the Company in accordance with the overall objectives of research at LMSC.

The work currently being conducted in the four Research Laboratories is described in the four sub-sections which follow. While the nature of the research activities requires frequent collaboration in many problem areas, each Laboratory is responsible for a particular area of investigation:

- Physical Sciences Laboratory - Interaction of radiation with matter
- Mechanical & Mathematical Sciences Laboratory - Flight
- Materials Sciences Laboratory - Materials and energy
- Electronic Sciences Laboratory - Information and communication

As a result of technical requirements for isolation, LMSC has located its Antenna Laboratory on the fringes of San Francisco Bay, a short distance from the Sunnyvale plant. Research on electromagnetic propagation and antenna systems is carried out there in conjunction with engineering design and

fabrication. Similarly, research involving hazardous quantities of chemicals and high-pressure fluids is conducted at the Santa Cruz Laboratories of the Engineering Organization, located high in the Santa Cruz Mountains.

Analysis of
Case History
of
The Development of Lockalloy

DESCRIPTION OF RESEARCH-ENGINEERING INTERACTIONS

a. Implications of work on composite Be alloys made by rapid solidification techniques (AVCO) or liquid phase sintering (Armour Research Foundation) focused attention on concept of composite approaches to achieve ductile Be alloys. Both of these findings were consequences of research programs to satisfy identified materials problems. Demonstration of concept was an outgrowth of an extensive background of national research effort on deformation and fracture behavior of polyphase alloy systems.

b. Recognition by Lockheed research people of potential applicability of concept for fulfilling particular class of aerospace structural materials needs with a particular alloy system; close interaction of materials research and structural design people at Lockheed provided basis for recognition of strong internal need for higher modulus material with sufficient ductility for fabrication and serviceability as a consequence of difficulties encountered in testing unalloyed beryllium structures.

c. Crash program with Lockheed funding for feasibility demonstration of practical process for making ductile Be-Al composite alloys. Again engineering requirements provided guide lines for metallurgical analyses in terms of composition and microstructural optimization and in terms of methods of preparation of alloy.

d. Determination of detailed property data and satisfactory techniques for forming, joining, etc. Again close interaction between research and engineering personnel promoted feedback for optimization of alloy and processing techniques to maximize combination of properties.

e. Pilot plant process development including alloy optimization, metallurgical control, and reduction of process costs. Continued interaction of research and process development personnel occurred.

STAGES AT WHICH REIs OCCURRED

		REI
0	Scientific Finding (knowledge)	a
1	New Material Recognition	b
2	Useful Material Creat. .l	c
3	Feasibility of Material Use in Hardware	d
4	Use of Hardware in System	
5	Production of Product (system)	e
6	Operation of Product (system)	

FREQUENCY OF FACTORS OPERATING IN REIs

	FACTORS	REIs					
		a	b	c	d	e	Total
1	High educational level (advanced degree) of principal investigator	x	x	x			3/5
2	Importance of management	x	x	x		x	4/5
3	Importance of Government-sponsored research	x	x	x			3/5
4	Importance of recognized need	x	x	x	x	x	5/5
5	Requirement of flexibility to change direction during work and local control of funds (easily available resources)		x	x	x	x	4/5
6	Industrial laboratory involved	x	x	x	x	x	5/5
7	Basic research in the laboratory (for inst. or org.)						0
8	Communications across organizations was important	x	x	x	x	x	5/5
9	Technical problem was the principal obstacle	x	x	x	x	x	5/5
10	Importance of a "champion"		x	x		x	3/5
11	Freedom for individuals		x	x	x		3/5
12	Broad spectrum of types of laboratories	x		x		x	3/5
13	Geographic proximity						0
14	Prior experience with innovation			x			1/5
15	Organizational structure (barriers and bonds)		x	x	x		3/5

SUMMARY ANALYSIS

Although Lockalloy is not yet established as a full-fledged member of the class of structural materials and is not yet in volume application, it represents an interesting case study with respect to the factors and climate motivating the transition from research into development. No direct link with a basic research phase emerges, but it is true, nonetheless, that the background of research on fundamental metallurgical principles, brittleness of beryllium and deformation and fracture of multiphase materials are some of the stepping stones of its development.

Several factors stand out as being key features of significance:

1. There existed a clear and recognized materials need (Factor 4) — both generic with respect to improvement of the brittleness of beryllium and specific with respect to particular high modulus-low density structural materials requirements of aerospace vehicles. This factor underlay all of the Research-Engineering interactions and particularly the acquisition of the initiating knowledge and the recognition of the applicability of the concept to solving a particular material need.

2. Factor 5 — flexibility of work direction and of use of a financial resource appeared to be valuable instruments in promoting the transition in a minimum of time. The flexible use of internal funds, particularly in stages b and c were critical events.

3. The role of a technical manager as both a "coupler" and "champion" is ideally illustrated — in point of fact, the coupler was the prime mover. Few, if any, organisational interfaces existed and the entire translation process fell within the responsibility of one laboratory. Thus, Factors 2, 10 and 15 jointly emerge as important features.

4. Timing as a factor was important — the availability of knowledge and resources at a given time in technological terms spurred the development. While the need did not change, later material development would not result in a similar transition sequence today.

5. The role of government supported research (Factor 3) is self-evident and is to be expected with a material development that is primarily oriented toward military and aerospace vehicle applications.

6. The key event was the recognition by the "coupler" of an urgent materials need and the conceptual implications of available technical information. Thus communication exchange (Factor 8) was a critical factor in stages a and b. Effective communication exchange was also important in Lockheed among the research staff, designers and systems engineers in establishing the need factor and the use requirement, which carried through stage c, d and e.

A CASE HISTORY
OF
THE DEVELOPMENT OF POLYSULFIDE POLYMERS

Prepared by
E. M. Fettes

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A CASE HISTORY
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THE DEVELOPMENT OF POLYSULFIDE POLYMERS

NARRATIVE

The founding of the Thiokol Chemical Co. was a direct result of the discovery of polysulfide polymers and their potential as synthetic rubbers. The spectacular growth of the company, from under one million dollars in annual sales in 1942 to 255 million dollars in 1962, was caused by the discovery of liquid polymers and their subsequent usefulness in such varied applications as sealing compounds and binders for composite solid propellants for rockets.

A discovery or innovation which can cause such a growth must necessarily be significant. The text which follows describes the history of polysulfide polymers and attempts to analyze the factors pertinent to the progress of the development in terms of interactions between science and technology.

In 1926, Joseph C. Patrick, an M.D. turned chemist, was a partner in an independent chemical laboratory in Kansas City, Mo. Dr. Patrick was investigating the hydrolysis of ethylene dichloride to ethylene glycol in an attempt to find a practical commercial process. The utility of ethylene glycol for an antifreeze component in radiators for the fast growing automobile industry was known. Union Carbide was producing ethylene glycol made from ethylene oxide and marketing under the tradename Prestone. Ethylene was available which could be chlorinated to ethylene dichloride. Patrick felt that an efficient method of hydrolysing the chlorine to hydroxyl would give a cheaper method of manufacture of ethylene glycol.

The hydrolysis of organic chlorides by common alkaline materials such as sodium or calcium hydroxide usually proceeds rapidly and well. With ethylene dichloride this was not true. The reaction was very slow and the yield of product low. From his background with Armour and the dehairing of hides,

Dr. Patrick decided to try adding sulfur to the hydroxide. The experiment was unsuccessful in producing ethylene glycol; instead, a gummy odorous solid resulted. He became interested in this unexpected result and, abandoning the original objective, followed investigation of the elastic solid. He and his partner applied for patents and a British patent (1) issued first in 1927. Patrick found local financial backing and the Thiokol Corp. (later changed to Thiokol Chemical Corp.) was founded in 1929 in Kansas City, Missouri.

To digress briefly from history to an assessment, the original discovery was unquestionably accidental. No one in the 1920's would have deliberately selected the reaction between ethylene dichloride and sodium tetrasulfide as a route to a synthetic rubber. The requirements in chemical structure for rubbery behavior in polymers were completely unknown. In fact, the concept of polymers as organic molecules of high molecular weight was just beginning to emerge. The pioneering work in the United States of W. H. Carothers had not yet even begun. The work by H. Staudinger in Europe had certainly started to show the nature of polymers in a preliminary way. It is extremely doubtful that Dr. J. C. Patrick was familiar with, or even had ready access to these foreign publications.

There is evidence in the literature that other investigators had found the same chemical reaction to occur as did Patrick. The main difference was that none of the others observed or believed important the elastomeric characteristics of the product. Any chemist would have realized that the objective of making ethylene glycol by this reaction had been unsuccessful; probably few chemists would have realized that their apparent failure had led to a significant discovery. Patrick not only realized this, but devoted the rest of his active scientific life to following up his accidental discovery.

The new synthetic rubber was deficient in physical properties compared to hevea rubber, more expensive, and malodorous. It did have extraordinary resistance to attack by light, oxygen, and organic solvents. The production was started in 1930 in which year the company moved to the vicinity of Trenton, New Jersey. It was soon realized that Thiokol rubber would never be a substitute for natural rubber, but did offer promise for applications where resistance to gasoline, oil, and solvents was necessary. The years from 1931 to 1941 were spent in improving the process for manufacture and the physical properties of the elastomers. A process for polymerization as a fine suspension was found. This "latex" was found to be useful in itself for coating storage tanks for aviation fuel. When coagulated with acid, the latex gave the solid rubber.

Dr. Patrick continued his research on the preparation, structure and properties of the polysulfide polymers. He investigated other organic dihalides, various polysulfides, and methods of formulating and vulcanizing. The scientific account of this work was presented (2) in London in 1935 at the first international meeting ever held on the subject of polymerization. One of the main results from this study was an improvement in the odor of the rubber, which was achieved by replacing ethylene dichloride in whole or in part with bis(2-chloroethyl) formal.

In 1940 when World War II commenced, Thiokol was still very small with less than 35 employees and annual sales under $500,000 a year. The products were essentially unchanged; the original elastomer (Thiokol Type A) and two modifications (Type FA and S), as well as two aqueous dispersions (MX and MF). The synthetic rubbers were used only in specialty applications where out-

standing resistance to solvents was needed - chiefly paint spray hose, printing rolls and blankets, and gaskets. The odor of the product and the physical properties of the elastomers had been improved to a tolerable level except for resistance to compression set. This so-called cold flow occurred when the rubber was kept deformed at elevated temperatures and presented a serious disadvantage for many uses of the rubber.

Mr. Harry R. Ferguson, a chemical engineer from MIT, with an extensive background in the rubber industry, was at that time in charge of production, engineering, and development of new products. He was keenly aware of the deficiency of the polysulfide elastomers in poor compression set and believed that the usage of the products could be greatly expanded if this handicap were removed.

Enough of the nature and characteristics of polymers was then known for it to be assumed that the poor resistance to a permanent stress was due to the lack of formation of a three dimensional network during the vulcanization with zinc oxide. It had already been found that introduction of tri- and tetrafunctional halides into the polymerization would produce a network structure, but crosslinked rubbers were much too tough to be handled on rubber mills.

Harry Ferguson conceived the idea of making the crosslinked network in the polymerization. By then reducing the molecular weight sufficiently by cleaving the chain, he hoped to achieve processability and then reform the original network during vulcanization. He had his staff investigate acidic cleavage of the formal linkage to produce terminal hydroxyl. This was successful but coupling of the hydroxyl groups could not be achieved. In a discussion

with Dr. Patrick, Ferguson asked him if it would be feasible to reduce the disulfide linkages to terminal thiol groups. Such terminals should be readily reformable. Patrick became interested in the possibility and assigned one of his staff to the project.

Although Joseph C. Patrick was a vice-president and the Director of Research of Thiokol, he devoted all of his time and thinking to research in this area. He was a creative inventor, preferring to work in the laboratory himself with only a few professional assistants. He would work only on problems which interested him and had no liking for organizing and planning for a large staff to support all of the technical areas of interest to the company. He had no interest in technical service to customers, attending technical meetings, writing or encouraging writing of technical articles. He was keenly interested in having his research covered by patents. Actually, a significant amount of research was carried out in the development department under Ferguson due to the disinclination of Dr. Patrick to pursue projects not of his own selection.

The research staff consisted of two Ph.D. chemists, one B.S. chemical engineer and one technician. The chemical engineer (E. M. Pettes) was assigned to follow up the program developed by Patrick and Ferguson. The problem was solved fairly easily and a process developed by which an aqueous suspension of crosslinked polymer was treated with inorganic reducing agents to form a soft millable crude rubber.

Ferguson then conceived the thought of cleaving even further the crosslinked elastomer to a sufficiently low molecular weight that it would be a liquid. At a meeting of the Board of Directors, he asked Frank Stoner,

Technical personnel at the Jet Propulsion Laboratory, run by California Institute of Technology, had heard of the liquid rubber. They thought it might be useful as a polymeric binder for composite rocket propellants. The asphalt then used as a binder was prone to cracking at low temperatures and slumping at high temperatures. Use of a liquid curable rubber as a binder alleviated this problem. It also allowed the elimination of insertion into the rocket case of cartridges containing propellant in favor of direct pouring of the liquid rubber into the case. This case-bonded propellant resulted in improved impulse.

The success of JPL in the development of polysulfide propellants with the advantages of wide temperature range and greater impulse did not result automatically in its usage. Aerojet was the only company producing rocket motors from composite propellants. They had some propellants of their own and had no interest in utilizing this new composite. Mr. Crosby, after months of persistent attempts to persuade someone to carry on with this use for liquid polysulfides, decided that the only route left was for Thiokol to enter the field of design and construction of rocket motors. He obtained a small government contract in 1948 and entrusted H. R. Ferguson with the task of setting up a rocket division. It was a large gamble for a small company with an historical and technical background solely in the area of specialty polymers, especially since the emphasis in the space field was almost entirely on liquid-fueled rockets rather than solid-fueled. The experiment was a success. The annual sales of the rocket division went from nothing in 1948 to 77 million in ten years and 271 million in fifteen years.

References

1. Patrick, J. C., and N. M. Mnookin, Brit. Pat. 302,270 (Dec. 13, 1927).

2. Patrick, J. C., Trans. Faraday Soc., 32, 347 (1936).

3. Patrick, J. C., and H. R. Fergusen (to Thiokol Corp.), U. S. Pat. 2,466,963 (Apr. 12, 1949).

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ANALYSIS OF CASE HISTORY OF POLYSULFIDE POLYMERS

For the purpose of analysis this case history has been divided into sub-cases as shown below.

Sub-case	Title
I	Synthetic Rubber
II	Liquid Polysulfide Polymers - Sealing Compounds
III	Liquid Polysulfide Polymers - Composite Propellants

DESCRIPTION OF REIs

REI	Description
	Sub-case I. Synthetic Rubber
a	Investigation of hydrolysis of ethylene dichloride and selection of sodium polysulfide.
b	Recognition that unexpected product formed had elastomeric properties
	Sub-case II. Liquid Polysulfide Polymers - Sealing Compounds
c	Concept that the compression set of polysulfide elastomers could be improved by crosslinking during polymerization and still maintain suitable processability by chemical cleavage of the polymer chain.
d	Laboratory investigation of methods to cleave controllable polymeric polysulfides.
e	Recognition that a low polymer that could reform to the high polymer was unique and should be a useful material.
f	Decision to look into the areas of caulking and sealing compounds for the liquid polymer.
	Sub-case III. Liquid Polysulfide Polymers - Composite Propellants
g	Possibility of using liquid polysulfide elastomers as binders for inorganic oxidizers to attain good physical properties at both low and high temperatures.
h	Investigation of the characteristics of polysulfide/oxidizer systems and developing suitable formulations.
i	Decision that polysulfide propellants would never succeed unless Thiokol went into the production of missiles and rockets.

STAGES AT WHICH REIs OCCURRED

Stage* No.	Sub-case I	Sub-case II	Sub-case III
0			
1	a	e	
2	b	d	h
3		c	g
4		f	
5			i
6			

* Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	Definition
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From the study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs and listed them as follows:

List of Factors Considered in Analyzing Events of REIs

1. High educational level (advanced degree) of principal investigator
2. Importance of management
3. Importance of Government-sponsored research
4. Importance of recognized need
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources)
6. Industrial laboratory involved
7. Basic research in the laboratory (or institution or organization)
8. Communications across organizations was important
9. Technical problem was the principal obstacle
10. Importance of a "champion"
11. Freedom for individuals
12. Broad spectrum of types of laboratories
13. Geographic proximity
14. Prior experience with innovation
15. Organization structure (barriers and bonds)

FREQUENCY OF FACTORS IN REIs

(Statistical Analysis)

Factor No.	Sub-case I			Sub-case II					Sub-case III				Total Frequency
	REIs			REIs					REIs				
	a	b	Totals	c	d	e	f	Totals	g	h	i	Totals	
1	x	x	2/2					0/4				0/3	2/9
2	x		1/2			x	x	2/4			x	1/3	4/9
3			0/2					0/4	x	x	x	3/3	3/9
4			0/2	x				1/4	x	x		2/3	3/9
5	x	x	2/2		x	x		2/4		x		1/3	5/9
6	x	x	2/2	x	x	x		3/4				0/3	5/9
7			0/2					0/4				0/3	0/9
8			0/2	x	x	x	x	4/4	x			1/3	5/9
9			0/2	x	x			2/4		x		1/3	3/9
10		x	1/2	x		x	x	3/4		x	x	2/3	6/9
11	x		1/2				x	1/4	x	x		2/3	4/9
12			0/2					0/4				0/3	0/9
13			0/2					0/4				0/3	0/9
14			0/2	x				1/4				0/3	1/9
15			0/2					0/4				0/3	0/9

SUMMARY ANALYSIS

The importance of the climate for research, the company's attitude toward research and development, the structure of the company, and many other factors which make up the typical case study are absent here. The three individuals concerned, Patrick from Research (Sub-case I), Ferguson from Engineering and Development (Sub-case II), and Crosby (Sub-case III) were themselves officers of the company and hence able to push projects without further management approval.

The original discovery of the polysulfide rubber by Dr. J. C. Patrick was unquestionably accidental. No one in the 1920's would have deliberately selected the reaction between ethylene dichloride and sodium tetrasulfide as a route to a synthetic rubber. The requirements in chemical structure for rubbery behavior in polymers were completely unknown. In fact, the concept of polymers as organic molecules of high molecular weight was just beginning to emerge.

There is evidence in the literature that other investigators had found the same chemical reaction to occur as did Patrick. The main difference was that none of the others observed or believed important the elastomeric characteristics of the product. Any chemist would have realized that the objective of making ethylene glycol by this reaction had been unsuccessful; probably few chemists would have realized that their apparent failure had led to a significant discovery. Accidental discoveries such as this are difficult to analyze in that only the successes become known. In the discovery of the polysulfide synthetic rubber and its subsequent evolution, Dr. Patrick was clearly the champion. In fact his whole scientific interest was in polysulfid

rubbers and then also the liquid rubbers. He was actually opposed to the later expansion of the company into other chemicals and into the field of rockets.

In the invention and subsequent search for uses for the liquid polysulfides, Ferguson was unquestionably the champion. Although the initial work on the preparation of the liquid polymers was carried out in Research under Patrick, Ferguson throughout the subsequent years pushed the project, not only in his Development Department, but also in Research and Technical Service which were not under his jurisdiction.

The decision to put Thiokol into the field of rocket motors as the only hope of furthering the progress of polysulfide propellants cannot be discussed as a typical business decision by management. It was an intrepid adventure. Thiokol had no mechanical aptitude, not even one mechanical engineer. It had practically no experience with government contracts and no site suitable for this type of operation. The growth of rockets and missiles that occurred since 1948 could hardly have been regarded then as a certainty.

Crosby had faith in the merits of polysulfide propellants and if Thiokol had to go into the business to prove it, go into it they would. The decision was the major one in the growth of the company from about 100 employees and annual sales of about 1 million in 1948 to about 9000 employees and sales of 271 million in 1963. It was the decision by Crosby that bridged the gap from the scientific and technological accomplishments of JPL to the final rocket motor.

A CASE HISTORY

OF

THE DEVELOPMENT OF SILICONES

Prepared by

F. E. Dickson and T. G Fox

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Preface

The following survey is a brief history of the development of silicone materials. Almost from the awakening of interest in the element silicon, its organic chemistry has been a focus of attention. Therefore, the survey must include some account of this early work. Even though we necessarily rely on earlier judgments for our knowledge of early research workers, we can still hope to attain insight into their personalities and motivations.

The material for the recent history (1930 to present) was obtained through conversations with Dr. E. L. Warrick and Dr. John Speier, whose cooperation and that of the Dow-Corning Corporation is gratefully acknowledged. Dr. R. R. McGregor, who for many years served as Head of the Dow-Corning Fellowship at Mellon Institute, died on April 8, 1965. His book, Silicones and Their Uses,[1] was most helpful in the preparation of this case history.

The limitations of our treatment, which will be apparent to the reader, are cited explicitly in the last section, the Summary Analysis. The limitations must be attributed to the authors, inexperienced in documentary histories and limited in time to devote to this assignment, rather than to the members of the Dow-Corning Corporation, who gave generously of their time in recalling the exciting events covering nearly thirty years.

Case History of the Development of Silicones

Narrative

Introduction

Liberally dispersed throughout the history of science one finds conjunctions of persons and events, that by chance, or by some logical consequence, spur outstanding discoveries. A careful chronological study of the discovery and subsequent practical application of a particular product may well yield valuable information regarding the factors contributing to its development and one might hope thereby to discern the outlines of some features common to all creative advances. The history of the development of silicones is an excellent example of such a product. The use of silicone products is commonplace in everyday life; yet silicones -- the generic name for high molecular weight organosilicon compounds -- do not exist in nature. The specific molecular structures and products are the rewards of much painstaking thought and investigation, by scientists and technologists who possessed in common at least one outstanding quality -- insatiable curiosity.

Crafts returned to the United States to become the Head of the Department of Chemistry at Cornell University and later the President of the Massachusetts Institute of Technology. Friedel maintained his interest in silicon, primarily because he was a mineralogist, and he was later joined in his work by the German chemist Ladenburg. Their interests, however, centered on learning more about the chemistry of silicon itself. If the preparation of compounds containing carbon could shed any light on this, they would attempt to prepare them, but otherwise it appears they were not particularly interested. This attitude was indeed unfortunate when one considers that at this point they were on the threshold of a silicone industry. Friedel and Ladenburg, however, did make many significant contributions to silicon chemistry, many of which remain basic to the modern technology. It is interesting to note that their last joint publication was in 1871, a year after the beginning of the Franco-Prussian War. Friedel, the Frenchman, and Ladenburg, the German, held conflicting political and religious views. For these reasons, Ladenburg returned to Germany; and thereafter Friedel maintained little more than a passive interest in organosilicon chemistry. One should observe, however, that in the twelve-year period that Friedel collaborated with both Crafts and Ladenburg, the foundations for modern silicone technology were laid. McGregor concludes "that in the silicon work with both Crafts and Ladenburg, Friedel must have been the activating force, or the catalyst, because of his interest in mineralogy ... While one would guess that Crafts and Ladenburg did most of the actual work on synthesis, neither of them would have continued with such zeal had it not been for the urging and encouragement of Friedel."

He further proceeded to replace the halogens with methyl groups and, on subsequent treatment with aqueous alkali, obtained an oily product similar to one which Ladenburg had observed many years before, $(C_2H_5)_2Si(OC_2H_5)_2$. Concerning this compound and the work of Stock, McGregor points out, "Again modern silicone preparation had been anticipated, but in such a hazy fashion that only a prophet of the first order could have been expected to see what the future had in store."

In contrast to the inquisitiveness and curiosity of these early experimenters, it should be noted in passing that a team of workers, Schlenk, Renning, and Racky, at the Royal Academy of Science in Munich, in a publication dated 1911,[3] investigated whether it was possible to prepare the triphenylsilane, $(C_6H_5)_3SiH$, which would be analogous to the free radical triphenylmethyl. They answered the question in the negative and then let the whole subject drop without ever asking the obvious question -- why? In addition, in the 1930's several Russian investigators published a number of papers, sensing that there might be some industrial value in the various types of resinous compounds that could be prepared through the use of organosilicon intermediates. Even though they were able to show that several of these compounds were remarkably heat stable, they could convince no one of their value. In view of the very encouraging results, the question arises as to why these workers were not more energetically supported.

In the period 1900 to 1940, while various investigations on the chemistry of silicon and organosilicon compounds were being carried on there appeared one man who apparently resolved to unravel the properties common to both carbon and silicon. He was Professor F. S. Kipping of the University of Nottingham. McGregor gives a brief description of Kipping as follows: "In the period from 1899 to 1944 he published 54 papers on this subject. As may be surmised from his long period of intensive work, he was one in whom the British tenacity

of purpose was evident to a superlative degree. He had one end in view and refused to be diverted from his target. He was confronted with problems which were difficult to resolve, and at times his products transformed themselves into unidentifiable oils and glues which, with typical British understatement, he frequently described as 'uninviting'. He was uncomprisingly interested in the chemistry of compounds containing silicon, and even in his later years, when shown some of the first commercial silicones, he could scarcely bring himself to take more than a passive interest in them."

The "uninviting" oils and glues that Kipping observed and later investigated turned out to be some of the forerunners of today's silicone compounds. Kipping demonstrated that many of these products were large molecules formed by the union of a number of small molecules. He showed that the result of the bimolecular reaction

$$-\overset{|}{\underset{|}{Si}}OH + HO\overset{|}{\underset{|}{Si}}- \rightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O$$

is elimination of water and formation of a chemical bond uniting two silicone chains and further that the reaction

$$-\overset{|}{\underset{|}{Si}}(OH)_2 \rightarrow \overset{|}{\underset{|}{Si}}=O + H_2O$$

does not occur. The last observation, showing that no two groups on the same silicon chain react with one another, is basic to organosilicon compounds; but this fact became clear only after long investigation.

The work of Kipping and others paved the way for further studies on the chemistry of organosilicon compounds. It should be noted, however, that apparently no interest or specific effort was directed toward preparing high molecular weight organosilicon materials. As we shall observe, the commercial development of silicones would at least have been severely hampered, and would perhaps have been impossible, without additional knowledge in an entirely distinct field -- that of high polymers.

Development of Polymer Chemistry and the Organic Polymer Industry

Even though a considerable amount of work had been performed in the area of organosilicon chemistry prior to 1940, very little attention had been paid to the "uninviting" oils and glues that Kipping had observed. Fortunately, however, during the long period over which the chemistry of silicon was being investigated, other chemists were studying various other oils, glues, and rubber-like materials. Pickle suggested, in 1910, that rubber was composed of eight-unit rings and termed these structures "polymers." Staudinger, who was studying natural products in Zurich in 1920, conceived the idea of macromolecules, or giant chain molecules held together by the normal covalent bonds long familiar in organic chemistry. He found that the properties of these macromolecules were not simply the summation of the properties of the individual units, but that the macromolecular architecture itself resulted in distinctive physical properties. These new macromolecules were termed "high polymers." While Staudinger was pursuing his work in Switzerland, similar studies were being carried on at the duPont Company laboratories by W. H. Carothers. Carothers, a brilliant experimentalist and penetrating thinker, was studying the principles underlying the preparation of various classes of high polymers. After thirty years, his classic work is still the basis for much of the synthetic aspect of contemporary polymer science and technology.

The work of Staudinger, Carothers and others, established the facts that macromolecular materials could be produced through reactions uniting small molecules into long chains through normal organic chemical procedures employing, generally, bifunctional instead of monofunctional species, and further that the specific important properties of such macromolecular materials as rubbers, fibers, oils, plastics, etc., depend both on the nature of the repeating chemical unit and the length of the molecular chain. These ideas led predictably and directly to the rapid profusion of a host of new synthetic organic polymers and the well known growth of the polymer industry. The period of the

thirties and forties was thus an exciting revolutionary time, of rapid development, both of knowledge in polymer science and of the industry born from this new specialized branch of chemistry. Synthetic substitutes for many natural products (nylon for silk, neoprene for rubber, plastics, adhesives and glazing, etc.) with new and tailor-made properties created an era of excitement and progress which continues to our own day.

Sub-Case I: Silicone Polymers for Heat Resistant Resins (Corning Glass Works). Needless to say, the advance of polymer chemistry during the 1920's and 30's set the stage for the inevitable joining of this science with organosilicon chemistry. Glass manufacturers seeing the new organic polymers and realizing their own product to be an inorganic polymer, became interested in the possibility of a hybrid polymer, part organic and part inorganic, combining the rubber-like flexibility of one with the thermal stability of the other. The Director of Research for Corning Glass Works at Corning, N. Y., Dr. E. C. Sullivan, engaged Dr. J. F. Hyde, an organic chemist, to investigate this area. In a short time, Hyde was successful in preparing high polymers containing both organic and inorganic constituents. Soon thereafter there occurred a coincidence that determined the future course of activity. McGregor describes it as follows:

> "The Corning Glass Works had just begun the development of glass fibers and was on the lookout for appropriate markets. One of the most promising outlets for this product appeared to be as a woven tape for use in electrical insulation. Cotton, impregnated with a resinous dielectric, had been used; but it would char at elevated temperature. This difficulty could be overcome by the use of glass tape in place of the cotton, but it was found that the resin impregnant would stand only slightly more heat than the cotton would. Thus there was but little advantage in using the glass. To realize the full value of the glass tape there was needed a resinous dielectric that was considerably more heat stable than the organic materials in common use.

> "Hyde was able to point out that the organosilicon compounds he had been developing could be made in resinous form and that certain types were unusually heat stable. The work then turned toward resinous compounds that would be of use as a heat-stable dielectric in tapes made of glass fiber.
>
> "...the [resulting] products were shown to officials of the General Electric Company in the hope that glass-fiber tapes would be recognized as the basis of high-temperature insulation. This approach to high-temperature electrical insulation was recognized as fundamentally correct, and the study of these organosilicon insulating resins was then taken up in the General Electric laboratories, as well, under the capable guidance of Dr. E. G. Rochow and Dr. W. I. Patnode."

Sub-Case II. High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning). The Corning Glass Works, realizing the potential which these new organosilicon products held, undertook intensified studies in this area at its Fellowship in Mellon Institute, Pittsburgh, Pa. These studies were aimed not only at the production of insulating resins but also at a general survey of the chemistry of the materials and the engineering required for their production.

Inasmuch as the research at Mellon Institute on organosilicon compounds plays a significant role in the development of this technology, it is desirable at this point to review briefly the history of the Institute and the founding of the Corning Glass Fellowship.

Mellon Institute was founded in 1913 by Andrew W. Mellon and Richard B. Mellon. The Mellon brothers were attracted by the idea of industrially sponsored research fellowships, which had been originated by Dr. Robert Kennedy Duncan of the University of Kansas. It was in 1906, while attending the Sixth International Congress of Applied Chemistry in Rome, that Duncan had formed a conviction that the resources and methods of physical science should be applied to the problems of American industry. In the following year, Duncan succeeded in finding

a sponsor for the first Industrial Fellowship at the University of Kansas In 1911 he was persuaded by the Mellons to come to Pittsburgh and, after a successful trial of his fellowship system at the University of Pittsbur Mellon Institute was established under Dr. Duncan's supervision. During the ensuing half century, the Institute has been successful in fulfilling the original goals of Robert Kennedy Duncan.

In the early 1930's one of the industrially sponsored fellowships at the Institute was sponsored by the Macbeth-Evans Glass Company. The personnel consisted of Dr. R. R. McGregor and Dr. E. L. Warrick, whose interests centered around various glass systems, such as opal glasses, containing crystallites. Typically, the goals and research objectives of the Fellowship under the direction of Dr. H. Blau, Research Director at Macbeth-Evans, were not very specific. According to Warrick, their commission was, "Do anything that looks interesting and which seems likely significant." This general research strategy was continued on the Fellowship after the Macbeth-Evans Company was acquired by Corning Glass Works in the middle 1930's. One of the research problems then under examination was the development of an adhesive for glass blocks. The adhesive used up to that time was an organic material, but it was not satisfactory for this application. In the course of this investigation approximately 100 different organic adhesives were tried -- none successfully. Ethyl silicate was suggested as a possible adhesive by a member of another fellowship, who had been using this material in his studies. After some investigation into the properties of ethyl silicate, it was found that a partially hydrolyzed form of this compound worked rather well, having considerably better adhesion than any of the organic compounds yet tried. With respect to the approach to this particular problem, Dr. Warrick mentions that "The atmosphere at Mellon Institute was such that you could walk into any laboratory and talk freely with other members of the staff, and as a result there was a sense of freedom and a complete dissemination of information."

Even though ethyl silicate was a good adhesive for the glass blocks, it was observed that after a short exposure to the atmosphere, it tended to hydrolyze. Inasmuch as this compound did show promise, however, Warrick decided to investigate other organosilicon compounds as adhesives. Although the interest of Corning Glass Works at that time was primarily in the field of inorganic chemistry, their attitude toward the organosilicon work was very free and the personnel of the Fellowship were permitted to choose any direction for their research. As mentioned earlier, Corning was interested in the intermediate field between plastics and glass and, concurrent with the interest at Mellon Institute in ethyl silicate as an adhesive for glass blocks, Corning had hired Dr. James Hyde who, by 1933, was working on the problem of finding a high temperature resinous material for glass tape. Hyde's work was specifically directed toward investigations on the aromatic organosilicon compounds, while the work generated through the adhesive problem at Mellon Institute was directed toward the aliphatic organosilicon compounds.

A major event in the course of the investigation of the hydrolysis of ethyl silicate was the uncovering by McGregor and Warrick of extensive literature on organosilicon compounds, including especially the work of Kipping. Aided and stimulated by this well of knowledge on organosilicone chemistry and interested in producing new useful materials, they were led to prepare many organosilicon compounds and derivatives of ethyl silicate. Dr. Warrick pointed out that the direction of investigation was at all times internally generated and that Dr. McGregor, who at that time was the Head of the Fellowship, created an atmosphere conducive to good exploratory research. He was willing to talk at any time to the staff about the problems on which they were working, but he <u>never</u> told them what course this research should take. In late 1939 and early 1940, from investigations of the aliphatic silicates, it was noticed that many of the reaction products were high viscosity fluids with temperature-viscosity relations radically different from that of common hydrocarbon lubricating oil. (On heating, the viscosity did not decrease as rapidly as in the hydrocarbon lubricating oil.) In addition, it was noticed that these materials were

extremely inert to attack by oxygen. Dr. McGregor, realizing the potential of these materials as oxidation resistant lubricants, mentioned them to a personal friend -- an employee of the Mine Safety Appliances Company -- at a meeting of the Pittsburgh Chemists' Club. By coincidence, Mine Safety Appliances was looking for just such a material for application in oxygen pumping systems. Some of the organosilicon materials were tried, and it was found that they served extremely well in this application. Up to this point, all the work in the area of organosilicon compounds was guided simply by observation and by the basic curiosity of the investigators. After the successful application of the oxidation resistant lubricants, Warrick felt that he ought to pursue some fundamental work on the oxidation stability of these materials.

In 1940, at the encouragement of Dr. McGregor, a pilot plant was established at Mellon Institute to manufacture small quantities of these various silicone fluids. Dr. John Speier, who joined the Fellowship in 1943, points out that Dr. McGregor was "quite a salesman" and that without this element of salesmanship many of the advances which were made during this period could not have been accomplished. It was necessary to "sell" the Corning Glass Works on the possibilities of this new avenue of research.

In the course of studies on the oxidation properties of the silicone fluids, it was noticed that many of the fluids became resinous and rubbery. Feeling that there might be something of interest in these resinous materials, McGregor and his colleagues determined to look further into their preparation and properties. In the meantime (1940-1942) Corning Glass Works had taken an increasing interest in the silicone materials. It was obvious to the company that they did not have people or facilities to explore the area properly. They subsequently made an agreement with the Dow Chemical Company to jointly pursue research in organosilicon chemistry, and in 1943 the Dow Corning Corporation was formed. The investigations into the resinous silicones revealed excellent dielectric

properties, and then an additional pilot plant was established at Mellon Institute for limited production of these materials. It is interesting to note that one of the factors leading to organization of the Dow Corning Corporation was the interest of Admiral Hyman Rickover in the silicone dielectrics for use in submarines. During World War II his recommendations enabled the company to secure money to build a complete plant to produce them. Subsequently these silicones were extensively used during World War II as electrical insulating materials in aircraft as well as in submarines. They were the first materials with a product motivation to come out of the Fellowship. Dr. Warrick points out, however, that the decision to investigate these materials was not dictated by Corning, yet the company encouraged continuation of the work whenever interesting properties were uncovered.

Sub-Case III: Silicone Elastomers (Mellon Institute and Dow Corning). While investigating the properties of various methyl silicone polymers in 1944, Dr. Warrick observed that many of them had properties similar to natural gums and rubbers, although they lacked the strength of polyester rubber. Warrick again took the opportunity to discuss these rubber-like materials with personnel of another fellowship at Mellon Institute who had been working on natural rubber. They suggested trying benzoyl peroxide to attempt to vulcanize the new silicone compounds since this agent worked very well on natural rubbers. There was no reason to believe that this material would react with methyl silicone compounds as it did with rubber and, as pointed out by Dr. Warrick, the method was simply one of trial and error. But in fact, the silicone material did gain rubber-like characteristics, including considerable strength, through the benzoyl peroxide treatment. As a result of this work, a patent application for the vulcanization of liquid silicone polymers was filed by Dow Corning Corporation in 1944, and eventually issued as U.S. Patent No. 2,460,795.

It was then decided that the work of the Fellowship should be directed toward some fundamental studies of these rubber-like compounds and the chemistry involved in their formation. As an extension of this work, a new research goal was established as the preparation of organo-silicon compounds with predetermined functional substituents. Dr. Warrick states, "This fundamental work on functional side groups, begun by Dr. Speier, was extremely successful. Today approximately 30 to 40 per cent of the 800 products marketed by Dow Corning Corporation are the result of these early studies."

The early silicone rubber materials were found to be rather limited in applications by their relatively low strength as compared to natural rubber. Maximum tensile strength was in the order of 500 lbs./in.^{2} and the material had the consistency of "tough cheese" rather similar to the common art gum eraser. Although Dow Corning was able to commercialize some of these rubbers, uses were severely restricted by the poor physical properties.

In the course of the studies on rubber-like materials, it came to be realized that two factors -- the molecular weight of the silicone polymer and the nature of the filler -- were extremely important to the ultimate properties of the rubber. The following is a brief account of how these observations were made.

In the winter of 1949 a significant breakthrough occurred which led ultimately to the high strength silicone rubber in use today. Dr. G. C. Akerlof of the Coal Products Fellowship at Mellon was studying methods for separating oxygen from air. He had heard that certain of the silicone resins were selectively permeable to gases. He discussed his problem with the silicones group, specifically inquiring whether any of the new resins could be made in the form of a thin membrane through which gas might diffuse. In an effort to accommodate Dr. Akerlof, it was decided to attempt to make such a membrane from a certain resin sample that had been on the laboratory shelf for some time. This material, designated as "K-gel", was then thought to be a silicone polymer composed of short

chains, and highly crosslinked. A filler of finely divided silica (SiO_2) had shown some success in improving the strength of the rubbers, and this material was chosen for the experiment. Upon vulcanization under high pressure the mixture gave a rubber with remarkable properties. The thin sheet that was formed was extremely elastic and behaved more like natural rubber than any previously prepared. Mr. Silas Braley, Jr., who was a member of the silicones fellowship at the time, and who is now Director of the Dow-Corning Center for Aid to Medical Research, described the amazement at the elastic properties of the material when a piece was stretched across a beaker and he was able to poke his finger almost to the bottom without the film breaking. This was the first time silicone rubber had behaved this way, and actually the sample had a tensile strength of 1000 to 1500 lbs./in.^{2}. Though the film was not useful as a membrane for removing oxygen from air, it did serve to point out a direction for future fellowship research in the field of high strength silicone rubber.

The reasons for the exceptional strength of the membrane film were not at first obvious. It was first thought that the high pressure treatment might have been significant, but the results could not be duplicated by similar treatment of other resins. Further investigation of the "K-gel" revealed that it was not composed of short but highly cross-linked chains, as had been thought previously, but actually had a rather high molecular weight and was only slightly crosslinked. It soon became apparent through experiments with other polymers that high molecular weight was significant in preparing a successful rubber. But it was not the only factor. Before the membrane experiment, fillers such as titanium oxide and diatomaceous earth had been used in rubber preparations; but when preparation of the oxygen-removing membrane was attempted, finely divided silica (SiO_2) was used in the hope of increasing the oxygen removing efficiency. As it turned out, the silica filler affected the strength of the rubber. Upon the recognition of this fact,

a considerable effort was undertaken to find appropriate fillers for high molecular weight polymers. Development of a rubber to the product stage form received great impetus from the Dow-Corning research group in Midland, Michigan, who gave all possible support to the group at Mellon and supplied them with various polymers for work on improving strength.

It was not clear in the beginning what properties of the filler were significant and therefore many materials were tried. Through empirical studies, it was learned that small particle size and large surface area were the important features to seek. Any material with small particle size was tried. Finely divided carbon, which is used as a filler in organic rubbers, could not be used because of its reactivity toward the vulcanizing agent. Ultimately, there was found a very finely divided silica (that has since come to be known as "Degussa" silica) manufactured in Germany by Deutsche Gold und Silver Scherdeanstalt.

After these initial observations by the Mellon Institute group, a considerable research and development effort was initiated at the Dow Corning research laboratories on preparation of fillers. It had been observed that on standing the mixture of filler and resin would vulcanize spontaneously. (Soon after the commercial introduction of the high strength rubber -- actually only six months after the first experiments -- many customers were receiving mixed polymer and filler for further use, and to their surprise found a solid mass, which could not be removed from the container.) It was suggested that a surface reaction was occurring with hydroxyl groups on the silica filler. An intensive research program was begun at Dow Corning to find a way to treat the surface of the filler so as to render it unreactive, or at least to slow down the reaction. Finally a method was developed to replace the hydroxyl groups of the silica with methyl groups, and this eliminated the problem of premature vulcanization. A patent application for this procedure was filed in December of 1951 by George Kunkle, Keith Polmanteer, and James McHard, the Dow Corning research men who developed

the process. Since the realization that the fillers are the most significant factor in the properties of high strength rubber, the investigation of various silica fillers has been a major research effort at Dow Corning.

In 1952 work was begun at Mellon Institute in another direction -- on radiation studies of silicone rubber materials. Warrick relates the beginning of this work as follows: "Purely by chance, a professor from the University of Pittsburgh Cyclotron Laboratory came to Mellon Institute and requested various compounds for his irradiation studies. We were happy to give him several of our vulcanized and unvulcanized silicone rubbers just to see what would happen. Much to our surprise, we observed that the unvulcanized material became vulcanized. To confirm our observations, we sent several samples to Stanford Research Institute to investigate the same type of reactions. We found the same results. Because of this we began to intensify our fundamental studies into the effects of radiation on our silicone materials. As a result of this work, radiation resistant rubbers were produced."

One of the fundamental characteristics of silicone polymers and rubbers is a low glass transition temperature. This property accounts for the extremely good low temperature flexibility. However, silicone rubber <u>per se</u> does not have the high tensile strength, and good elongation and tear resistance, of organic rubbers. During the 1950's studies were conducted on the Mellon Fellowship, in cooperation with Dr. L. E. Alexander. It was found that at normal temperatures silicone rubbers are much less prone to crystallize on stretching than natural rubber. Obviously what was needed was a silicone rubber which either would crystallize more readily on stretching or which contained some degree of crystallinity in the relaxed state. Subsequently, and with the aid of the Dow Corning Corporation, Dr. R. L. Merker developed a series of silicone block copolymers based upon combinations of silphenylene siloxane blocks and dimethylsiloxane blocks. The resulting silicone rubber polymers have tensile strengths in the vicinity of 3000 lbs./in.^{2}

in the unvulcanized state. A patent application for this invention was filed in 1960 and resulted in U.S. Patent No. 3,202,634 in August 1965.

Other fundamental studies were also encouraged in the early 1950's. Dr. Paul Lauterbur who had previously become interested in nuclear magnetic resonance spectroscopy joined the Fellowship. He was able to convince Drs. McGregor and Warrick that Si^{29} NMR spectra had potential for studies of silicon-containing materials. They agreed that this technique might add to the knowledge of silicone technology and encouraged Dow Corning to support the purchase of the NMR equipment. Lauterbur not only studied silicon-containing compounds, but also investigated the newly developing field of C^{13} and P^{31} NMR spectroscopy. It should be pointed out that during the course of his studies Lauterbur, through the Institute policy of encouraging personnel to obtain advanced degrees at the neighboring University of Pittsburgh, was able to complete the work for his doctor of philosophy degree. (The same is true of Warrick and Speier who obtained their Ph.D.'s at Carnegie Institute of Technology and the University of Pittsburgh, respectively, while working at Mellon Institute. Warrick and Speier both mentioned several times during the course of conversations that this educational opportunity was one of the important values of the fellowship system at Mellon Institute.)

Sub-Case IV. Biomedical Applications (Dow Corning). A notable offshoot from the development of high strength silicone rubber has been the interest of the medical community. Late in the 1950's, after the high strength rubber had been commercialized for some time, Dow Corning began to receive inquiries and requests from surgeons for samples of the material molded in specific shapes and forms. It had been observed in several instances that, when introduced into the human body, silicone rubber did not cause adverse reactions observed with many other materials. Specifically, in several applications, silicone

rubber did not cause the severe blood clotting that has generally been seen with foreign materials used in various prosthetic devices.

Mr. Braley, who transferred from the Mellon Fellowship to the Dow-Corning product engineering group in Midland, took an interest in these applications and tried to satisfy each individual request. As experimental prosthetic devices were disseminated throughout the medical circles , publications began to appear lauding the use of silicone rubber. Soon Dow Corning was overwhelmed with requests for the material -- not for large amounts, but for very small quantities molded in specific shapes. The company decided that, even though potential sales of large volumes of silicone rubber for these applications could be not be anticipated, the prospect of practical benefits coming from the research warranted the forming of a group specifically for the study and dissemination of information relating to the use of silicone rubber in medical applications. In 1958, Dow Corning formed its Center for Aid to Medical Research under the direction of Dr. McGregor, the long-time Administrative Fellow in charge of the Mellon Fellowship. Mr. Braley, whose original interest in this work added impetus to the development of these devices, served as McGregor's assistant at the Center. Upon the death of McGregor in 1965, Braley assumed the duties of Director. The Center has continued to grow as new and important medical applications have been found. Silicone rubber has found use in artificial blood vessels, in a drain tube for hydrocephalic children, in heart valves, and in many other substitutes for parts of vital organs. Today the Center publishes a brochure which describes new uses of silicon rubber as they are developed in medical practice.

Retrospect

The names McGregor, Speier, and Warrick figure prominently in this account of the initial work leading directly to the development of organosilocons as useful commercial materials. It is therefore of

interest to record some of their thoughts in retrospect concerning the nature of some of the events which produced the successful result.

Dr. McGregor's views are recorded in many places including especially his book on "Silicones and Their Uses" published in 1954. We reproduce as Appendix B his section on the "Commercial Development of Silicones". Here we quote from the latter part (pp. 24-26) of the introductory chapter on early studies in Organosilicon Chemistry:

> "The stage was at last set for the appearance of silicones. And it is only right that we should recognize who was responsible for the setting. Long years of earnest work by scientists who were curious about natural phenomena had been rewarded by a wide knowledge of the peculiarities of silicon chemistry. Others who were curious about large molecules, how they were formed naturally and how they could be produced synthetically, had learned fundamental truths about them and had shown principles governing their formation. It was not too much to expect that these two lines of activity should be brought together, that the knowledge of silicon-containing compounds and the knowledge of the principles governing the formation of large molecules should result in the synthesis of large molecules containing silicon. What the properties of such compounds would be one could only guess, but the fact that the two necessary lines of information had been developed assured the appearance of the joint product. Now it was simply a matter of time.
>
> "But it should not be assumed that the beginning of 'applied' research marked the end of 'pure' research. Although the importance of the commercial applications of silicones had become recognized by industry the intriguing nature of their chemistry was being attested by numerous academic publications. Work that had been started as a result of scientific curiosity a century earlier was now bearing fruit that had not been foreseen. It had been assumed originally that results would show silicon to be simply an analogue of carbon. While this proved to be the case in a limited sense, the differences were much more evident than the similarities. What had been started as a search for further knowledge proved to be the groundwork for technological advance that has proved helpful to industry and in so doing has contributed its part to improving our standard of living.

"It would be a mistake to consider this the end of the story from the standpoint of either pure or applied science. While industry is naturally doing a great deal to further its knowledge of these compounds and to develop more economical methods of preparing them, the centers of pure research are doing their share to clarify points in organosilicon chemistry that are still obscure. The number of papers of this latter type appearing between the years 1945 and 1950 have been about 100 times as great as in the century preceding. Industry has recognized the fact that it has eaten up in 10 years the pure research of 100 years. Without this type of research, technology would wither. Thus we see a greater and greater overlapping of the fields of pure and applied research, the only point of distinction between the two being the motivation of the individual who does the work. And who shall say that the mental satisfaction of the one is any less real than the material satisfaction of the other?"

The recollections of Dr. Speier are of special interest:

"In 1943 I came to M.I. with a M.Sc. degree from the University of Florida where I worked on terpenes and other natural products. These I liked. They are highly reactive complex molecules that are forever rearranging and reacting with all kinds of things. The silicones struck me as, in Kipping's term, 'uninviting.' The silicones we were settling down to, all had methyl or phenyl groups attached to silicon. The intermediates all reacted with water and sooner or later ended up as polymers with nothing but methyl or phenyl groups attached to an SiOSi chain or network. These may have been and are great dielectrics, etc. but chemically they are nearly inert and they are useful chiefly for this reason. I couldn't get real excited about making hundreds more like these. Further, rubbers and fluids were never very intriguing to me for some unknowable reason. I wanted to put organically reactive groups on silicon in place of the methyls and phenyls. These I wanted to attach to the Si-C bond to come up with families of silicon-substituted organically functional molecules, which would give the opportunity to study the effect of an atom like silicon upon the chemical properties of organic functional groups.

"The trouble with this idea was that such molecules were practically unknown. Friedel and Crafts had made $Et_3SiCHCH_3$ (Cl), $Et_3SiCHCH_3$ (OAc) and $Et_3SiCHCH_3$ (CH). Kipping had made a few sulfonic acids having groups like Si-CH_2- -SO_3H, and a few nitro compounds such as $Si(C_6H_4NO_2)_4$. That was about all there was, and these were not what I wanted. I wanted structures that were functional at the silicon atom, i.e., with groups like $-SiCl_3$, $-Si(OMe)_3$, $-SiMeCl_2$, $SiMe_2OH$, etc., and also functional on the organic group. I had some ideas of how these might be made in systematic series to given an idea of 'silicon' effect on organic molecules and the effect of other atoms and groups on silicon upon the effect of that silicon.

"I talked to Dr. Bernard Daubert at Pitt about how such molecules might be incorporated into fats, proteins, and other natural products (which hasn't been done yet!) and he agreed to be my faculty advisor on such a project and accept work like this for my Ph.D.

"I talked to Dr. McGregor, and in his usual manner he encouraged the whole thing and said go ahead. I talked to Warrick, he was much interested in making silicone fluids with at least a few organically functional sites in them to serve as means for vulcanization to make rubbers. Also such groups might have led to stronger rubbers which he greatly desired.

"So the three of us talked to Shailer L. Bass, who was Dow Corning's director of research (now president). He said okay; we could try if we wanted to. Daubert insisted that anything we did for a degree had to be published. Bass and the legal department at Dow Corning and at Corning agreed to this with only a few days of discussion (six months would be needed today) and we took off.

"The results of this line of research have been for the most part gratifying. Dow Corning has many patents on such compounds now. I have about 45 myself and the people working with or around me must have about as many more. There has been much unexpected fallout in every area of Dow Corning's present business. The commercial use of such functional silicones is now a new thing. They are now appearing on the market and no one knows really where they will end up. The story may be more, or less interesting in 1975."

Today he Dow Corning Corporation is the largest company in the field of organosilicon products and holds approximately 60% of the total market. Although much of the early work in this area was performed at Mellon Institute, a good deal of the subsequent engineering and fundamental work on silicones was performed at the Dow Corning laboratories. In estimating the value of Mellon Institute to organosilicon chemistry, Dr. Warrick states, "The value of the Institute was pretty high; but, of course, the same information would have been found eventually without the Institute. However, the Fellowship certainly accelerated the science of organosilicon chemistry." When asked what at Mellon Institute contributed to the acceleration, Warrick stated, "The freedom to work on subjects of interest and the proximity and existence of people in other fields were the major contributing factors. Also, the general relaxed climate and pace of work contributed a great deal." Dr. Warrick felt that the single motivating factor for the studies at Mellon Institute was the accumulation of fundamental knowledge in the field of organosilicon chemistry. He added that the very informal channels of communication with the sponsor organization contributed to the general atmosphere of this research effort.

Concerning "the relaxed climate and pace" Dr. Speir added:

> "In a way Warrick is right, if he means unregimented. We came and went pretty freely with little supervision or comment by anyone. If we took two hours for lunch, no one objected.
>
> "On the other hand, if we worked till midnight and we did many, many times -- no one said anything either. The pace of work was self-imposed but very fast. Very few of us worked a 40 hour week, and those that did usually left after a bit (by their own choice).
>
> "McGregor could usually be found working on Sundays, Saturdays, anytime at night, even if he might disappear in the middle of the morning when a good organization man would be at his greatest prominence. The same for Warrick. I was trying to work full time and get a Ph.D. as fast as I could. So during 1944-1947 I practically lived in the Institute. After I got the degree, I don't think I slowed down very much except I did quit working on Sunday.

"If there is a moral in all this I guess it has to do with the freedom we enjoyed at Mellon Institute to depart from urgent, obvious needs of a struggling young company, to attack problems that seemed important to a struggling young student. It is not possible that everyone can enjoy this kind of freedom; but somehow it is imperative that some must enjoy it. How any manager can select who should have it and who should not, and when, is a mystery to me. Fellowship 222 at M.I. was a good and profitable one. Was this an accident of history or can similar things be brought about repeatedly by careful design?"

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(1) R. R. McGregor, "Silicones and Their Uses," McGraw-Hill Book Company, Inc., New York, 1954.

(2) M. Persoz, Ann. chim. et phys. (2), 44, 315 (1983).

(3) W. Schlenk, F. Renning, and G. Racky, Ber. 44, 1178 (1911).

APPENDIX A

Mellon Institute: Organization and Character

"Mellon Institute is an endowed nonprofit corporate body for conducting comprehensive investigations in the natural sciences, for training research workers, and for providing technical information for the benefit of the profession, the public, and industry."

The above brief descriptive paragraph appearing on Mellon Institute literature expresses the purposes motivating all activities at the Institute. Research activities and the scientists who perform them fall into two categories, the Fellowships and the Independent Research Groups.

A Fellowship is a group of scientists (one or more) working on fundamental or applied problems of interest to a particular sponsor, either a single firm or an association of companies, which bears all costs, including overhead charges, for the activities of its Fellowship. Although support for Fellowship activities is usually on a year-to-year contract basis, most of the Fellowships have been stable with regard to personnel and sponsor for many years. Three hundred investigators are engaged in Fellowship activities.

As compared to other research institutes, Mellon Institute is unique in several ways.

--Founded over fifty years ago as part of the University of Pittsburgh, it was the first of the institutes to undertake research aimed at the utilization of science for the development of industrial technology. During its early years, it served as a prototype for other institutes and a training ground for industrial research departments that have come to constitute much of the strength of the chemical and petroleum industries. Companies like Union Carbide and Dow Corning trace their early successes, or even origin, to work done under contract at Mellon Institute.

--Heeding the lessons of academic experience, Mellon Institute, alone among the institutes, requires that contracts involve the effort of at least one research worker for one year, and that the individual researcher normally engages during any given period in work exclusively for a single sponsor. Indeed, in the university tradition, he is designated as a "Fellow" and his project as a "Fellowship" for a given sponsor. There is a requirement that significant results be published, when the sponsor's interests have been protected, and that projects shall have social merit.

--Thus, Mellon Institute personnel have long been engaged in pioneering applied research based on research competence in chemistry and related areas of physics, much of it for materials producing companies and in continued close contact with their personnel. Advanced development work, better done in industrial plants or requiring more advanced engineering, has not generally been undertaken.

Mellon Institute evolved to provide a transitional stage between the scientific community in the university and the industrial-research community; it has some of the features of each and is closely allied with both.

While evolving from the University, Mellon Institute has retained informal semiautonomous positions for the "Research Director", the "Fellowship Head," and the "Research Fellow", who are somewhat akin to a Department Head, Professor and senior postdoctoral student, respectively, in a university. Research tends to be deeply rooted in chemical, physical, and biological science, and such that one or two problems occupy an investigator full time for a year or more. The sponsor is, in a sense, in the position of supplying "fellowship support" for progress in a new area. Further, the Research Fellows regard themselves as temporary, though loyal, members of the Institute, destined to go on to industry or academic posts elsewhere. Freedom of

inquiry, lack of administrative detail, and informality, lend the Institute something of the atmosphere of the university instead of the stringently managed atmosphere sometimes necessary in industrial development work.

On the other hand, members of the Fellowships, unlike their university cousins, are generally highly motivated towards pioneering applied research, i.e., to using their creative talents to pioneer new technology. They are aided in this task generally by close contact with personnel from industry, including especially the sponsor but also other members of the institute, visitors from other sponsors, alumni of the Institute and members of industry locally. In addition, travel to the sponsor laboratory or plant, and to scientific and engineering meetings is encouraged. Thus the Fellow at Mellon Institute generally is exposed to a number of sources of knowledge of new science, of new technology and of some of the "open problems" or "needs" in each.

It is pertinent to mention the "alumni" of Mellon Institute. Perhaps uniquely among "mission-oriented" laboratories, the Institute regards it as a basic goal to train personnel and to encourage recruiting of its personnel by the outside world. A great number of the Institute's 3000 alumni today hold responsible positions in the industrial and academic research-oriented community.

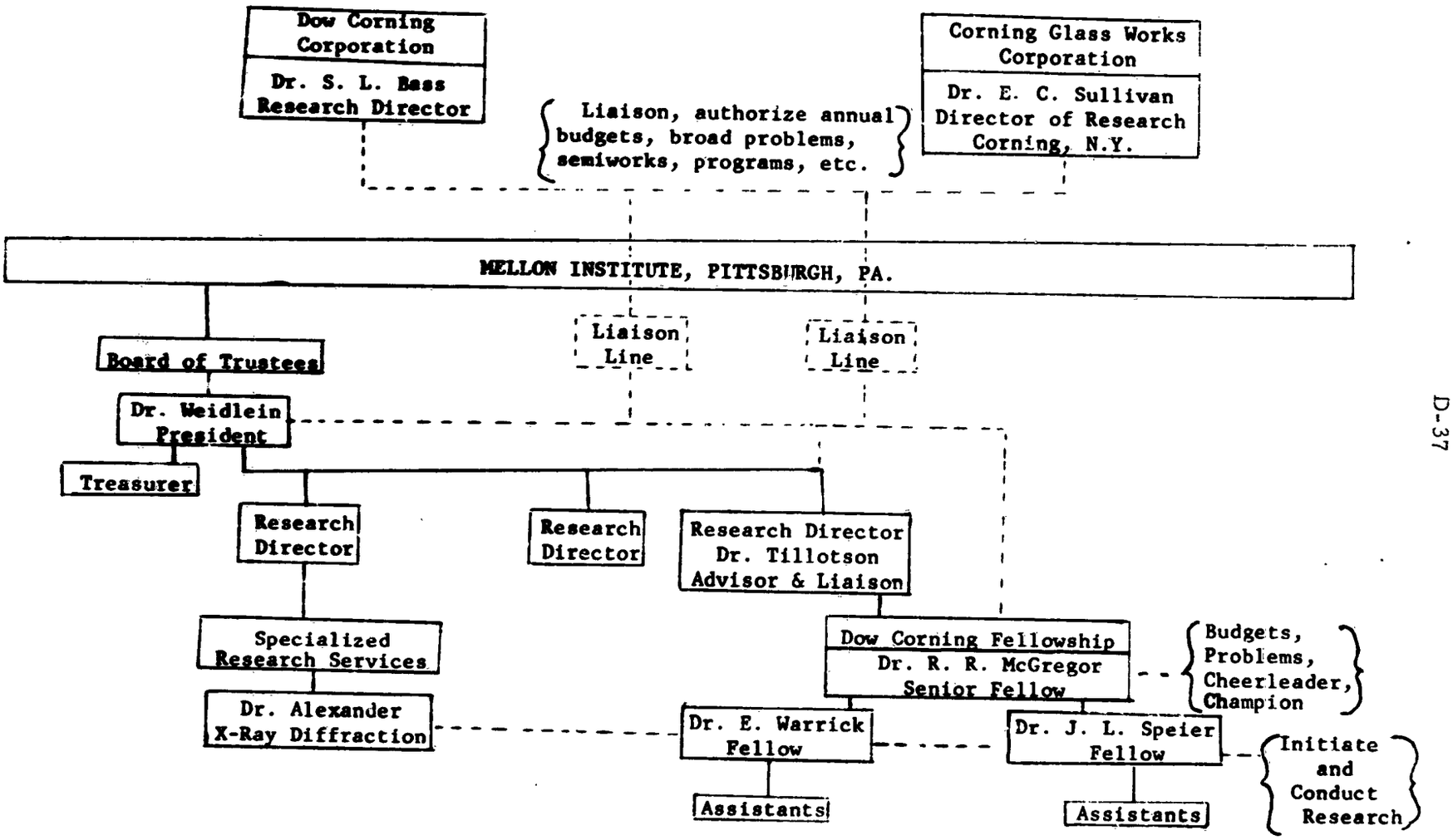
The disciplines represented at Mellon Institute over the years include chemistry, and materials especially, together with biochemistry and certain areas of physics and mathematics.

The Independent Research within the Institute is supported by income from a Fundamental Research Trust established in 1957 and by grants and contracts from government agencies. The twin goals are new fundamental scientific knowledge and the development of promising young scientists. Publication of significant findings is mandatory. A total of nearly

one hundred and fifty investigators are involved in these fundamental studies -- a permanent staff of about twenty Senior Fellows and about fifty Fellows on two or three year tenure appointments. Althougn the Institute has always supported basic science studies, the program of the present scope emerged since 1957 subsequent to most events in this case history. Consequently the Independent Research is not emphasized here.

ORGANIZATION FOR CORNING AND DOW CORRNING SUPPORTED SILICONE RESEARCH AT MELLON INSTITUTE

(As Seen from Mellon Institute Files)



APPENDIX B

"Commercial Development of Silicones," excerpt from Silicones and Their Uses, R. R. McGregor, (McGraw Hill, 1954)*

"In view of the wide background of knowledge just described the question may be asked: Why was the commercial development of silicones so long delayed? The previous history provides some of the answers. The classical chemists had long been schooled in investigation methods that called for the separation, by distillation or crystallization, of pure compounds. Large, poorly definable polymeric bodies did not lend themselves to this method of approach. No doubt Kipping expressed the sentiments of many other chemists of his day when he described such products as 'uninviting glues.' There was little commercial background at the time to suggest that these 'glues' had any practical significance. Further, those interested in chemical research had few, if any, connections with industry. Without the backing which industry could furnish there was great difficulty and little incentive in embarking on a study of such indefinable products.

"The word 'polymer' had been in common use for years, but it was not until Staudinger voiced his concept of 'macromolecules' in the 1920s that there was a major interest in the study of them. The recognition that these undistillable and non-crystallizable bodies were built up by known chemical reactions and could be considered simply as very large molecules opened up the enormous field of polymer research. This heralded the beginning of the 'plastic age', and high polymers of many types began to appear as commercial products. Some of these products were transparent and could be used, with more or less success, in the place of glass.

"The possibility of a hybrid polymer -- a cross between the organic polymers (plastics) and the inorganic polymers (glasses) -- appealed to some glass manufacturers as a desirable possibility. Dr. E. C. Sullivan, then Director of Research for the Corning Glass Works of Corning, N.Y., engaged Dr. J. F. Hyde, an organic chemist, to investigate this matter.

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* Permission for this quotation granted by McGraw-Hill Book Company

"Hyde was acquainted with the literature describing organosilicon research, and he had the advantage of the rapidly accumulating knowledge of large polymers. By using knowledge from both these fields he was able to prepare large polymers containing both organic and inorganic constituents.

"At this point there arose one of thos coincidences that often direct a course of action. The Corning Glass Works had just begun the development of glass fibers and was on the lookout for appropriate markets. One of the most promising outlets for this product appeared to be as a woven tape for use in electrical insulation. Cotton, impregnated with a resinous dielectric, had been used but it would char at elevated temperature. This difficulty could be overcome by the use of glass tape in place of the cotton, but it was found that the resin impregnant would stand only slightly more heat than the cotton would. Thus there was but little advantage in using the glass. To realize the full value of the glass tape there was needed a resinous dielectric that was considerably more heat stable than the organic materials in common use.

"Hyde was able to point out that the organosilicon polymers he had been developing could be made in resinous form and that certain types were unusually heat stable. The work then turned toward resinous compounds that would be of use as a heat-stable dielectric in tapes made of glass fiber.

"Studies and experimental work were then conducted along these lines. When sufficient progress had been made to justify a demonstration, the products were shown to officials of the General Electric Company in the hope that glass-fiber tapes would be recognized as the basis of high-temperature insulation. This approach to high-temperature electrical insulation was recognized as fundamentally correct, and the study of these organosilicon insulating resins was then taken up in the General Electric laboratories as well, under the capable guidance of Dr. E. G. Rochow and Dr. W. I. Patnode. About this time the Corning Glass Works

Fellowship at Mellon Institute, Pittsburgh, under the headship of the author, undertook similar work, aimed not only at the production of insulating resins but also at a general survey of the chemistry of the materials and the engineering required for their production.

"The knowledge of this work catalyzed similar investigations by other industrial laboratories, and soon the technical literature showed that ever-increasing attention was being given to organosilicon compounds.

"By 1942 work had progressed with the Corning group to the point where commercial production could be considered. As the manufacture of these materials was in the nature of an organic synthesis rather than a glassmaking operation, the Corning Glass Works approached the Dow Chemical Company with a view to obtaining engineering and research assistance. The result was that in 1943 the formation of the Dow Corning Corporation, financed jointly by the Dow Chemical Company and the Corning Glass Works, was announced. The fury of World War II was then at its peak and high priority was granted to Dow Corning for the erection of a factory and procurement of equipment, as Dow Corning was the only source of several organosilicon products demanded by the military forces. While these materials were being produced in commercial quantities, research on their improvement continued and it was inevitable that new and valuable products would be found. With the close of the war it was therefore possible to offer to industry commercial quantities of a wide range of products with properties that had not been known previously.

"Meanwhile other companies, though not actually producing, had been conducting vigorous research. In 1946 the General Electric Company announced the opening of its plant for the production of silicones. In 1949 the Plaskon Division of the Libbey-Owens-Ford Glass Company advertised silicone products for sale, directing attention largely to materials useful with alkyd coatings. About this time the Linde Air Products Company, a division of Union Carbide and Carbon Corporation, commenced pilot-plant work in Tonawanda, N.Y. At this writing they are planning for full-scale production of a broad line of silicone products.

"Although the original aim of the investigations carried out had been to develop electrical insulating resins, the first materials to be made commercially were the silicone fluids.

"The limited amounts of fluids that were first available restricted their use to applications such as damping fluids in sensitive instruments used by the Air Force. The stability of the fluids and their small change of viscosity with temperature were the properties that proved the most valuable here. As production increased the fluids were formulated into a greaselike material that proved to be of great value as an ignition sealing compound for use in the spark-plug wells of military aircraft engines. The resins had by this time reached the point of development where it was possible to use them, in conjunction with glass-fiber tapes, as the insulating medium in motors. Cooperative work with the armed forces helped in their development and appraisal.

"The usefulness of the fluids as antifoam agents in petroleum oils had been demonstrated and some military specifications demanded their addition to many types of oils.

"In 1945 both the Dow Corning Corporation and the General Electric Company announced the development of a silicone rubber that was useful at temperatures too high for the functioning of organic rubber.

"All these products were so necessary for military requirements that little or none of them was available for civilian use. When hostilities concluded in the summer of 1945 the military demands ceased and silicones were left without a market. But the versatility of these materials was such that energy and ingenuity soon showed how they could be adapted to a peacetime economy.

"The fluids were found to be excellent mold-release agents in the molding of rubber tires and other rubber goods, as well as of many types of plastics. Polishes and lubricants were developed, and the damping fluids were adapted to peacetime requirements. The resins were improved and developed into high-temperature coatings and laminating

materials. The silicone rubber was given improved physical properties and was formulated to maintain its properties at extremely low temperatures while still retaining its high-temperature stability. Application to the waterproofing of textiles was developed.

"Evidence accumulated that the silicones in one form or another could be profitably applied in almost any industry one could name. Demand for peacetime applications soon surpassed the requirements for early military use, and expansion of facilities became necessary for all producers.

"The pattern of growth is familiar, for as production has been increased prices have dropped. This allows application to a greater variety of industries and products; more production is then required and the cycle is repeated. The conclusion of the matter appears to be still far distant, and nobody short of a professional soothsayer is willing to hazard a guess as to the position of silicones in the industries of the future."

ANALYSIS FOR A CASE HISTORY OF THE DEVELOPMENT OF SILICONES

For the purpose of analysis, this case history has been divided into sub-cases as shown below.

Sub-Case	Title
I	Silicone polymers for heat resistant resins (Corning Glass Works)
II	High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning Corporation)
III	Polysilicon Elastomers (Mellon Institute and Dow Corning Corporation)
IV	Biomedical Applications (Dow Corning Corporation)

DESCRIPTION OF REIs

Stage*	REI	Description
		Sub-case I. Silicone Polymers for Heat Resistant Resins (Corning Glass Works)
0	a	Development of silicone chemistry and polymer science
1	b	Recognition of possibility of new class of polymers with silicon as part of chains (Sullivan-Hyde)
2	c	Recognition of need for high temperature resin for dielectrics (with glass fiber) and that new silicon resins could do the job (Hyde)
3,4	d	Corning takes result to General Electric
2	e	Recognition at GE of a new class of polymers and assignment of Rochow and Patnode
		Sub-case II. High Temperature Lubricants and Dielectrics (Mellon Institute and Dow Corning)
3	f	Recognition that ethyl silicate may be useful adhesive for glass blocks (McGregor-Warrick)
1	g	Recognition of treasure of literature on organosilicon chemistry and possibility of making useful new materials (McGregor-Warrick-Kipping)
3	h	Recognition of viscosity-temperature properties and oxidati resistance of new aliphatic silicone fluid as possible high-temperature, stable lubricants for oxygen pumping systems (McGregor-Warrick)
5	i	Establishment, in 1940, of a pilot plant at Mellon Institute for the manufacture of small quantities of silicone fluids

* See Page 49 for identification of the stages of development considered he

0	j	Decision to look at the fundamentals of oxidation stability of silicone fluids (McGregor)
1	k	Recognition that resinous rubbery materials with good dielectric properties could be made by oxidation of silicone fluids (McGregor-Warrick-Speier)
5	l	1940 pilot plant at Mellon Institute for production of dielectric resins
6	m	Formation of Dow Corning with a Government contract for production of dielectric materials for submarines (and lubricants for aircraft)
		Sub-case III. Polysilicon Elastomers (Mellon Institute and Dow Corning)
1	n	Recognition that silicone polymers were elastomeric (McGregor-Warrick-Speier)
2	o	Vulcanization to useful rubber (Warrick)
0	p	Decision to investigate fundamentals of organosilicon chemistry with view to synthesis of polymers of varied structure (various side groups) (McGregor-Warrick-Speier)
0	q	Chance exploratory work on radiation of silicone resins showed possible vulcanization route
1	r	Decision to investigate fundamentals of radiation effects on silicone rubbers led to development of radiation resistant silicone rubbers
1	s	Chance exploratory work on vulcanized silicone resins with SiO_2 filler (as gas preferential diffusion membrane) showed extremely high strength.

2	t	Intensive studies at Mellon Institute and later at Dow Corning led to the development of superior polymer-filler combination
0	u	Recognition by Dr. Alexander, Warrick, et al., that silicones are less prone to crystallize than normal rubber, and acceptance of crystallizable structure as a goal
1,2	v	Development by Merker et al at Mellon Institute of crystallizable block copolymers which behave as high modulus crystallizable rubber. (1958-1965)

Sub-case IV. Bio-Medical Applications (Dow Corning)

1	w	Recognition by medical community that silicone rubber had unusual nonthrombogenic tendencies when implanted in the body (prosthetic devices)
2	x	Decision to form a research group for the study and dissemination of information relating to the use of silicone rubber in medical applications (1958). Center for Aid to Medical Research at Dow Corning
3	y	Tests and demonstrations by surgeons of utility in artificial blood vessels, heart valves, etc.

STAGES AT WHICH REIs OCCURRED

Stage No.*	Sub-case I	Sub-case II	Sub-case III	Sub-Case IV
0	a	j	p,q,u	
1	b,e	g,k	n,r,s,v	w
2	c		o,t,v	x
3	d	f,n		y
4				
5		i,l		
6		m		

* Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

FREQUENCY OF FACTORS FOR REIs

(Summary)

Factor		Total Frequency
4	Importance of recognized need	20/25
5	Requirement of flexibility to change direction during work and local control of funds (easily available resources)	20/25
8	Communications across organizations	18/25
11	Freedom for individuals	17/25
1	High educational level (advanced degree) of principal investigator	14/25
7	Basic research in the laboratory (or institution or organization)	14/25
12	Broad spectrum of types of laboratories	14/25
15	Organizational structure (barriers and bonds)	13/25
2	Importance of management	12/25
6	Industrial laboratory involvement	12/25
10	Importance of a "champion"	11/25
14	Prior experience with innovation	10/25
13	Geographic proximity	9/25
9	Technical problem as the principal obstacle	2/25
3	Importance of Government-sponsored research	1/25

FREQUENCY OF FACTORS FOR REIs

(Statistical Analysis)

Factors	Research-Engineering Interactions																											Total Frequency
	Sub-case I						Sub-case II									Sub-case III										Sub-case IV				
	a	b	c	d	e	Total	f	g	h	i	j	k	l	m	Total	n	o	p	q	r	s	t	u	v	Total	w	x	y	Total	
4		(X)	X	X	X	4/5	X		X	X		X	X	X	6/8	X	X	X		X		X	X	X	7/9	X	X	X	3/3	20/25
5	X	X	X		X	4/5	X	X	X		X	X			5/8	X	X	X	X	X	X	X	X	X	9/9	X	X		2/3	20/25
8			X	X	X	3/5			X	X		X	X	X	5/8	X	X		X		X	X	X	X	7/9	X		X	2/3	18/25
11	X	X	X		X	4/5	X	X	X		X				4/8	X	X	X	X	X	X		X		7/9	X	X		2/3	17/25
1	X	X			X	3/5		X	X		X	X			4/8	X		X		X	X		X	X	6/9	X			1/3	14/25
7	X		X		X	3/5	X	X	X		X	X			5/8	X		X		X		X	X	X	6/9				0/3	14/25
12	X			X	X	3/5	X		X				X	X	4/8	X	X		X		X	X	X	X	7/9				0/3	14/25
15	X	X	X			3/5	X		X					X	3/8		X		X		X	X	X	X	6/9		X		1/3	13/25
2		X		X	X	3/5				X	X		X	X	4/8			X		X		X		X	4/9		X		1/3	12/25
6		X	X	X	X	4/5								X	1/8			X		X		X	X	X	5/9		X	X	2/3	12/25
10	X	X	X			3/5				X	X		X	X	4/8			X				X			2/9		X	X	2/3	11/25
14	X	X	X	X	X	5/5									0/8			X		X			X	X	4/9		X		1/3	10/25
13			X	X	X	3/5	X		X					X	3/8		X		X		X				3/9				0/3	9/25
9						0/5									0/8								X	X	2/9				0/3	2/25
3						0/5								X	1/8										0/9				0/3	1/25
Stage:	0	1	2	3-4	2		3	1	3	5	0	1	5	6		1	2	0	0	1	1	2	0	1-2		1	2	3		

Summary Analysis

In the editing of this report, nearly a year after the narrative of the case history was completed, limitations of our treatment became apparent:

(1) The developments under review are generally twenty to thirty years old; and, therefore, the participants in the discussions are often unable to recall specific details which are of crucial importance in this kind of analysis.

(2) The participants at Mellon Institute were more immediately involved in stages 0, 1, and 2, and consequently these receive the greatest emphasis. Interactions influencing stages 3, 4, 5, and 6 are generally given little attention. Thus, inadequate attention is given to the contribution and interaction in the research and engineering departments at the Dow Corning Corporation.

(3) The treatment of the four subcases is very uneven, though none is treated in its entirety. For example, the treatment of subcase I is obviously inadequate. Similarly, the role of the Dow Chemical Company and the government in the formation of Dow Corning is not made explicit.

(4) Some of the happenings reported here occurred in a different era, before research in industry (generally) was highly organized; and they involved a new company with research-oriented management at a time before the development of divisional lines, etc. Thus, contact between top-level management and the research chemist was close and the many communication barriers that can exist in a larger and older organization had not appeared.

Any strength in this review lies, perhaps, in the picture it gives of the ways in which highly motivated scientists use basic scientific knowledge, observed behavior, awareness of needs, and tricks of existing technology in various adjoining fields, to find their way to novel applications. To a degree there is little that is systematic in this.

Implicit in the present case was faith on the part of the investigators and their sponsors that there were opportunities to take advantage of the growing understanding of organosilicon chemistry in making new materials with unusual combinations of properties and finding profitable new applications for them. The "formula" for success amounted to this: alert, perceptive, intellectually flexible men motivated by curiosity and the will to succeed, working in an atmosphere that exposed them, perhaps haphazardly, to ideas and needs from many directions. To a degree, this exemplifies the advance of basic science, unpredictable and unprogrammed, yet often swift. The emphasis is necessarily on the individual scientist, on his training and environment. The tremendous importance of the contribution of a few individuals is impressive. The function of communication to management, fulfilled by the champion or "salesman", is illustrated here by instances showing how well it can work when the conditions -- and the men -- are right.

The thesis that new science and new materials will lead to new, perhaps unforeseen, applications has been the guiding philosophy, more often than not, in the development of the organic polymer industry. Perhaps this was the natural result of the circumstance that the synthetic arts were more advanced than the physics of materials. Today, with more severe demands on materials and better physics to guide us, explicit definition of needs and goals becomes commonplace and taken for granted. This may represent, in part, a limitation -- a danger to innovation through hardening of attitudes as to what is and what is not feasible.

A CASE HISTORY OF HIGH TEMPERATURE POLYMERS: THE POLYBENZIMIDAZOLES

Prepared by

W. E. Gibbs

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INTRODUCTION

This case history* describes the events and surrounding circumstances leading to the development of a new class of polymers (the polybenzimidazoles) which are currently entering several areas of use. These polymers were discovered by Professor C. S. Marvel and Dr. H. Vogel of the University of Illinois under a contractual program sponsored by the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory. The discovery and subsequent exploitation of these polymers is important technologically because these polymers possess outstanding resistance to high temperatures. As such, they are being actively pursued for use as fibers and plastics in aeronautic and astronautic applications and other applications where resistance to high temperature is of major importance. The discovery of these polymers is important scientifically because the principles learned from the discovery have a broad and important impact on the field of not only thermally stable polymers, but other types of polymers as well. From the historical point of view, this case history enumerates a method by which a presumably successful research and development program can be conducted within the general framework of federally sponsored research and development. Further, the overall program involved a number of individuals in organizations of quite different perspectives (eg. university, industry and government laboratories) who were widely separated geographically and each of whom had, or has, an important role to play in the outcome of the overall program.

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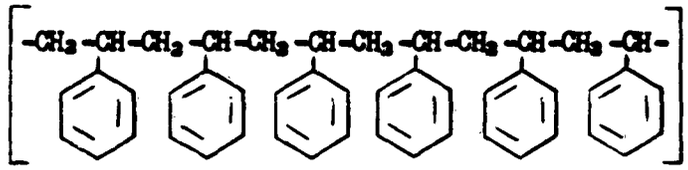
*APPENDIX gives a brief chronology of events.

BACKGROUND

Polymers are a broad category of organic, inorganic and semiorganic materials which find general application as plastics, fibers, elastomers, coatings films, fluids, adhesives, etc. Polymers are chemical compounds of very high molecular weight composed of large numbers of chemically similar recurring units linked together to form long, essentially linear, molecules by primary chemical valence bonds. For example, the polymer polystyrene is composed of a large number of recurring styrene residues:



Whereas the parent styrene has a molecular weight of about 100 molecular weight units, polystyrenes may have molecular weights, depending upon the method of preparation, ranging up to several million. Therefore, a single polystyrene molecule may contain over 100,000 styrene residues in a single chain.

Depending upon the chemical composition of the recurring unit, the size of the molecule and the temperature of observation polymers may be strong, hard plastics, extensible rubbers, or liquids.

Prior to the early part of this century, the chemist, physicist and engineer had only the naturally occurring or slightly modified naturally occurring polymers to work with. However, as the scientist began to understand how to prepare synthetic polymers and to modify the properties of both natural and synthetic polymers the versatility of polymers increased manifold. An ultimate goal of polymer science is to understand the relationships between the properties of polymers and their physical and chemical constitution and to learn how to prepare polymers of desired chemical and physical constitution to yield an optimum balance of chemical and physical properties. In the past few decades considerable progress has been made in these directions. However, much is still yet to be revealed and understood.

HIGH TEMPERATURE POLYMERS

Improvements in the properties of polymers are continually sought. New polymers are constantly being prepared with improved resistance to solvents, better abrasion resistance, better strength, etc. Progress in aviation, missiles, and space exploration have led to pressing needs for polymers which can withstand high temperatures, low pressures, high radiation fluxes, etc., and have useful properties. These applications include structural materials, such as reinforced plastic laminates for radomes, missile cases, etc., for electrical purposes such as insulation, thin film dielectrics, etc., elastomers for fluid transport, seals, sealants, tires, etc., plastics for thermal protection such as ablative nose cones, rocket engine throats, etc., fibrous materials for reinforcement in ducting and tires, for high speed recovery systems such as decelerators, etc. Nearly all functions which normally are required for polymeric materials in ordinary use under ordinary conditions are found in aeronautic and astronautic applications, but with more severe condition of operation.

Faced with these needs, and other needs which preceded the aeronautic and astronautic applications, a number of organizations became interested in polymers with improved high temperature properties. A few organizations have been sufficiently interested to conduct or sponsor polymer research with improved thermal stability as a major goal. The United States Air Force, through the Air Force Materials Laboratory (AFML)* has been pursuing such polymer research and development since the early 1950's. This program had evolved from applied work on modifying and reformulating available polymers, to a broad based fundamental and applied research program of some few million dollars effort, involving both internally and contractually conducted programs.

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*The titles of organizations appearing here are current as of this writing, rather than the title at the time.

Toward the end of the 1950's, in the Nonmetallic Materials Division of AFML, headed by Mr. R. T. Schwartz, and particularly in the Polymer Branch headed by Dr. A. M. Lovelace, this effort had been devoted to the preparation of a variety of new polymers. An effort conducted internally and with the M. W. Kellog Company, Peninsular ChemResearch Incorporated, the Dow-Corning Chemical Company and Minnesota Mining and Manufacturing Company had successfully synthesized a variety of new high temperature, solvent resistant fluorinated rubbers. These polymers solved certain critical needs in jet aircraft and received very general acceptance. Several other programs in the Division had as successful, although perhaps not as dramatic, an impact.

Within the Division exploratory research on new polymers on a rather broad base was encouraged and stimulated. Pressing and well-recognized needs existed which supported this interest. Management of the internal and contractual research programs was in the hands of people who understood these needs, the general problems of research and how to fit the conduct of productive research into regulations and customs best equipped to support line organizations. Experience gained during the past several years had led to an ability to select and originate technical programs which generally were productive.

The major influence which set the pattern of research and development in the Division, was the attitude of Schwartz. He provided the overall orientation of research and development, yet depended upon his personnel to recommend and exploit fruitful areas. He strongly supported exploratory polymer synthesis. However, the derivation of the technical approaches to new polymers, and the conduct of the research rested with the bench scientist and first-line supervisors.

The staff of the Polymer Branch in Schwartz's Division, consisted of some twenty professionals, 2/3 of which held the Ph.D. in chemistry. They represented a cross-section of backgrounds in chemistry from classical organic, semiorganic and inorganic synthesis to specialists in polymer chemistry

and physics. These personnel devoted a majority of their time to internal research, but in addition conducted a contractual research program of some 150 man-years/year effort. The Branch Chief, Dr. A. M. Lovelace, in particular, had been closely associated with the discovery and development of the high temperature and solvent resistant fluorinated rubber program. His training was in the synthesis of fluorine containing monomers and polymers, and he was a recognized authority in this area.

The development of fluorinated elastomers appeared to solve, for a time, the most pressing problems in the elastomer area and effort was directed more toward other critical areas: high temperature plastics, adhesives and fibers. The state-of-the-art materials in the high temperature plastics field were the phenolics and modified phenolics. However, these materials fell considerably short of current and projected requirements mainly in respect to resistance to high temperatures. In the fibrous materials area, the state-of-the-art materials were the aliphatic polyamides (commonly referred to as nylons) and a new fiber recently provided by the duPont Company. The proprietary material, originally referred to as HT-1 and later as Nomex* was significantly better than the nylons in thermal resistance, but requirements still existed which were beyond the capability of this material.

The general problem in the high temperature plastic and fibrous materials area was two-fold. First, the basic polymer must resist chemical attack and degradation at higher temperatures. Secondly, the polymer must not soften or flow at these temperatures. These two characteristics might be related, ie., the polymer might chemically degrade due to oxidation and the degraded polymer might soften and flow. However, it was also possible that the polymer might be chemically stable, yet of too low a softening temperature to be useful. It appeared that the best approach would be to look for polymers of high softening temperatures which would be chemically stable. This was the basic approach which had been attacked by a number of workers, but with a notable lack of significant success.

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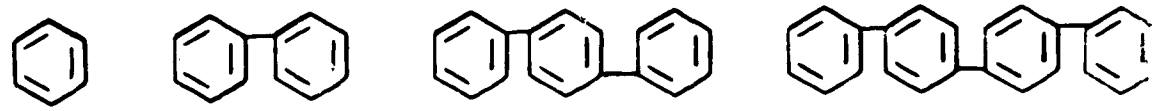
*Registered trade-mark, the duPont Company.

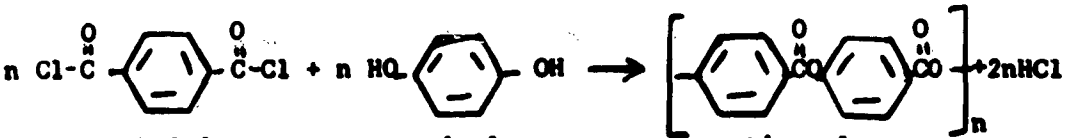
The major problems encountered were that when one attempted to synthesize polymers which were expected to have enhanced stability the polymer forming reactions (polymerization reactions) proceeded sluggishly and yielded products of too low molecular weight. In those few cases where products of apparently high enough molecular weight were obtained, they completely resisted all attempts to do something with them. They were insoluble in all solvents tried. When heated in an attempt to mold them, these polymers did not soften or flow at any point short of decomposition temperatures. These materials came to be known as "brick dusts". They were typical products of many high temperature polymer synthesis programs.

Another basic problem which faced this field was termed the "weak link" problem. Some of the most chemically stable compounds known in organic chemistry are the aromatic hydrocarbons, such as benzene and its homologs, biphenyl, terphenyl, quaterphenyl, etc.



benzene biphenyl p-terphenyl p-quaterphenyl

At this time, no good procedure existed for the preparation of polyphenyls of even moderate molecular weight. Therefore, a common approach was to react chemically substituted benzenes with other aromatic, co-reactive compounds to form polymers which contained a high proportion of aromatic nuclei in the recurring structure:



terephthalyl chloride resorcinol aromatic polyester

While the aromatic units in these type polymers were still quite stable, the ester group (-COO-) was of considerably less stability. Therefore, the stability of the polymer was limited not by the aromatic group, but by the

ester group. In general, the conventional polymer forming condensation reactions all left such "weak links" in the chain. Therefore, if one allows some oversimplification, the most serious problems at this point in time could be represented:

(1) Those polymerization reactions which could yield polymers of preferred stability generally proceeded sluggishly and gave products of too low molecular weight to be useful materials.

(2) In some cases, polymers of possibly high enough molecular weight could be prepared but they resisted all efforts to dissolve, mold or otherwise shape them into useful forms.

(3) Those conventional reactions which could yield high molecular weight polymers which were fabricable generally left residual "weak links" in the structure which seriously limited the polymer stability.

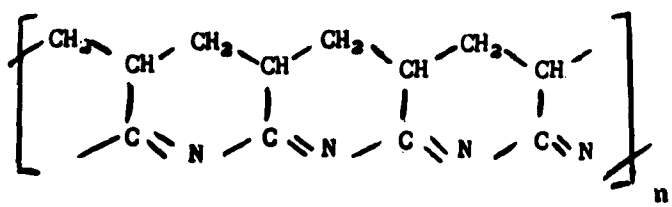
Professor Carl S. Marvel of the University of Illinois Chemistry and Chemical Engineering Department for a number of years had been recognized as a leading authority in the field of polymer synthesis. During the Second World War, he was very active in the government sponsored synthetic rubber research and development program. During the middle 1950's, he became a contractor of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, in the area of thermally stable polymers. Shortly after this, the University of Illinois program was expanded to include investigations by Professor John C. Bailar on coordination polymers and Professor Ludwig Audrieth on inorganic polymers. Marvel, Bailar and Audrieth worked independently, although Marvel was the administrative head of the total program. Marvel, a very aggressive and talented scientist, had become very highly interested in the preparation of thermally stable organic polymers. He was strongly affiliated with the interests of the Air Force in pursuing such materials. Due to his high motivation in this direction and to his obvious talents, he was given rather broad license to conduct research in this area.

Marvel's association with the Polymer Branch by the late 1950's had been satisfactory, in general, both to Marvel and to the Air Force personnel. No lack of communication appeared to exist between these two groups.

Discussions were candid and informal. Marvel had little patience with tangential effort, which although interesting, did not contribute toward the objectives of his research. The research always appeared purposely directed. The staff of Marvel's part of the program generally consisted of Ph.D. candidates, although occasionally a single post-doctoral would be taken on.

In addition to the Air Force sponsored program, Marvel was also supported by funds from the Department of Agriculture, the duPont Company and at times by funds from other organizations such as the National Science Foundation. Thus, a rather wide variety of work was underway concurrently having fairly dissimilar objectives.

The research underway on the Air Force program at about the time of discovery of the polybenzimidazoles (PBI) is summarized in Appendix II. It is apparent from this summary that Marvel believed that the future of high temperature polymers rested primarily with polymers having cyclic or ring structures in the main chain, and moreover, with structures having large proportions of aromatic nuclei. He was greatly impressed that "Black Orlon" (a polyacrylonitrile that had been pyrolyzed in a specific manner to give what was believed to be a double-chain or ladder structure):

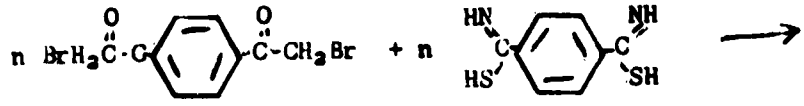


Black Orlon

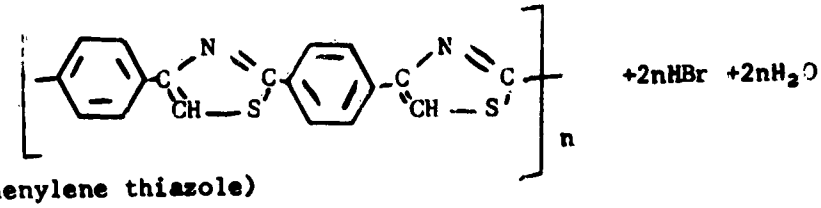
could be heated in a flame to red heat without visible change. He was attempting to prepare similar polymer structures by other methods. He had also pursued the preparation of polyphenylenes.

In the latter part of 1958, Marvel became interested in an approach which had been followed by Erlenmeyer in 1944. Erlenmeyer[1-6] had prepared a type of aromatic-heterocyclic polymer, a poly(phenylene thiazole), by a novel

kind of reaction:



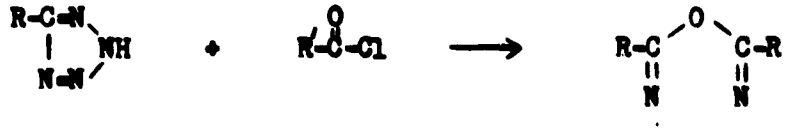
p-bis(bromacetyl) benzene p-phenylene bis(thionamide)



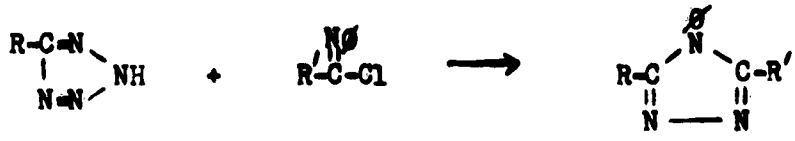
poly(phenylene thiazole)

This reaction was novel because it was a condensation reaction which did not leave a "weak link" in the polymer structure. The thiazole ring (a heterocyclic unit) has a stability in the same range or higher than the phenylene unit. This type of polymerization reaction, a ring closure reaction, it appeared, could be used to circumvent the "weak link" problem mentioned earlier. Marvel repeated the work of Erlenmeyer, et. al., since in the original work the reaction products were not fully characterized. The polymers obtained by Marvel and coworkers were of good stability but of low molecular weight and very limited solubility.

In the latter part of 1958 and in 1959, Huisgen and coworkers[7-9] published procedures for the preparation of other types of heterocyclic compounds, the oxadiazoles and triazoles:

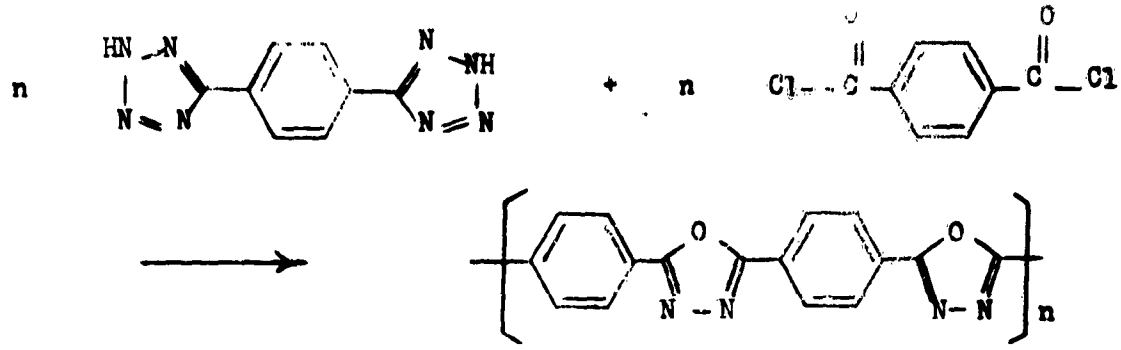


aryl tetrazole acyl chloride substituted oxadiazole

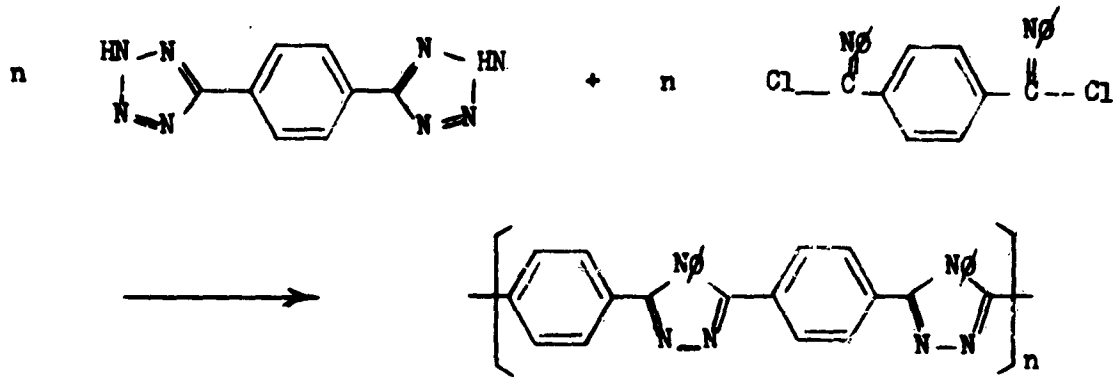


acylimino chloride substituted phenylene triazole

Marvel recognized that the oxadiazoles and triazoles were stable structures, and immediately undertook the preparation of polymers via a ring closure reaction forming these units:



poly(phenylene oxadiazole)



poly(phenylene triazoles)

The poly(phenylene oxadiazoles) were of very good stability; however, they were insoluble in all solvents. The poly(phenylene triazoles) were of nearly the same stability, and while soluble in organic acids such as formic acid, the molecular weights were too low.

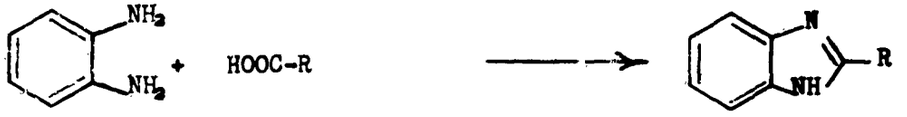
From the time that research had begun in the Polymer Branch directed toward high temperature polymers, programs had been conducted, internally and contractually, to determine the thermal stability of various classes of organi semi-organic and inorganic compounds. The research covered basic studies of the mechanisms of decomposition and extended to screening studies of a large number of different types of simple and complex compounds. The intention here was (1) to provide basic information on general chemical reactions involved in decomposition of model compounds, and (2) provide a general library of semi-quantitative information on the gross thermal stability of organic model compounds. This information was placed in the hands of the synthesis chemist to help guide his search for more stable chemical systems.

In the period from 1958 to 1960, a program was in effect at Monsanto Chemical Company, led by Dr. J. W. Dale, directed toward polymeric fluids stable at temperatures in the order of 800 to 1000°F. A portion of this

effort was involved in screening model compounds for thermal stability by means of the isoteniscope method. A large number of compounds were screened in this program, including aromatic and heterocyclic structures. Since reports generated by one Branch contractor were automatically distributed to other contractors of the Branch, Marvel received the results of this work. In January 1959, one report[10] issued from this work which listed, among many other compounds, the isoteniscope results for imidazole. These results indicated that imidazole had a very good stability. Marvel read and noted these results, but recalls that no direct synthesis of polymeric imidazoles occurred to him at the time. At about that time, January to March 1959, Marvel was the recipient of a National Science Foundation grant. An applicant from Germany, Dr. Howard Vogel, was accepted to work on this grant.

In the interval between March and June 1959, Marvel visited the Polymer Branch to discuss progress under the research contract. He met with Lovelace (mentioned earlier) and Dr. W. E. Gibbs. Gibbs, who had joined the Branch during the previous year, was the project scientist for Marvel's program. His background was polymerization kinetics, dilute solution properties, and diene synthetic rubbers.

At the outset of the meeting, Marvel was quite despondent over the lack of positive results from the current program. Further, he felt that he did not have any better ideas on which to work. Although progress toward stable polymers on the present program was disappointing, Lovelace and Gibbs were of the opinion that the present course of work was good and strongly encouraged Marvel to continue. They encouraged Marvel to seek related systems where the principle of ring-closure condensation reactions could be employed. About four hours were spent in a detailed review of the present approach and results and discussing possible future effort. Although memories now of those present are all somewhat vague about the exact situation, Lovelace recalls (then confirmed by Gibbs) that Marvel brought up the imidazoles as a potential polymer. This was explored further when Marvel recalled a specific reference in the literature to the preparation of benzimidazoles. The three then went to the Branch library and looked up the reference. It appears that this reference was: M. A. Phillips, J. Chem. Soc., 1415 (1930)[11]. This reference gives the preparation of benzimidazoles by condensation of aromatic ortho diamines with an organic acid in an acidic media.



o-phenylene diamine organic acid substituted benzimidazole

Marvel planned to try this approach.

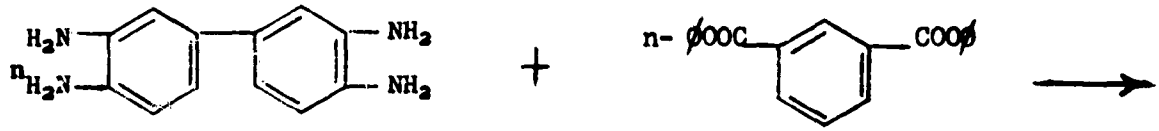
Following this discussion, Marvel was in an optimistic frame of mind and visibly encouraged about the research.

On 1 August 1959, Vogel reported for work. Marvel outlined some four possible research projects. Included in these was the synthesis of aromatic benzimidazole polymers based on the reactions of aromatic di-acids with aromatic di-ortho diamines. This program was selected by Vogel.

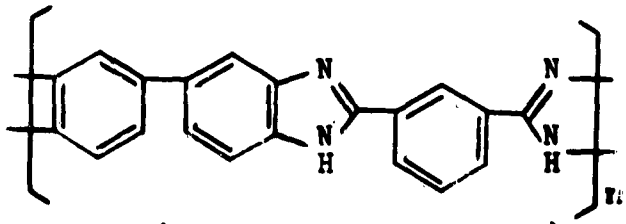
Very shortly thereafter, Vogel began work along the lines suggested. It was found that the reaction of aromatic acids and aromatic di-ortho diamines did not go well and poor yields were obtained. The work was extended to cover various solvent systems along lines suggested in the literature but with limited success. Following conventional approaches of reactions of carbonyl compounds with amines, they attempted the reaction of methyl esters rather than the free acids, but the methyl esters proved too volatile at temperatures required for reaction. They then tried phenyl esters to minimize volatility.

At once a dramatic change took place. The reactions proceeded smoothly to yield soluble polymers of much higher molecular weight. This inherent viscosity indicated that the molecular weight of the polymer was in the range required for useful properties. Vogel recalls that the first high molecular weight PBI was prepared just prior to Christmas recess in 1959. It had an inherent viscosity of about 0.5 dl./g.

At once Marvel telephoned the results to Gibbs and recommended shifting the work to the AF contract in order to expedite the work and to get it into channels where the material would be used. This was approved and changed. Further work was conducted on the AF program.



diaminobenzidine diphenyl isophthalate



poly(phenylene bibenzimidazole)

$+2n\ \phi\text{-OH} + 2n\text{-}H_2O$

Samples of the polymers were forwarded to the Polymer Branch where Dr. G. F. L. Ehlers conducted thermogravimetric analysis. The results were on the early polymers, but still, the weight loss characteristics were quite good.

For several years, Marvel had been a consultant for the duPont Company. Shortly after this time he visited duPont and for the first time became aware of the work of Brinker and Robinson[12] there, who had synthesized polybenzimidazoles based on aliphatic dicarboxylic acids and aromatic diortho diamines. These partially aromatic polymers, however, had much lower stability than their aromatic cousins. Interestingly, the aliphatic free acids readily form the imidazoles, whereas in the aromatic series this reaction is unsatisfactory. Either during this visit or another made rather soon after, duPont expressed a willingness to conduct a six month program to determine the potential of the PBI's as fiber-forming materials. This offer was communicated to the AF who agreed to the plan. Very shortly thereafter, duPont initiated this effort, utilizing their well-known capabilities to prepare fiber and evaluate the properties, particularly the high temperature properties.

Although the data were slow in arriving, and the lack of adequate communication between the AF and duPont was felt to contribute to this, Marvel relayed the tentative results to AFML. Fibers prepared from dimethyl sulfoxide solution gave tenacities over 2-3 grams/denier at room temperature and they retained very high percentages of that strength at temperatures up to 350°C and perhaps higher. Further, the overall properties of the fiber were such that it could undergo any conventional textile processing operations. These results were extremely encouraging.

Larger scale follow-on research directed particularly toward the preparation of high temperature fibers was next of concern. The duPont Company was awarded a contract for this and related effort. In a matter of some 3-4 months, the work was underway under the direction of Dr. A. Fraser of the Textile Fibers Department. During the program the polymerization was more fully investigated, larger quantities of PBI were prepared and the fiber forming process at the laboratory level was investigated in some detail. The first comprehensive data on the mechanical properties of the fibers and yarns under a wide range of conditions were obtained. The fiber was found to have an advantage of some 200°F+ over the formerly used nylons, and a significant but smaller advantage over other new polymers under development.

As a result of the duPont program, it was clear that this new fiber should be of considerable value for a variety of applications such as decelerators, reinforcement for high temperature ducting, high temperature tire cord, etc. The strength at temperature was greater than any other available system. In 1964 a program was initiated by the Manufacturing Technology Division of the Air Force Materials Laboratory at Celanese Chemical Corporation for the development of a commercial process for the production of high grade PBI fiber. This included process work on the starting materials, polymerization, isolation, fiber spinning and preparation of yarns and woven articles. This program was successfully completed in December 1965. The yarn and woven articles are now under evaluation.

With the success realized in the fiber preparation work during 1960 and 1961, the adaptation of this chemical system to other uses was planned. However, the means of utilizing this new polymer in applications, such as high temperature plastics, laminates and adhesives, was not at all obvious.

Plastic, laminate, and adhesive uses require that the polymer, at some stage in the process, must be capable of being molded or formed. For nonreinforced plastics this is accomplished either by molding the conventional polymer at, or slightly above, the softening temperature, or by the use of a pre-polymer technique. The pre-polymer technique involves the use of a polymer that is only partially polymerized. This partially polymerized polymer generally softens at temperatures lower than the fully polymerized material and is easier to handle. Alternatively, the pre-polymer is dissolved in a solvent which is then allowed to volatise and deposit the pre-polymer in a desired form, e.g., sheets or films. The partially polymerised material is then heated, usually under pressure, to continue polymerisation to completion to yield optimum properties. Basically, the same approach is used for the plastics which are reinforced by fiber glass, or other filamentary reinforcing materials. However, it is essential, in order to realise reinforcement, for the polymer to come into intimate contact with the reinforcing media to form an adhesive bond. This is generally termed "wetting" the reinforcing media. The same "wetting" phenomena is required for adhesive applications. The partially polymerised material is then heated under pressure to complete the polymerization. For plastic and adhesive applications

it is vital, therefore, that the polymer be capable of significant softening and flow to permit molding and formation of the adhesive bonds.

PBI, however, in high molecular weight form does not soften or flow significantly, even under pressure, below temperatures where the polymer decomposes. There was no assurance that enough softening and flow could be obtain even from polymers of lower molecular weight (pre-polymers). Further, there no assurance that if the polymerization was stopped short of completion, that the reaction could be made to continue in the mold or press in the presence o other materials, eg., the reinforcing media or other substrates. Lastly, it thought necessary to provide some means by which crosslinking between polymer chains could be effected. Conventional reinforced plastics were crosslinked polymers, and the additional strength provided by this was thought necessary provide adequate high temperature strength properties.

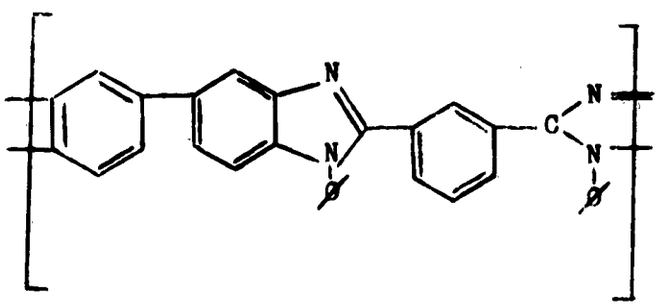
Mr. R. T. Schwartz, Chief of the Nonmetallic Materials Division of AFML was the prime moving force behind starting research on the development of approaches for plastics, laminates and adhesives from PBI. A program was initiated for research on plastics, laminates and adhesives from PBI and othe candidate systems with Narmco Research and Development, a division of Whittak Corporation. The most active participants in this program were Mr. Sidney Litvak, Plastics and Composites Branch, Nonmetallic Materials Division, AFML (see organization chart Appendix III) and Mr. Harold Levine, senior staff chemist, of Narmco R & D. Early approaches were concerned with conducting the polymerization with an imbalance of amine and ester to yield a lower molecular weight polymer which, hopefully, would soften and flow. This was unsuccessful and stoichiometric relations were attempted and interrupted shortly after reac tion commenced to yield very low molecular weight pre-polymer averaging about dimer or trimer. This pre-polymer was found to soften and flow under pressure Equally important, it was found that this pre-polymer would continue to polymerize in the presence of filamentary high temperature fiber glass to yield small scale laminates with very good strength. This demonstrated that a satis factory adhesive bond was forming.

Initially this pre-polymer was dissolved in a solvent and cast onto fiber glass which then would be plied into a laminate. The first two-ply laminates were prepared and tested in about April 1962. The results were very encouragi With this success, all other work in the program was halted and the entire eff

placed on PBI. In addition, the overall effort of the program was expanded. This shift in emphasis was justified when the experimental laminates were found to possess exceptional strengths at temperatures of 800°F and higher. In addition, metal-to-metal adhesives formed from the PBI pre-polymer were found to be very exciting. The first samples yielded 2200 psi lap shear strength (stainless steel) after aging one hour at 700°F.

An important by-product of this work was the demonstration that it is not necessary to have crosslinked polymer structures to obtain good high temperature properties, if the material has a high enough softening temperature. The interchain forces in the glassy solid, the physical state below the softening temperature for amorphous polymers, are sufficiently strong to give good strengths.

A continuing series of developments made the PBI resin work a source of satisfaction. A melt process was found for the pre-pregging operation which avoided the use of solvents. Techniques were developed for the larger scale purification of intermediates and polymerization which led to ample supplies of polymer for the work. Successively lower cure temperatures and pressures came out of further work. The dielectric constant and loss of the laminates were found to be almost temperature insensitive. The use of mixed esters of diphenyl-isophthalate and diphenyl terephthalate gave improved high temperature strength properties, a new polymerization reaction using the diamides rather than diesters were found to give superior aging at high temperature as a result of the lowered amount of volatiles produced during reaction. This latter development led to the first pure molded specimen of PBI. In addition the preparation of N-phenyl substituted PBI's has further improved the long-term aging qualities of laminates.



In the fall of 1962, at the request of the Air Force to define their commercial position in this PBI area, Whittaker decided to conduct the development of certain PBI resins and adhesives as a corporate venture. This group was headed by a vice-president of the company. This has culiminated in the Imidite* line of Narmco products. This satisfied an objective of AFML in that a source of these materials was now available to the Air Force, other military agencies and to the aircraft industry.

Further development of the PBI resins and adhesives toward specialized objectives has been continued within the Air Force. A variety of programs to explore the utility of PBI in honeycomb, foam, sandwich, and filament winding applications as well as other areas is underway.

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* Registered trade-mark name, Whittaker Corporation.

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APPENDIX I

General Chronology

Prior to June '58	1 - C. S. Marvel:	History of long participation to polymer field. Contractor closely affiliated with objectives of AFML. Held opinion that future of organic polymer for high temperature lay mainly with aromatic polymers.
	2 - AFML	History of productive research with follow-on into development. Management aware of research and objectives. Control of the research program in hands of working level personnel.
	3 - Others:	Very small amount of effort overall in high temperature polymers. Some few selected programs under industrial supports, on aromatic or heterocyclic polymers.
June-Dec '58:		Marvel becomes interested in preparing aromatic-heterocyclic polymers via ring closure polymerization. Series of papers by Erlenmeyer described polymerization of p-bis-bromocetyl compounds with bis-thioamides to give polythiazoles. This is followed in late '58 by a series of papers by Huisgen describing preparations of monomeric oxadiazoles via reaction with acid chlorides.
Jan-Feb '59:		Work on above systems continue, Marvel becomes aware that simple imidiazoles have good stability via Monsanto report. No method of synthesis is at once apparent. Marvel is awarded NSF grant. Invites Dr. Herward Vogel to come from Germany for post-doctoral.

May '59	Marvel visits AF Materials Laboratory and in discussion with Lovelace and Gibbs, the idea of preparing PBI's by ring closure polymerization of aromatic tetraamines and aromatic diacide comes out. Marvel plans to try.
Sep '59	Vogel reports. Marvel outlines four possible programs. Vogel selects work on preparing PBI.
Dec '59	First high molecular weight PBI's are synthesized. Work transferred to AF contract.
Jan-Nov '60	DuPont becomes interested and initiates a six-month program to do preliminary spinning and fiber evaluation. Results come to AFML.
Mar '61	Contractual program with DuPont begins.
Jan '62	Program on PBI resins begins with Narmco.
June '62	First small scale preparations of prepolymers, laminates and adhesives show promise.
Jan-Mar '63	First 14 ply laminate.
Nov '62	Narmco decides to take-on PBI resins and adhesives as commercial venture.
Jun-Aug '63	Melt coat process found for laminates.
Oct '63	New route to PBI resins via di-amides instead of di-esters.
Dec '63	AFML, Manufacturing Technology Division, process development work on PBI fiber begins.
'64	Process development work begins on laminates with Narmco.
Dec '65	Full scale evaluation of PBI, fibers, yarns, tapes and woven fabric begins.

APPENDIX II

Research in Progress Under Direction of C. S. Marvel Just Prior to and at th Time of Discovery of FBI

A. Polyaromatics

1 - polyphenylenes via polymerization of 1,3-cyclohexadiene and aromatiz tion.

2 - polymers and copolymers of aromatic hydrocarbons, e.g., ethylenanth cene, and pyrene.

B. Polymers Based on Inter-Intramolecular Propagation

1 - psn. of 1,5; 1,6; 1,7; diolefins

2 - psn. of diallyl silanes

3 - transannular psn.

C. Polyschiff Bases

D. Polyphthalocyanines

E. Polymeric Basic Beryllium Carboxylates

F. Heterocyclic Polymers

polypyridines via oximation of polyvinyl ketones and ring-closure.

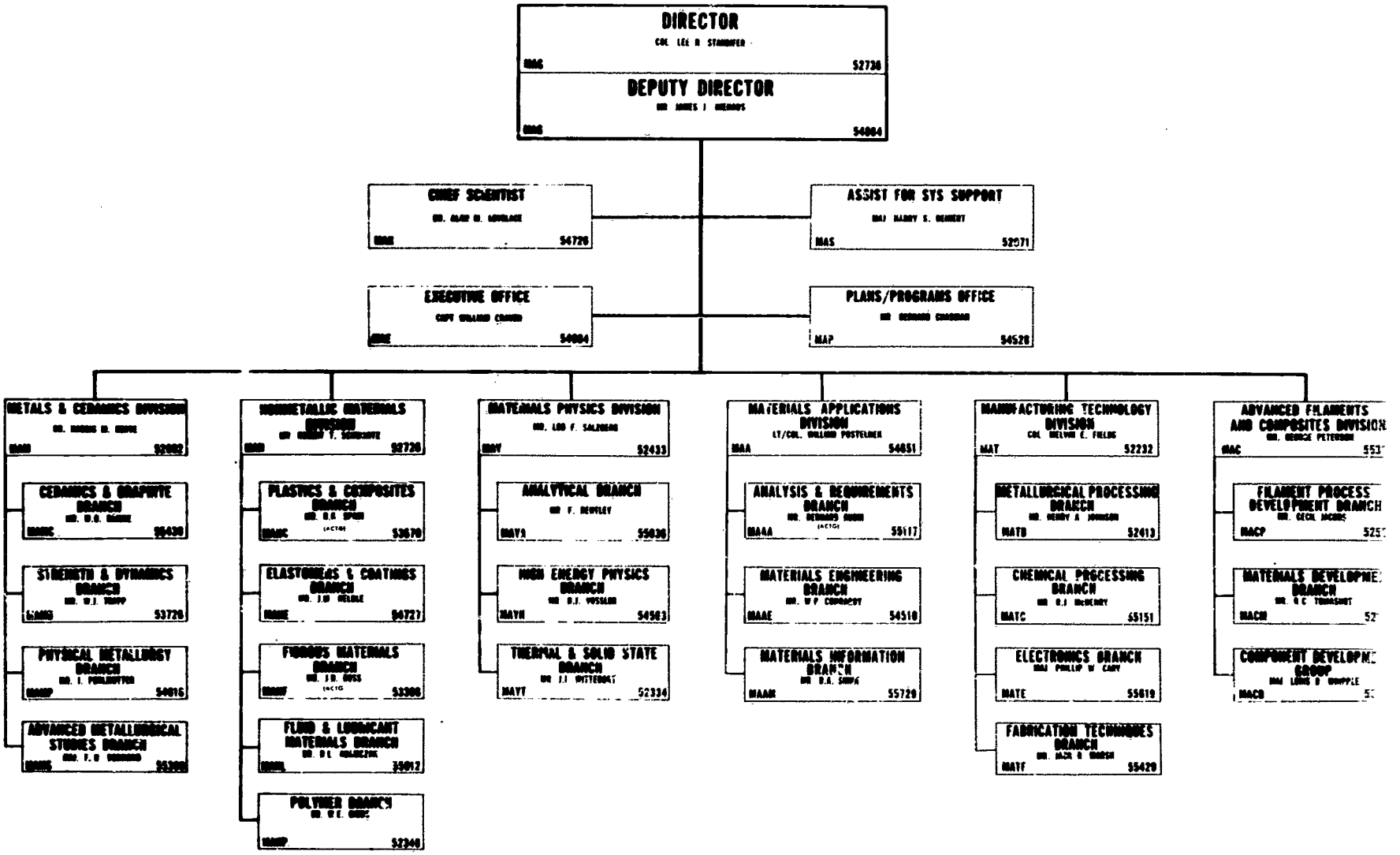
G. Ladder Polymers - via cyclic psn. of diacrylylmethane, oximation and rin closure

H. Aromatic-Heterocyclic Polymers

1. Polyphenylene thiazoles: via ring closure polycondensation of p-bis· biomacetylbenzene with phenylene bis thioamides

2. Polyphenylene Oxadiazoles and Triazoles: via polycondensation of ar matic bis tetrazoles with bis acid chlorides and bis imide chlorides

AIR FORCE MATERIALS LABORATORY



ANALYSIS

DESCRIPTION OF MEI'S AND STAGES

STAGES IN PBI FIBER DEVELOPMENT

0. In discussion between Marvel, Lovelace and Gibbs, it is suggested that reaction of diaminobenzidine and aromatic acids will lead to useful hi temperature stable polymers.

1. Marvel and Vogel find that the polymerization of diphenyl isophthalate diaminobenzidine form a high molecular weight polymer. Preliminary te show the polymer has very good thermal stability.

2. DuPont finds that the PBI's can be spun into strong fibers with outstan properties at elevated temperatures.

*3. Woven and braided articles can be prepared from PBI following work on p cess which provides quantities of fiber.

*4. Demonstration that woven and briaded articles from the fibers have supe properties in application such as: decelerators, expandable structures reinforcement in tires, ducting, etc.

STAGES IN PBI RESIN DEVELOPMENT

0. In discussion between Marvel, Lovelace and Gibbs, it is suggested that reaction of diaminobenzidine and aromatic acids will lead to a useful h temperature stable polymer.

1. Marvel and Vogel find that the polymerization of diphenyl isophthalate diaminobenzidine forms a high molecular weight polymer.

2. Levine, et al., at Narmco finds that the polymerization can be stopped to yield soluble, fusible polymer which can be used to form a laminate.

3. Demonstration that laminates based upon PBI have outstanding strength a retention of strength at elevated temperatures and can be made in large sections.

*4. Laminates of configuration similar to that to be used in future systems are prepared and evaluated.

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*currently underway

FACTORS* CONSIDERED IN ANALYZING EVENTS OF REIs

From the study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs and listed them as follows:

List of Factors Considered in Analyzing Events of REIs

1. High educational level (advanced degree) of principal investigator
2. Importance of management
3. Importance of Government-sponsored research
4. Importance of recognized need
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources)
6. Industrial laboratory involvement
7. Basic research in the laboratory (or institution or organization)
8. Communications across organizations
9. Technical problem as the principal obstacle
10. Importance of a "champion"
11. Freedom for individuals
12. Broad spectrum of types of laboratories
13. Geographic proximity
14. Prior experience with innovation
15. Organizational structure (barriers and bonds)

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* The discussion in the section on FINDINGS in the main body of the report amplifies the meaning of these factors in the context of the analysis of the cases.

FREQUENCY OF FACTORS IN REI'S

Factors	PBI Fibers 0 1 2 3 4 5 6	Frequency	PBI Resins 0 1 2 3 4 5 6	Frequency
1.	X X X X X - -	5/5	X X X X X - -	5/5
2.	X O X X X - -	4/5	X O X X X - -	4/5
3.	X X X X X - -	5/5	X X X X X - -	5/5
4.	X X X X X - -	5/5	X X X X X - -	5/5
5.	X X O O O - -	2/5	X X X O O - -	3/5
6.	O O X X X - -	3/5	O O X X X - -	3/5
7.	X X O O O - -	2/5	X X O O O - -	2/5
8.	X X X X X - -	5/5	X X X X X - -	5/5
9.	X X X X X - -	5/5	X X X X X - -	5/5
10.	O O O O O - -	0/5	O O O O O - -	0/5
11.	X X O O O - -	2/5	X X X O O - -	3/5
12.	O O O O O - -	0/5	O O O O O - -	0/5
13.	O O O O O - -	0/5	O O O O O - -	0/5
14.	X X X O O - -	3/5	X X X O O - -	3/5
15.	O O O O O = =	0/5	O O O O O = =	0/5
Totals	10 9 8 7 7 - -		10 9 10 7 7 - -	

SUMMARY ANALYSIS

1. Fibers: This case would appear to differ substantially from most other cases due to the fact that a number of different organizations are actively involved in the research and development as well as in the technical and administrative direction of the program. These include a government laboratory, a university and two industrial concerns. All of these participants played a major role. The case gives a good basis on which to examine particularly such features as communication across organizations, geographical proximity, the importance of government sponsored research, the role of management and the importance of a recognized need and the inter-relation of these factors in a research and development program.

This case is primarily characterized by the high incidence of Factors 1(5/5) 2(4/5), 3(5/5), 4(5/5), 8(4/5) and 9(5/5). The importance of management comes up strongly in several ways: (a) nature in which the AF laboratory is permitted to approach the problem, (b) a constant level of support available for conducting the research over periods of much less fruitful activity, (c) the dependence of at least laboratory management upon the advice and opinions of the working level technical personnel and, (d) keeping the research personnel informed of the kinds of needs that exist. As the research proceeds the management assumes a greater role in determining where the areas of application are and hence the direction of the applied research and development work.

The program has been fully funded by the government, with the exception of the six-month phase funded by DuPont. The use of government funds, therefore, was vital to the inception and progress of this work.

The need for the improved material is probably the most important factor in the case. The need was recognized by personnel at every phase in the program.

Due to the fact that several organizations were involved at least adequate communication between these groups at the working level or first echelon of supervision was necessary. The normal means of communication utilized were visits, telephone, and transmittal of reports. Due to the geographical non-proximity of these groups the number of personal contacts was probably fewer than desirable. However, no particular effect of this was noted in the program.

Perhaps as significant as the Factors occurring in a high incidence : those of low incidence: 10(0/5), 12(0/5), 13(0/5), 15(0/5), 5(2/5) and 1 Some weighting should be done with Factor 11, since this Factor, believed important to the inception of the program, became somewhat less important the program proceeded toward development.

From this analysis it would appear that certain of the Factors selec for evaluation of the committee are more important toward the beginning o program or toward the middle to end phases and are not nearly representati of the program as a whole. A likely next step would be to isolate all 0, 2, 3, 4, 5 and 6 type stages in the several cases and compare the 0's, 1's 2's, etc.

2. Resins: As may be noted from the frequency of Factors indicated for t sub-case, it is almost identical with the Fibers case above, and the comm made in the discussion there are valid here.

A CASE HISTORY OF ANTIOZONANTS FOR SBR RUBBER

Prepared by
M. P. Marks*

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* Most of the information used in preparation of this case was provided by Rock Island Arsenal and other Army activities.

A CASE HISTORY OF ANTIOZONANTS* FOR SBR** RUBBER

NARRATIVE

PROBLEM

Prevention of ozone cracking of diene-type rubbers.

BACKGROUND

Natural rubber as an engineering material was in use by natives of the new world before Columbus discovered America. It wasn't until 1839 with the discovery of sulfur vulcanization by Charles Goodyear that the technology of rubber made a significant advance. Since then many improvements have been made in the characteristics of rubber and the processes used in natural rubber technology. One of the difficulties which has a historical background was the problem that stressed rubber developed cracks when exposed to the atmosphere. At first this was attributed to the sun or to light but was later shown to be due to a relatively low (below 50 pphm) ozone concentration in the air. These cracks in natural rubber were small but numerous and, although unsightly, they did not usually result in failure of the item. Also it was considered that rubber had a relatively short life and that a ready supply of new items was always available.

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*"Antiozidant" is an occasional synonym for this term.
**"SBR" is a common term for a class of Styrene Butadiene copolymer Rubbers.

Onto this scene came the problems associated with World War II: shortage of natural rubber, the use of reclaimed rubber, and the short supply of knowledge, compounding experience and long-term aging data o a new material variously called Buna S, GR-S, or SBR. This butadiene-styrene copolymer was very susceptible to ozone cracking and differed natural rubber in that the first cracks formed did not relieve the sur stress and as a result, grew in size and depth so as to destroy the st rubber. In contrast to this large volume, general purpose, nonozone-r rubber, were the higher cost specialty rubbers such as Neoprene, Butyl Silicone, and Thiokol that have inherent ozone resistance. Since thes specialty rubbers were much higher in price and unsuitable for many ap cations, SBR became the material of choice for all automotive tires ex the largest sizes. Today it is still a major polymer in the tire indu Much development effort was undertaken to protect it from ozone attack such means as surface coatings, compounding with waxes and antioxidant and by designing to eliminate stress points. However, none of these e was completely satisfactory. At the same time, considerable effort wa expended by various investigators to measure the ozone content of air many literature references are available on this subject.

ANTIOZONANT DEVELOPMENT AT ROCK ISLAND ARSENAL (RIA)

The necessity for protection and storage of the large stock of equipment on hand at the end of World War II, including rubber goods,

prompted the Army Ordnance Corps to let a contract in May 1945 with a nonprofit institute for a "Literature Survey on Aging and Storage of Vulcanized Rubber Goods."[1] This survey served to point out that there was then no good way to preserve rubber items and that appropriate methods needed to be developed. As a result, it was decided to probe further and a second more definitive contract was let to determine the factors responsible for aging of rubbers. The prime contractor was one of the major national rubber companies and it was supported by a subcontract with an academic institution.[2,3] The purpose of this effort was to provide a well-grounded and rational basis for a systematic attack on the problem. Although much worthwhile work of good quality was done with respect to oxygen and its reaction kinetics with rubbers, ozone was not recognized as a significant quantitative factor. However, the qualitative significance of its presence was by now generally recognized. At about this time a paper[4] by Crabtree and Kemp of Bell Telephone Laboratories came to the attention of R. F. Shaw, Chief of RIA Rubber Laboratory.* Bell Telephone had an interest in the subject associated with the weather cracking of cable insulation.

During this era, Shaw's early work at RIA emphasized various means of defeating ozone attack in an empirical way: development of coatings using

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* A brief discussion of the "Climate" of the RIA Rubber Laboratory (also referred to as the Elastomer Unit) is given on pages F21-F23. A short statement of its history, resources and capabilities is given on pages F17-F19.

ozone-resistant rubbers,[5,6] compounding with waxes and conventional antioxidants, and studies of various polymers to determine their intrinsic ozone resistance (using Crabtree-Kemp type cabinets for accelerated testing).

In 1949 an event occurred that sharply emphasized the criticality of the problem. To crosscheck Shaw's concern for the Army's stake in the problem, a research manager responsible for nonmetallic materials in the Office of the Chief of Ordnance arranged to use old, but unused, tires on trucks involved in a lubricants field wear test being conducted at Benicia Arsenal. During this test these tires failed in large numbers after a very small fraction of their expected normal life.[7] This confirmed Shaw's concern and gave additional impetus to his efforts. It also smoothed the way at higher headquarters for acceleration of his program to solve the problem.

In response to this new stimulus Shaw did two things: (1) he initiated a study to determine the service life of old but unused Ordnance rubber items, and (2) he accelerated work at RIA concentrating on methods[8] to reproduce, measure, and compare ozone cracking to obtain reliable data with which to study the problem systematically. In connection with his own laboratory program he dispatched chemists to the Bell Telephone Laboratories to learn more details about their ozone cabinet construction. Duri

this visit Bell workers also discussed uses to which their cabinets were put and the compounding work that was evaluated in them. A few months later these Rock Island Arsenal chemists also went to the University of New Mexico to observe apparatus for measuring atmospheric ozone content because it was anticipated that it might become necessary to ascertain ozone concentrations at various Army storage sites. With this information added to background developed during the contract study of aging factors, Shaw placed further contracts in 1952 with the National Bureau of Standards[9] and the Mast Development Company for development of reliable ozone test apparatus. He intended this apparatus to be used initially to obtain data meaningful for laboratory studies and ultimately to be suitable for use in government specification tests. In both these efforts Shaw was project officer. The Mast cabinet subsequently was deemed suitable for its purpose and a significant number were marketed.

Although much empirical engineering-type compounding was generally underway (including at Rock Island), Shaw finally decided that the problem warranted concentrated fundamental study. Accordingly, in June 1951 he let a contract with the Augustana Research Foundation to study the kinetics of the ozone/diene rubber interaction with the aim of understanding the mechanism well enough to control it. This Foundation was an arm of Augustana College, conveniently located in Rock Island, Illinois.

Meanwhile work continued in the Rock Island Arsenal Laboratory on the screening of compounding ingredients that were felt to have the slightest promise. Although practically none of these proved useful, including the antioxidants, Shaw and his staff noticed that Tenamene II, an antisludge additive for fuel oil, did show specific antiozone activity in rubbers.[10] This confirmed information previously acquired by Rock Island chemists during their visit to Bell Telephone Laboratories for the purpose of discussing ozone cabinets. At that time, although this material seemed to be effective, the means by which it worked were not understood. Further, it was generally considered too toxic for safe use in rubber.

Based on his earlier recourse to research in this program and the developing progress of the Augustana contract, Shaw concluded that this kinetics investigation, although of good quality, would not produce definitive information soon enough to provide a theoretical basis for early development of a practical solution. Furthermore, he was acutely aware that production of unprotected tires continued and that the Army was buying a significant proportion of them.

After approximately six months' work on the purely basic scope of the Augustana investigation, Shaw decided to split his effort. He would

continue the systematic study of the ozone/diene reaction mechanism in hope of ultimately understanding the fundamental aspects. However, he would also use a portion of the Foundation's effort to follow up the Tenamene II clue. Here was something that did work even though it was considered too unsafe to use.

Basing his thinking on the pharmacologist's approach, Shaw reasoned that higher molecular weight and bulkier homologs of this chemical compound would probably retain antiozone potency. Also they would have lower vapor pressure, would be retained in the rubber longer, and at the same time be less toxic. Accordingly, he modified the contract scope to include synthesis of new ozone inhibitors based on phenylene diamine derivatives and similar compounds. This was the class to which Tenamene II belonged. Under the supervision of Prof. E. R. Erickson, chemists of the Foundation synthesized many compounds to Shaw's specified pharmacological goals. These compounds were regularly evaluated at the RIA Rubber Laboratory for their efficacy as ozone inhibitors in rubbers. This laboratory fully studied the better ones from all aspects of rubber compounding and practical processing. The best were tried out in experimental tires. Eventually the survivors were biologically evaluated and approved with respect to freedom from toxic hazard by a laboratory of the Army Surgeon General.

As the result of close personal communication with Rock Island and regular receipt of its reports, Detroit Arsenal engineers responsible for rubber automotive components became fully aware of the ozone cracking problem. They decided to supplement Shaw's work with a contract[11] of their own and Shaw furnished all available data from his own and his contractors' laboratories.

This resulted in a contract between Detroit Arsenal and Burke Research and the subsequent acquisition, in September 1953, of experimental samples of phenylene diamine compounds from the Universal Oil Products Co. These samples had been prepared originally for entirely different purposes, i.e., as a protective agent in the processing of alfalfa for Vitamin K, and as an oil sludge inhibitor.

As the certainty of a practical antiozonant grew, Shaw contacted several chemical suppliers in 1953 to insure a potential commercial source of supply, which would be necessary if specifications were eventually to require ozone-resistant tires. At that time the chemical suppliers proved reluctant to commit themselves unless their proprietary rights could be protected. This was not feasible because the unique application of these compounds resulted from Army-funded effort.* Eventually many rubber

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* Military Invention Record filed by R. F. Shaw, 29 June 1953.

chemical companies did enter the field, including at least one that had originally demurred. Their ultimate judgment to produce these materials appears well founded since the present market is estimated at well over 14 million dollars per year.

As a hedge against its possible failure, alternate in-house and contract[12] work continued throughout the Augustana/RIA effort. Shaw continued to explore coatings[13] and other means of tire protection, such as covers.[14] Eventually, as the Augustana compounds became available, the RIA Laboratory tried them in paint-on solutions and coatings for stock tires. Although solvent applications of experimental antiozonants were of measurable benefit, it became apparent that their optimum employment was with waxes as part of the rubber compound and this is how they are used today.

The successful development of practical nontoxic antiozonants was documented in subsequent technical reports during 1953 and 1954.[15-16] Other agencies[19] began to confirm these results, and in August 1954 a definitive technical article was published by Shaw, Ossefort, and Touhey.[20] As part of this program, work on test methods[21] and measuring devices[22] continued and an extensive bibliography on ozone was issued.[23]

The official implementation of this development in behalf of the Army was sponsored by Detroit Arsenal through the Tire and Rim Association[24]

and by the issue, in January 1955, of an Engineering Change Order[25] to the military tire specification. It required ozone resistance in tires for the first time. Further implementation followed later with establishment of MIL-STD-417, Ozone Resistance Tests, in September 1957. Throughout this period of the mid and late fifties a substantial number of open literature publications, internal reports, and patents were issued as a direct result of the program.[26-41]

After a long delay in Category 35 USC 267, caused by a shortage of legal personnel in Washington, a patent[42] was issued to Shaw in 1962 based on the Military Invention Record he filed in 1953. The long-term storage protection of these antiozonants in rubber was conclusively proven after ten years of outdoor exposure[43] at Rock Island Arsenal.

Industrial interest is now clearly evident because there are fifteen suppliers who provide forty chemicals of this kind to the market at the present time. The most recent indication of the value of this development was shown in a paper[44] given at the American Chemical Society Rubber Division meeting in March 1965. It stated: "It is conservatively estimated that the annual usage of anticonsants in the United States in passenger tires exceeds 24,500,000 pounds." To this must be added the many other it in the mechanical rubber goods field.

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** AD - Defense Documentation Center Reference Number
*** PB - Office of Technical Services (now Clearing House for Federal Scientific & Technical Information) Reference Number

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APPENDIX A
TO
CASE HISTORY
OF
ANTIOZONANTS FOR SBR RUBBERS

The Elastomer Unit - RIA Laboratory*

I. Historical Background

The Ordnance Research Program at Rock Island Arsenal in the area of synthetic rubber was first funded in FY 47. Rubber development work, however, began on artillery and tank end items in 1935 on a specific problem basis. This background assisted Rock Island Arsenal in becoming established in the rubber field. It was recognized that the Ordnance Corps was the largest user of rubber products within military agencies and that a continuing effort should be made to keep "in house" capabilities in the forefront in this rapidly changing field. All areas including basic research, applied research, end item development, testing and standardization were included in the assignment and scope of effort.

Specific Accomplishments Include:

Antiozonants: The class of dialkyl-p-phenylene diamine antiozonants was discovered. These are now widely used in rubber products to the extent of several million dollars worth per year.

Heat Resistant Inhibitors: A family of inhibitors for improving thermal stability of elastomers in the 250F-300F range was developed. These are useful in heavy duty military hardware applications.

* These data were prepared for another purpose in 1963. However, the elements of information are essentially valid for the period of this case.

Low Temperature Performance Measurement: Tests for low temperature flexibility and brittleness of elastomers devised and described by this laboratory and accepted by ASTM and ISO as standard.

Machine Gun Components: Most recently elastomeric coverings having outstanding properties were developed for use in the M60 machine gun.

The laboratory also acts as general consultant for elastomer hardware problems encountered in other former Ordnance installations, i.e., Picatinny Arsenal, Redstone Arsenal, ATAC, etc.

II. Personnel

By Degree

1 - Ph.D.
2 - M.A.
9 - B.A.
2 - Technicians

III. Facilities

13,000 sq. ft. of space is available for experimental work.

IV. Specialized Equipment

A complete line of rubber compounding processing and testing equipment is available. Specialized equipment includes cryogenic test chamber, and a high intensity cobalt 60 source. Also available are the necessary laboratory facilities and equipment for monomer synthesis and polymerization. A rubber processing and fabrication pilot plant is available for small production and semi-work studies.

V. Type of Work

A. Test & Evaluation of New Elastomers & Compounding Ingredients

B. Development & Improvement of Rubber Formulations for Army Applications

C. Liquid Butyl Rubber Systems for Radiological Shielding

D. High Bulk Modulus Cellular Rubber for Army Applications

E. New & Improved Elastomers Resulting from Grafting and Cross-linking

F. Polymer Physical Properties & Structure

G. Dynamic Low Temperature Test for Elastomers

H. Development of Improved Rocket Motor Case Insulation Liners

I. Improved Thermal-Oxidative Stability of Fluoroelastomers & Silicones

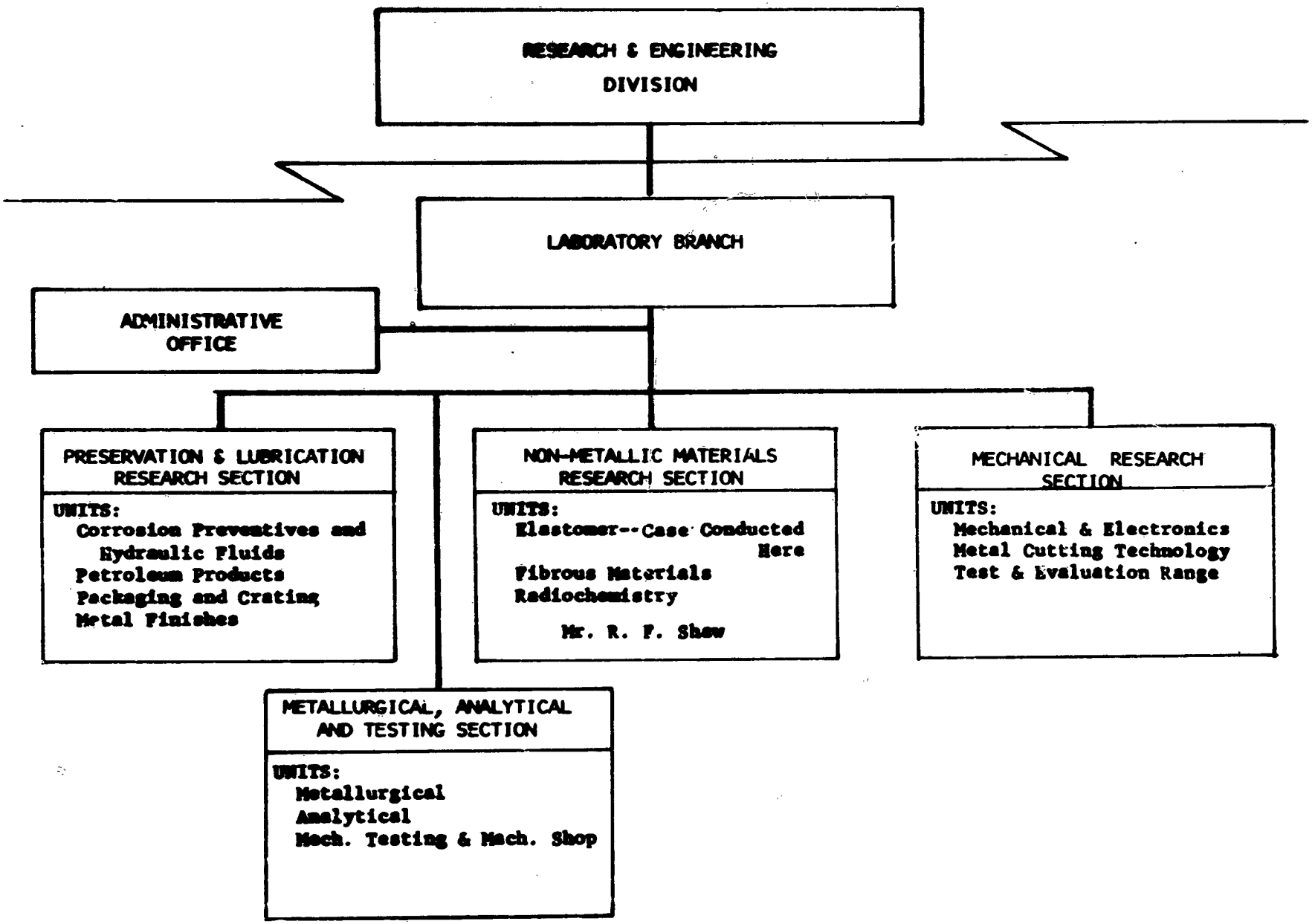
J. Silicon-Nitrogen Polymers (Midwest Contract)

K. Low Temperature, Oil Resistant Polyurethanes (Wyandotte Contract)

L. Polyphenyl Ether-Siloxane Copolymers (Naugatuck Contract)

M. Development & Evaluation of Polyurethane Track Pads

N. Development of an All Purpose Brake Cup


RESEARCH & ENGINEERING
DIVISION
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PRESERVATION & LUBRICATION
RESEARCH SECTION
UNITS:
Corrosion Preventives and
Hydraulic Fluids
Petroleum Products
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NON-METALLIC MATERIALS
RESEARCH SECTION
UNITS:
Elastomer--Case Conducted
Here
Fibrous Materials
Radiochemistry
Mr. R. F. Shaw
MECHANICAL RESEARCH
SECTION
UNITS:
Mechanical & Electronics
Metal Cutting Technology
Test & Evaluation Range
METALLURGICAL, ANALYTICAL
AND TESTING SECTION
UNITS:
Metallurgical
Analytical
Mech. Testing & Mech. Shop

THE CLIMATE

During the period of this case, the RIA Laboratory was charged with a dual mission: a. direct support of Arsenal manufacturing, i.e., process control, product testing and trouble shooting, and b. national responsibility in rubber research for the entire Army Ordnance Corps. Although nonmetallic materials were a minor concern within the Arsenal itself, the rubber work had national significance. Army truck tire inventories exceeded $75,000,000 and mechanical rubber parts were often critical components in military weapons and vehicles.

At the beginning of this case the Laboratory Director was a metallurgist whose interest in nonmetals was minimal. Subordinate to him and working with a fair degree of autonomy was a chemist in charge of Nonmetallic Materials Research. This individual had taken his Ph.D. in Physical Chemistry at University of Iowa in the 1930's and later had specialized in rubber chemistry. During World War II he served as a technical staff officer in Washington dealing with rubber matters. In 1946 R. F. Shaw was hired to head up RIA Laboratory packaging work. However, his previous background (details in another section) and inclinations caused him to be put in charge of a newly established Elastomer Unit. Somewhat later the metallurgist retired as Laboratory Director and the then Chief of Nonmetallic Materials

succeeded him. At about the same time Shaw stepped up as Chief of Non-metallic Materials Research. Thus, throughout this case the principals remained in the same relation to each other.

The new Laboratory Director was a competent and conscientious person convinced of the merits of fundamental research. Shaw, then in his late twenties, was enterprising, pragmatic and on the lookout for major Army problems for his new Elastomer Unit to solve. In a short time he built an informal network of contacts linking his national Ordnance customers. These included rubber technical service people at large Ordnance installations and key staff people at the Washington level.

Soon the higher staff was sold on the importance of his program and they promoted it with personal encouragement and program funds. Similarly close liaison grew between his own laboratory staff and engineers elsewhere in the Army responsible for using rubber items, e.g., Ordnance Tank-Automotive Center, Detroit Arsenal. This was achieved by personal visits, notes and telephone calls as well as by the more formal exchange of reports. Within the Elastomer Unit Shaw provided strong motivation, leadership and technical direction. However, he judiciously balanced these with broad delegation of responsibilities to the more competent investigators. Accordingly, the group had the sense of being a team on which all played with enthusiasm a

expectation of success. Simultaneously, close working relations were cultivated with the academic and industrial communities in a climate of mutual respect. This was done not only by funded research contracts but also by extensive voluntary participation in cooperative technical activities of national societies.

Thus effective communications existed within the working groups that produced results, with higher echelons that shaped policy and controlled funds and with the customers for whose benefit policies were promulgated and programs funded.

PERSONAL INFORMATION

Shaw, Robert F.

1940	- AB (Chemistry) Augustana College, Rock Island, Illinois
1940-42	- Chief Chemist, American Container Corp. (battery cases)
1942-46	- Engineering Officer, USN w/station at USN Engineering Experiment Station and later aboard ship
1946 to date	- Chief, Elastomers Unit, RIA Laboratory Chief, Nonmetallic Materials Research
Member	- American Chemical Society and its Rubber Division; American Society for Testing Materials and Society of Automotive Engineers. Active in rubber committees and working groups of the latter two.

ANALYSIS OF CASE HISTORY OF ANTIOZONANTS FOR SBR RUBBERS

DESCRIPTION OF RESEARCH ENGINEERING INTERACTIONS (REI's)

REI	Description
a	Determination of the nature and extent of the rubber aging problem. (a nonprofit research institute) Interaction between an Engineering Requirement and Applied Research.
b	Attempt to: (1) identify and measure all factors (i.e. light, oxygen, ozone, stress, etc.) responsible for rubber aging, and (2) determine their significance alone and in combination. (research staff of a national rubber company supplemented by an academic institution.) Interaction between an Engineering Requirement and Applied Research.
c	Decision that the problem warranted fundamental study of the ozone-diene interaction in order to understand the mechanism well enough to control it. (Phase I - Augustana Research Foundation) Interaction of Engineering Requirement with Fundamental Research.

d Shaw's decision based on results of research to date that: (1) the fundamental study of the ozone-diene interaction would not produce theoretical understanding soon enough to provide an early solution, and (2) that he would divert part of the effort to following the Tenamene clue to an early engineering solution.
Interaction between Fundamental Research and an Engineering Requirement.

e Synthesis of higher molecular weight phenylene diamines by Prof. E. R. Erickson et al coupled with proof of their antiozone potency in elastomers and development of optimum engineering application by RIA Laboratory. (Phase II - Augustana Research Foundation)
Interaction between Applied Research and Engineering Applications.

STAGES AT WHICH REI's OCCURRED

Stages*	REI	
0	a, b, c	Knowledge
1	d	Recognition of possibility of new material product
2	e	Creation of useful material form
3		
4		
5		
6		

* Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	Definition
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From its study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REI's. The statistical analysis of the frequency of these factors in this case is shown below.

FREQUENCY OF FACTORS IN REI's

(Statistical Analysis)

Factor No.		REI a	b	c	d	e	Total
1.	High educational level (advanced degree) of principal investigator					x	1/5
2.	Importance of management						0
3.	Importance of Government-sponsored research	x	x	x		x	4/5
4.	Importance of recognized need	x	x	x	x	x	5/5
5.	Requirement of flexibility to change direction during work and local control of funds (easily available resources)				x	x	2/5
6.	Industrial laboratory involved				x		1/5
7.	Basic research in the laboratory (or inst. or org.)						0
8.	Communications across organizations was important				x	x	2/5
9.	Technical problem was the principal obstacle				x	x	2/5
10.	Importance of a "champion"			x	x	x	3/5

Factor No.		REI a	b	c	d	e	Total
11.	Freedom for individuals				x	x	2/5
12.	Broad spectrum of types of laboratories				x	x	2/5
13.	Geographic proximity				x	x	2/5
14.	Prior experience with innovation						0
15.	Organizational structure (barriers and bonds)						0

SUMMARY ANALYSIS

This case is not necessarily typical nor is it an example of Research Engineering Interaction of the same order of magnitude as silicone or polysulfide rubbers. However, it did produce significantly better useful properties in the military's largest class of elastomeric materials and its impact on civilian rubber industry is evidenced by an annual consumption of 14.5 million pounds of antiozonants for passenger tires alone.

The sequence of events does not evolve directly from pure Science into Engineering (rubber technology is treated as the equivalent of engineering in this case). Rather it is nearer to an Engineering/Science/Engineering cycle. First there was recognition of the need for a better engineering material. Next came the recourse to science to: (a) define the problem, (b) isolate pertinent parameters, (c) understand the major uncontrolled parameter (ozone attack). Finally came the synthesis of a new material effective for safe engineering application.

Throughout all stages, Factor 4, the "Importance of Recognized Need," is a major driving force. This is not surprising in the case of a military laboratory assigned to supporting research for ordnance systems. It is interesting to note, however, that the emphasis on this need was highlighted by Factor 10, the "Champion" who promoted the program, maintained its impetus and produced results.

Factor 3, "Importance of Government-Sponsored Research" is noted in four out of the five stages. Again this is to be expected in a case conducted principally by a military laboratory and its research contractors. (Government-sponsored research in this instance is research directly associated with this particular case and not with research precursor to it.)

However, during what is perhaps the most critical Interaction d, Factor 3 is not present. Rather Factors 5 and 11, "Flexibility" and "Freedom," predominate. Shaw's decision to use part of his resources to synthesize a safe phenylene diamine was possible only because he had the personal freedom to control his own course and the flexibility to change its direction.

In Interactions d and e many of the other identified factors are also present. Of these, Factors 8, 12, and 13, "Communications," "Broad Spectrum of Laboratories," and "Geographic Proximity" are next in significance. They allowed Rock Island to work closely with Erickson of Augustana as a complementary team to implement Shaw's key decision with maximum effectiveness. As used here "Geographic Proximity" refers to the nearness of the RIA applied research and engineering laboratory to the basic research capability of Augustana Research Institute. It does not refer to the distance between the RIA Laboratory and Detroit Arsenal, the systems designer, several hundred miles away. It was good "Communications" stimulated and maintained by the "Champion" that effected this essential link.

The absence of Factors 2 and 15, "Importance of Management" and "Organizational Structure," are primarily attributable to qualities of the principal investigator who was the arch type of "Champion" cited in Factor 10. He created his own management support as needed, and by acting as a good communicator and promoter, he eliminated whatever organizational barriers may have existed. At the same time he made maximum use of organizational bonds. (See "Climate.")

The absence of Factor 7, "Basic Research in Laboratory," is partially compensated by the nearness and close working relations with Augustana during the crucial and productive Stages d and e.

Fortunately Factor 1, "High Educational Level of Principal Investigator," is not the only criterion provided in this procedure to characterize the key individual. In this case, and several others, Factor 10, "Importance of a Champion," is worthy of special recognition. Shaw highlighted the need, acted as the focus of communication, promoted the program, maintained its impetus and produced results. In many ways this is very close to that combination of qualities referred to by Shepard: "A creative but pragmatic imagination; psychological security and an autonomous nature; an ability to trust others and earn the trust of others; great energy and determination; a sense of timing; skill in organizing; and a willingness and ability to be Machiavellian where that is what the system requires."*

* Shepard, H. A., "Innovation-Resisting and Innovation-Producing Organization Paper presented to the Institute of Managerial Sciences at the Meeting of t American Association for the Advancement of Science, 30 Dec. 1964, Montreal Canada, p. 8.

CRITICAL POINTS

Departure from the idea of protective coatings as a suitable solution to the problem.

Rock Island Arsenal's recognition that ozone deterioration was a significant problem. Failure of truck tires during the Benicia lubricants test pointed up the Army's big stake in this problem area.

The switch from measuring ozone and development of measuring devices and test apparatus to active measures aimed at solving the problem.

Realization that Tenamene II was a real key and that similar compounds more acceptable for rubber processing could probably be synthesized.

Prediction that increasing the bulk and weight of phenylene diamine molecules would overcome deficiencies while retaining antiozone specificity in diene rubbers.

Expansion of the Augustana contract from a basic reaction mechanism study to include half its effort in synthesis of new materials.

The break away from evaluation techniques for assessing ozone cracking and emphasizing prevention and zero cracking criteria for acceptance testing.

8. Issue of Military Specification MIL-T-12459 Engineering Change Order 40996-4.

9. Issue of U. S. Patent 3032520 to R. F. Shaw.

A CASE HISTORY
OF
THE DEVELOPMENT OF PYROCERAM® BRAND GLASS-CERAMICS

Prepared by
M. G. Britton

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PYROCERAM® is a registered trademark of the Corning Glass Works.

Corning Glass Works
May 15, 1966

A CASE HISTORY OF THE DEVELOPMENT OF PYROCERAM® BRAND GLASS-CERAMICS

NARRATIVE

In the period between 1941 and 1953, Dr. S. D. Stookey had been investigating the photosensitivity of glass. He had progressed to the point of developing compositions in which colloidal metal crystals were precipitated by ultraviolet light. Upon heat treatment, silicate crystals formed in the glass on the metallic nucleation sites, thereby opacifying, or rendering the material translucent. Work on composition, process, and product development was under way to exploit this research.

In this research in photosensitive glass Stookey began to realize what profound changes could be brought about by a trace quantity of an effective nucleating agent. This realization was brought into sharp focus by an accident, which turned out to be one of the most important factors in the development of glass-ceramics. This accident was the fault of a furnace temperature controller, which allowed the furnace to heat a plate of exposed photosensitive glass 300° C hotter than the control setting. Expecting to find a pool of melted glass when he opened the furnace, he found instead a plate of opaque, predominantly crystalline material that was much stronger and harder than the original glass. This was the first ceramic-from-glass.*

This material, a valuable material in itself, still required photonucleation. It soon became obvious that controlled crystallization involving thermal nucleation in glass was both feasible and useful. The next stage, the development of thermally nucleated materials, involved the expansion of the knowledge gained in the photosensitive experiments described above to a general theory of nucleation, the search for other nucleating agents, and their use in a wide range of compositions.

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* In 1958, Dr. Stookey described the events in a paper presented at the Industrial Research Institute.

As soon as Stookey realized how broad the range of glass-ceramic compositions might be, the nature of the research was changed to a team effort, directed toward two goals. Additional staff was assigned to composition research, and additional time in the experimental melting shop was allocated. One objective was to explore the important composition fields and obtain the necessary information for preparing patent applications. The other was to select a few promising compositions and begin the development of processes and products.

Pursuant to previous experimental work in the evaluation of glass as a material for radomes, some samples of glass-ceramics from the first crucible melts were subjected to tests including whirling-blade rain erosion. The results indicated that the crystallized materials had greater strength and remarkably high resistance to high-speed impact compared to glasses and most ceramic materials. This immediately focused attention on radomes for high-speed missiles as a possible application. Indeed, some of the earliest thermally nucleated glass-ceramics were found to have still higher strength and hardness, better thermal shock resistance, and better dielectric properties at radar frequencies than the photo-nucleated material. Tests by defense agencies verified that these glass-ceramics had good properties for radomes; so, although production was still in the crucible stage, a development contract to determine the feasibility of radome production and to obtain radomes for evaluation by the defense agencies was undertaken and successfully carried out. This involved pilot plant production of radomes under Dr. Ben Allen, whose coordination of melting, forming, and finishing development produced usable items within a very tight timetable.

The Research Director had by this time alerted the company's top management to the radical nature of the discovery, and the President charged line management with exploiting the discovery in every way possible.

From this point on, as other compositions having new and useful combinations of properties were developed, it became necessary to establish product-development groups. Other company divisions outside the Laboratory

began to take part, and the rapidly mushrooming number of problems became complex for all levels of management.

A wise decision was made to expand the fundamental research group and not to yield to the temptation to concentrate entirely on product development for immediate marketing. However, as interest in consumer skillets developed, supporting services of R&D division were brought in by:

a. The Melting Research melt shop to speed up experimental melts.
b. The Technical Services group to measure electrical properties.
c. The Product Development group to evaluate proposed applications.
d. The Consumer Marketing groups for shape, design, decoration, service test and market evaluation.

Also, backup by technicians and administrative services speeded up experimental work.

The next episode in the story of PYROCERAM® Brand materials was a successful run of a general-purpose glass-ceramic in a specially-rebuilt full-scale production tank. This glass-ceramic was used for many kinds of articles, e.g., ball-bearings, pipe, skillets, sheet, and large telescope mirror blanks. This production represented a million-dollar gamble by the Company, with a glass that had to be formed 100°C hotter than any production glass made previously, in addition to posing many other new problems for production.

A very difficult management problem was to decide when and how to make public the new developments. It was known that an invention of such complexity and broad scope would probably require years to perfect completely, so that immediate public announcement in some respects would be premature. On the other hand, incomplete and distorted stories were beginning to circulate through grapevines. The announcement was made at the time of the dedication of the new Corning Laboratory, on May 23, 1957.

The response to this announcement amazed everyone at Corning. A deluge of about 10,000 requests for information resulted. In order to cope with these successfully and to tie together the activities of the various divisions of the Company in this field, a coordinator for glass-ceramic materials was appointed by top management.

After this, under the urging of Mr. Waterman, and the product development work under Mr. Voss, a major effort was made to produce consumer cookware. First production runs were under a project engineer, Dr. George Bair, and the need for meeting a favorable market date spurred the effort.

APPENDIX A
TO
CASE HISTORY
ON
THE DEVELOPMENT OF PYROCERAM® BRAND GLASS-CERAMICS

The Corning Glass Works

A. GOALS AND STRATEGY OF THE COMPANY

1. Competitive Situation of Company

The glass industry tends to distinguish itself from the ceramic industry in that its fundamental processes, unlike its materials, are distinct. Further, the processes are the basis of the classification of the industry into the flat glass, container glass, pressed and blown glass, and glass specialty groups. The 1958 sales volumes were:(1)

Flat Glass	$385 million
Containers	862
Pressed & Blown	445
Specialties	469
	$2,161

The Corning Glass Works had sales of $159 million in that year, with research and development costing $7 million. Its product divisions reflect the kinds of markets which the company served: electrical products, including: light bulbs, radio bulbs, television bulbs, fluorescent tubing; technical products, including: laboratory glassware, chemical industry process ware, optical glass; Consumer products, including houseware, tableware, ovenware, and new products, including radomes, aircraft windshields, glass resistors and glass capacitors.

In regard to the successful applications, radomes and cooking ware, there existed at the time no market in the sense of competing against materials or products of similar properties. That is, the missile industry, previously content with fiberglass reinforced plastic radomes was confronted for the first time with high velocity flight through a rainstorm. Erosive destruction of such radomes provoked a search for a strong, hard, dielectric material. In the cooking ware line, competition came primarily from metallic containers, ceramic cookware never having been highly developed technically nor marketed aggressively.

(1) Ceramic Age, January 1965

In this period, sales rose from $149 million in 1953 to $201 in 1959. Net income per share rose from $1.86 to $3.57.

2. Company Policy Influencing R&D Efforts

Company policy is best indicated by the establishment of a laboratory in 1908, one of the first industrial laboratories in the nation. Its first full time employee, Dr. E.C. Sullivan, was active in the company's technical program as an advisor in 1960. He had in those years been Research Director, President of the company, Research Director, and finally, honorary Board Chairman. He brought to Corning W. C. Taylor, J. T. Littleton, and H. P. Hood, all pioneers. They spent their entire professional lives with Corning and became respectively Vice President and Director of Technology, Vice President and Director of Research, and Head of Chemistry. The present research director, Dr. W.H. Armistead is a corporate Vice President. Attitude is reflected by a statement from the 1961 Annual Report "Corning has long believed that corporate growth can best be achieved and accelerated by vigorous continuation of a large and expanding program of research and development. Research and Development expenditures (for 1961) rose to a new peak of $10,714,482, or 4.7 percent of sales. This ratio is considerably higher than the average for all manufacturing industry in the United States." The research effort has constantly been supported with new buildings. In 1908 the laboratory occupied 1200 square feet. In 1939 a new building of 61,000 square feet was built, in 1957, a new complex of 189,000 square feet was built, and in 1965, a new complex of twice this size was under construction.

Growth of Sales and Research Budget in period 1952-1959:

1952	$126 million	$3.29 million
1953	149	5.22
1954	148	4.49
1955	150	5.32
1956	163	4.79
1957	159	5.63
1958	159	6.90
1959	201	8.13

All materials research, most product development, and most process development during the period 1952-1959 was done in Corning, New York area within a geographic radius of 1/2 mile.

3. Limitations Imposed by Management

Limitations imposed by management on the research program were those of the Research Director. To a major degree, the consideration of the needs, capabilities, and guidelines set by the product divisions was influential.

4. Orientation of Laboratory

The competitive situation was primarily on the basis of costs rather than technical competition, since few glass companies had a financial position to justify large research programs. Those companies which were large were flat glass and container producers, and did not at the time enjoy a major position in "pressed and blown" glass such as consumer or technical glass. The Corning laboratory had been well known, and in the industry's circles was recognized for its orientation towards exploratory research in glass chemistry and physics. However, at the time of the discovery of the glass-ceramic, only a very small fraction of the technical effort was allocated to basic research; a rival, existing product, television bulbs, was consuming practically all available people.

B. CLIMATE FOR WORK

1. History

During the early fifties, the company tended to shift its publishing philosophy to greater freedom, particularly in the research on the chemistry and physics of the glassy state. Prior to that, publication, particularly of manufacturing details, was quite limited. Patents had always been vigorously sought for compositions or processes which were to be marketed. Other details of technical knowledge were considered proprietary. Formal reporting systems developed as memoranda until about 1945 when a system of laboratory records was imposed, with a system of individual progress reports being developed about 1953.

2. Facilities and Personnel

The laboratory had operated as a formal group since 1908 under Dr. E.C. Sullivan. By 1938, the staff consisted of 100 chemists, physicists, engineers, glass technologists and assistants. By 1956, the staff reached the level of 350. In 1939 Dr. Sullivan, who had been President of the Company in the twenties, was Director of Research. He supervised Dr. Littleton, in charge of physics, and Mr. Taylor, in charge of chemistry. In 1944, Littleton became Director of Research and Taylor became Director of Glass Technology, a

manufacturing advisory group. Littleton continued until 1959, when Dr. E.U. Condon became Director. In 1954, Dr. W.H. Armistead became Director of Research, and latter became a Vice President and Director of Technical Staffs. The position of Research Director reported either to the President, or in recent years, to a Vice President for staff groups. Also in recent years the company had formed product divisions, i.e., Technical, Consumer, Electrical, and New Products which also reported to the President through General Managers, usually vice presidents.

3. Organizational Structure

The Laboratory during the mid-fifties was organized into departments, each with a Manager reporting to the Research Director. In addition, a process research and development group headed by the late Dr. Ben Allen reported to the Research Director, forming with other research groups a "Melting Research" group. This team played a vital and multiple role in bringing new developments into production. Part of the group was housed in the Research Laboratory and its staff had traditionally worked closely with the Research Staff. Other parts of this group were housed in a pilot plant, and its staff had worked closely with manufacturing groups through process development and break-in stages.

The research groups, having been physically located prior to 1957 in a laboratory surrounded by the manufacturing plants, had been accustomed to closely watching melting and forming operations which were in a transition from laboratory results. That is, since the pilot plant concept had been of recent introduction, much experimental work was accomplished in the manufacturing plants, and research people took a personal interest in progress.

The laboratory prior to 1950 had little formal structure other than the chief physicist and chief chemist. New personnel were assigned to "work with" senior scientists in various areas, but there was no hierarchy of titles. The general philosophy in the fundamental field was that the individual best knew the areas of interest in which he should work, and assignment of research objectives was rare.

4. Channels of Communication

In the late thirties, the staff reported daily its work, by dictating a few notes which were typed and then read by the Research Director. Later, monthly reports were prepared. By 1951, a formal system of reporting research

results was adopted, each report being in effect a summary representing a significant amount of work or a significant innovation. Later, a system of monthly technical staff division reports was initiated, and summaries were widely distributed to executives and "new product" people in manufacturing divisions. Also a semi-annual progress meeting was held in the Research Director's office, and concerned persons from division sales, marketing, engineering and development were welcomed. These communication channels were actively promoted by an Associate Research Director performing all staff functions.

Communications at research level were accomplished by:

a. Six-month project review meetings to which operating division people are invited.
b. Divisional monthly meetings to which R&D administration is invited.
c. Circulation of monthly laboratory progress reports to research, product, process and manufacturing division people.

5. Pressures and Controls

Problem definitions and new business opportunities were usually orally or, occasionally by memo, communicated by division managers to the research director, who was in complete charge of allocation of the research budget. At the time of the PYROCERAM® brand glass-ceramics work, however, the extreme pressure for work on television products captured a major proportion of the staff's attention. This pressure was very great in the early fifties, and then receded.

6. Motivation and Morale

One important feature of the quickness with which the technical and non-technical people grasped the significance of the PYROCERAM® brand material was the company's product history. Since 1912, when the low expansion borosilicate glass had been invented to withstand heat shock, the company had recognized the great importance of a low thermal expansion. This awareness permeated the company. When the first glass-ceramic had such a property, better than most glasses, coupled with higher useful strength, the commercial application was immediately appreciated. It may seem trite to say that "morale is high," but reasons for this are strong. First, the laboratory was established in 1908 by Dr. Sullivan, who for over 50 years continued to be the senior technical man

in the company. He shaped the philosophy of generations of executives to an appreciation of the value of research investment. Thus, the scientific staff has been given excellent facilities and a climate of patience to which the creative person responds. Nevertheless, the staff was physically close to the plant, and direct involvement was encouraged. In later years, a generous attitude toward travel for technical meetings and for memberships in technical societies, along with a good library and supporting staff, created an environment that the staff appreciated.

7. Leadership

The organization structure, as it developed in the fifties, followed much more the line of fitting the structure to the skills of the people available, than to fitting the people available to a structure. Thus, emerging leaders could be suitably advanced, thus strengthening the whole team. This was particularly valuable in the process development and pilot plant area, where a leader was established who worked well with both research, engineering and executive level people.

Fortunately, formal and informal leadership seemed to be coincident. Armistead, who had become Research Director by the time the glass-ceramic started to get fresh attention (due to the relief in pressure from television product problems) had shared an office with Stookey, and was quite familiar with his ability in research. At the same time, Armistead himself had always lived close to the effort to get new compositions for new products, and was therefore quick to exploit what was obviously a basic invention. Furthermore, he had worked on projects so vital to the company that top management had known him for a long time and at first hand.

C. BIOGRAPHIES OF KEY PERSONNEL

Allen, Ben

Experience:

1950 - CGW Research Chemist

1955 - CGW Manager, Melting Department

1958 - CGW Director of Melting Technology

1960 - CGW Director of Engineering

Education:

Cornell University, Chemistry 1946 B.S.

Cornell University, Inorganic Chemistry - 1950 Ph.D.

Critical Period

1956 - CGW Manager, Melting Department

1957 - CGW Manager, Melting Department

Memberships in
Technical Organizations:

American Chemical Society

American Ceramic Society

Sigma Xi

Armistead, William H.

Experience:

1941 to 1954 - CGW Research Chemist

1954 - CGW Manager, Melting Department

1954 to 1956 - CGW Research & Development Director

1956 to 1961 - CGW Vice President & Director of Research and Development

1961 to Present - CGW Vice President & Director of Technical Staffs Division

Critical Period

1956 - CGW Research & Development Director

1957 - CGW Vice President & Director of R&D

Education:

Vanderbilt, Chemical Engineering 1937 B.E.

Vanderbilt, Chemistry 1941 Ph.D.

Armistead, W.H. (Cont'd.)

Memberships in Technical Organizations:

American Ceramic Society	Director of Industrial Research
American Chemical Society	Society of Glass Technology
American Institute of Chemists	Sigma Xi
American Management Association	Industrial Research Institute

Bair, George J.

Experience:

1927 - 1931 - Pennsylvania State University, Instructor
1931 - 1936 - Pennsylvania State University, Asst. Professor
1934 - 1935 - M.I.T. Teaching Assistant
1936 - 1937 - Fellow, Mellon Inst. of Industrial Research
1937 - 1942 - Senior Fellow, Mellon Inst. of Ind. Research
1942 - 1944 - Research Chemist (CGW)
1944 - 1946 - CGW Manager of Multiform Pilot Plant
1946 - 1952 - CGW Manager of Optical Glass Plant
1953 - 1961 - CGW Manager Quality & Process Engineering
1961 - 1964 - CGW Manager of Development Engineering
1964 to Present - CGW Director of Technical Staff Services

Education:

Pennsylvania State University, Ceramic Engineering 1927 B.S.
M.I.T., Ceramics, 1936 Sc.D.

Critical Period

1956 & 1957 - CGW Manager Quality & Process Engineering

Memberships in Technical Organizations:

Fellow, American Ceramic Society
National Institute of Ceramic Engineers
American Chemical Society
Society of Glass Technology
International Commission on Glass
Sigma Xi
Tau Beta Pi
Sigma Gamma Epsilon

Stookey, S. Donald

Experience:

1940 to 1955 - CGW Laboratory - Research Chemist

1955 to 1963 - CGW Manager Fundamental Chemical Research Dept.

1963 to Present - CGW Director of Fundamental Chemical Research

Education:

Coe College, Cedar Rapids - Chemistry 1936 - B.A.

Lafayette College, Easton, Chemistry 1937 - M.S.

M.I.T. - Chemistry 1940 - Ph.D.

Critical Period

1956 - Manager of Fundamental Chemical Res. Department

1957 - Same as above

Memberships in Technical Organizations:

American Ceramic Society

American Chemical Society

Society of Glass Technology

Sigma Xi Club

Voss, R.O.

Experience:

1942 - CGW Chemist

1944 to 1956 - CGW R&D Research Supervisor

1956 - CGW Manager of Ceramic Research

1957 - CGW Supv. of Consumer Product Development

1958 to 1963 - CGW Mgr., Consumer Product Development

1963 to present - CGW Director of Product Development

Education:

Stetson University, Chemistry 1941 - B.S.

Critical Period

1956 - CGW Manager of Ceramic Research

1957 - Supervisor of Consumer Product Development

Membership in Technical Organizations:

American Chemical Society
American Ceramic Society

Waterman, R. Lee

Experience:

1926 - 1933 - W.T. Grant Co. Manager

1933 - 1940 - Montgomery Ward & Co., National Retail Merchandise Manager & Div. Manager

1941 - W.T. Grant Co., Director of Sales Promotion and then Vice President & Director of Merchandising

1951 - Sloane-Blabon Corp., President

1955 - CGW, General Manager of Consumer Products Division

1956 - CGW, Vice President

1962 - CGW, Director

1964 - CGW, President

Education:

Bates College, 1926 B.S.

Critical Period

1956 & 1957 - CGW Vice President

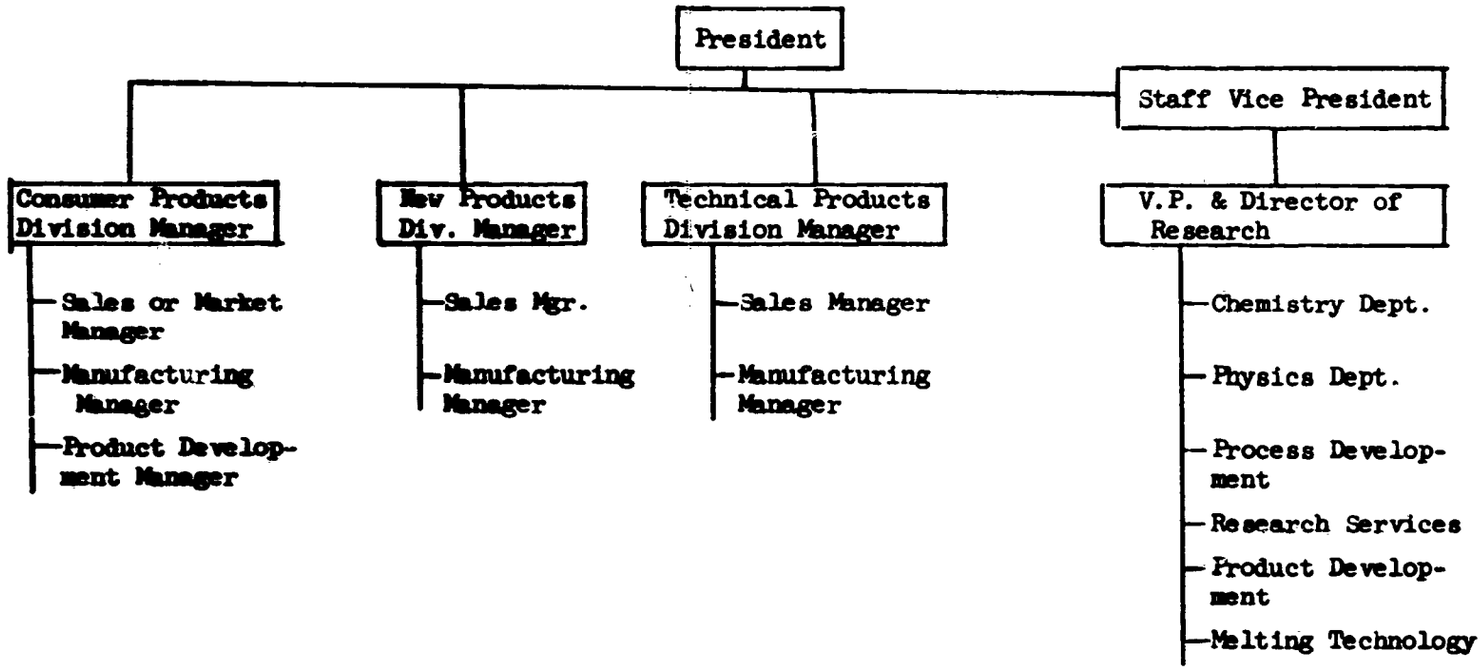
He is also chairman of the board of CGW of Canada Ltd., and a director of Corning, Nederlandse Fabrieken, N.V., and Corhart Refractories Co., and a trustee of the CGW Foundation.

Also, past president of the National Housewares Manufacturers Association, Vice President of the Marketing Division of the American Management Association, and a member of the Advisory Board of the American Hardware Manufacturers Association.

He is President of the Board of Trustees of the Wooster School, Danbury, Conn., and a trustee of Bates College, Lewiston, Maine.

CORNING GLASS WORKS LABORATORY

Organizational Structure - 1952-1958



NB. This is only a typical chart since there were several reorganizations in the period. For the most part, the structure reflects the character of the people available at any particular time rather than fitting the people to a rigid structure.

ANALYSIS OF CASE HISTORY OF GLASS-CERAMICS

For the purposes of analysis, this case history has been divided into subcases as shown below.

Sub-case	Title
I	Glass-ceramic radomes
II	Glass-ceramic cookware

DESCRIPTION OF REIs

REI	Description
	Sub-case I. Glass-Ceramic Radomes (Corning Glass Works)
a	Military need proposed by Navy; a glass radome was furnished for rain erosion test, but erosion was very high.
b	Composition research Chemists supplied glasses for evaluation of materials to be used in glass melting furnaces; glass also supplied for evaluating forming methods.
	Sub-case II. Glass-Ceramic Cookware (Corning Glass Works)
c	Properties adjusted to produce test items by normal glass forming processes.
d	Additional composition research to eliminate micro-cracks and to develop decorations.
e	Development of special process controls for full scale manufacturing operations.

STAGES AT WHICH REIs OCCURRED

Stage* No.	Sub-case I	Sub-case II
0		
1		
2		
3		c
4	a & b	
5		d
6		e

*Stages were defined by the Committee for purposes of this study, as follows:

STAGES

No.	Definition
0	Scientific finding (knowledge). Research on photosensitive nucleated glass, then thermally nucleated.
1	Recognition of new material (process) possibility. Determination of physical properties.
2	Creation of useful material (process) form. Melt shop made slabs.
3	Possibility of using the material (process) in hardware. Pressed and blown ware from pots and day tank.
4	Possibility of using the hardware containing the material in a system Recognition of product usefulness.
5	Production of the system (product). Factory melts and pilot plant melts forming.
6	Operation of the system (Product). Charleroi-Baden City melts.

FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From the study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs and listed them as follows:

List of Factors Considered in Analyzing Events of REIs

1. High educational level (advanced degree) of principal investigator
2. Importance of management
3. Importance of Government-sponsored research
4. Importance of recognized need
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources)
6. Industrial laboratory involved
7. Basic research in the laboratory (or institution or organization)
8. Communications across organizations was important
9. Technical problem was the principal obstacle
10. Importance of a "champion"
11. Freedom for individuals
12. Broad spectrum of types of laboratories
13. Geographic proximity
14. Prior experience with innovation
15. Organizational structure (barriers and bonds)

FREQUENCY OF FACTORS IN REIs
(Statistical Analysis)

Factor No.	Sub-case I			Sub-case II				Total Frequency
	a	b	Totals	c	d	e	Totals	
1		X	1/2		X		1/3	2/5
2		X	1/2				-	1/5
3			-				-	-
4	X	X	2/2	X	X		2/3	4/5
5	X		1/2		X	X	2/3	3/5
6		X	1/2		X		1/3	2/5
7	X	X	2/2				-	2/5
8	X	X	2/2	X	X	X	3/3	5/5
9			-		X	X	2/3	2/5
10			-				-	-
11				X			1/3	1/5
12		X	1/2	X	X	X	3/3	4/5
13		X	1/2				-	1/5
14	X	X	2/2	X		X	2/3	4/5
15					X	X	2/3	2/5

SUMMARY ANALYSIS

COMMENTARY ON SIGNIFICANCE OF FACTORS IN CASE HISTORY

The analysis shows Factors 4, 8, 12, and 14 as those most frequently occurring. Factor 4, the importance of a recognized need, permeates the case. Research exploitation moves faster, as opposed to simply moving, if there is an urgent need. In the case of the ceramic radome, composition research quickly identified a dielectrically satisfactory material, and the furnace people learned how to melt it. Furthermore, the need was more real than simply a paper study. The Navy's missile was in existence, and operationally limited, so that the Navy's response time was shorter than usual.

Factor 8, communications across organizations, was important. All the engineering and research people involved in the interactions reported to the same executive. Since he had complete authority to shift program emphasis, the various departments involved could be committed as need be. Equally important was the charge by the corporate president. He had been persuaded that the new discovery was revolutionary, and directed all operating groups, i.e., their process and product engineers, to exploit the new materials as quickly as possible.

Factor 12, the broad spectrum of technology, reflects an ability to summon in-house experts on each technical problem as it arises. Their availability also is a result of the unification of the technical staff under a single executive.

Factor 14, prior experience with innovation, is certainly valid for the research-engineering interaction. However, a prime reason for the speed of the process, which required the support of manufacturing groups, was the drive of the new general manager for whom a new product was essential. An innovation had not been a strong characteristic of that particular group, as was the case for the research people.

The role of two factors is especially important: the Navy had asked Corning for a glass radome. Its rain erosion resistance was poor, and this fact was known to the laboratory staff. The hardness of the glass-ceramic

indicated it was an obvious candidate. The additional requirement for dielectric constant stability and low loss provoked composition research. Thus, the Navy, with its urgent requirement for defense, played a significant catalytic role. The second factor was the low expansion of the lithia glass-ceramics. Here, the Company's long market orientation to consumer products alerted the Division Manager to the opportunity for rapid exploitation; and this opinion was shared in a meeting with the Research Director, the Consumer Product Development Manager, and others.

As the project developed, the person-to-person contact of the Division Manager, who needed the product, and the Development Manager, who was in this case an informal leader more than the formal one, was very frequent. Summary reports by the Development Manager were widely circulated.

In summary, I believe that the key points of a well-integrated technical and marketing program reflected the importance of management in defining the high priority, and therefore a massive effort on creating a product of recognized need.

CHRONOLOGICAL SUMMARY OF THE HISTORY OF GLASS-CERAMICS

Date	Event	People Responsible	Motivation
Fall 1952	During composition & process research on metal-nucleated photosensitive glasses, furnace accidentally over-heated and a glass-ceramic of unusual strength was produced.	Stookey	Serendipitous observation on printing plate research.
Late Fall 1952	Added TiO_2 as a nucleating agent.	Stookey	Had realized that thermal initiation was more desirable than optical.
Winter 1952	Larger melts of thermally nucleated glass (pot and day tank)	Stookey	Needed quantity of material to explore heat treating schedules.
Spring 1953	Glass chemistry staff expanded to explore compositions.		
January '54 June '55	A slow-down period: optically nucleated aperture masks and printing plates pre-empted research time.	Stookey	Color Television markets vital.
Fall '55	Rain erosion test focused interest on glass-ceramic for radome.		Navy seeking high speed capabilities.
Spring '56	Accelerated program Mg-Al-SiO_x (good dielectric) used to spin radomes from glass melted in pilot plant.	Allen	Process research function.
Spring '56	Extension composition research using TiO_2.	Stookey & Tech. Staff	Determine the universality of TiO_2 as a nucleating agent
Jan. '57	Melts of Li-Al-SiO_x glass to get samples and test processes for pressed consumer products.	-	Opening of new lab in May 1957.
Jan. '57	Check out pressed consumer products for properties	Waterman & Voss	General recognition of low expansion needs.

Chronological Summary (Cont'd.)

Date	Event	People Responsible	Motivation
Fall '57	Consumer product composition research renewed. (8 pilot plant melts had preceded this.)	Stookey et al	Micro-cracking detected.
Jan. '58	Major tank melt for market test.	Bair & Waterman	Normal role, project manager.
April '58	Final product specification.		
Summer '58	Production run.	Bair	Fall Housewares market.

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A CASE HISTORY OF MISSILE-GRADE GRAPHITE

Prepared by
E. M. Glass

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A CASE HISTORY OF MISSILE-GRADE GRAPHITE

BACKGROUND

This study reviews the development of a number of graphite advances as seen through their history and the actions of a major producer of graphite materials and a number of organizations in the Department of Defense (DoD). This case was selected as an example of a DoD attempt to transform scientific research findings into engineering applications.

It was believed that the study of a case in which the DoD was closely involved would provide valuable insight into the process of interaction that exists-or then existed-between the Federal Government and industry. The selection of one company for discussion in this study was due partly to the availability of information and partly to the fact that the DoD chose that company to scale up a number of processes offering unusual potential for satisfying Defense needs with respect to performance, uniformity and reliability.

All the information for this case study was provided by Mr. W.A. Steiner, retired Vice-President (Technology) of the Union Carbide Corporation, Mr. J.J. Krochmal of the Air Force Materials Laboratory, and Major I.K. Holdener, Headquarters, U.S. Air Force. Without their contributions, the study would not have been possible.

A General Perspective of Graphite Technology

Graphite is unique as a refractory structural material owing to its great binding energy which makes it the highest-temperature-stable elemental solid. The strength-weight ratio of graphite is above that of any known material from 3100°F to more than 5500°F. It has no liquid phase below a pressure of 100 atmospheres and sublimes at 6700°F at atmospheric pressure. Although in the class of brittle refractories, it is inherently plastic at room temperature and limited deformation at small load relieves stress concentrations. Graphite has a very high degree of resistance to thermal stress and shock.

Many materials have individual properties that far exceed those of carbon. For example, copper's electrical conductivity is thousands of times better than that of graphite, but its strength drops to practically zero at 1800°F. Fused quartz has lower thermal expansion but no electrical conductivity. For chemical inertness, only metals like platinum or tantalum equal carbon. For high-temperature strength, carbon is in a field all by itself; no other substance (with the exception of carbides of tantalum and columbium) can approach carbon.

The graphite business is based on the material's unique intrinsic physical and chemical properties, such as the following:

Sublimation at 6700°F (Does not melt at atmospheric pressure.)
Useful strength up to about 4300°F (Steel melts at 2500°F.)
Low coefficient of thermal expansion (ne-eighth that of steel)
Thermal conductivity (three times that of steel)
Chemical inertness
Neutron characteristics

To meet specific service needs, other desirable characteristics related to structure and composition can be built into the graphites by suitable processing, for example:

Resistance to severe thermal stress and shock
Impermeability to liquids and gases
Hardness varying from unctuous and soft to very hard

The physical properties of fabricated graphite can be made to vary over a wide range, because the highly anisotropic hexagonal plane crystal allows such control by the selection and processing of the raw materials; and further variations can be effected by an increasing number of basic fabrication processes for the formulation of grain texture and structure.

The properties of a graphite article are determined by its composition and structure as follows:

Composition - major phase(s),
minor distinct phase(s)
intergranular material or binder

Microstructure - continuous phase(s)
discontinuous phases
disposition of phases (i.e., within or among)
crystal structure of phases

Macrostructure - density or porosity
pore size, shape, distribution
grain size, shape, distribution
grain orientation
structure of grain interfaces
cracks, flaws, inclusions

The carbon atoms making up soot, charcoal, natural graphite and diamond are identical. The wide differences in these materials' properties arise from the differing arrangement of carbon atoms with respect to each other.

Carbon materials (such as cokes, charcoals, blacks) that have not been heated to high temperatures possess an embryonic crystal structure; the carbon atoms are arranged in layers which are wrinkled and warped. The high temperatures of graphitizing simply flatten out the wrinkles of crystal layers already present in the carbon at the instant it was formed by the decomposition of carbon-containing compounds.

The ultimate physical properties of a graphite article depend largely upon the nature and processing of the raw materials, which must also have the intrinsic crystalline structure required to produce the desired properties in the resulting article.

The graphite article's physical properties are also dependent upon the nature and quantity of the bond carbon cementing the carbon particles. The quality of the bond carbon, which governs strength and conductivity, is affected by the processing temperature. Further, the relative quantity of binder is critical; for example, as quantity is decreased, strength and conductivity fall off rapidly.

A key operation in carbon manufacture is carbonizing the binder into an infusible solid, which occurs when the baking temperature goes beyond about 900°F. Because of binder pyrolysis and physical and dimensional changes, the baking process is very sensitive to many factors, such as thermal gradients, supporting of the "green" shapes, volatile venting, oxidation, etc. Baking must be controlled within the limits defined by the type of process; for instance, in bulk baking the total cycle may be 55 days, but it may be only minutes for some shapes under suitable pressure.

Because of the need to balance many factors in both the processing and the use of carbon products, there are intrinsic relationships between the size of an article and its physical properties. That is, the properties and structure of small pieces may be quite different from those of large pieces; or what can be made in small sizes may not be duplicated in larger sizes. Similarly, it is not possible to test small samples and extrapolate results to performance of large pieces without first developing adequate correlation data.

History of the Carbon and Graphite Industry

To understand the present status and future prospects of the carbon and graphite industry, it may be of interest to look back to its scientific and technical origins.

The industrial uses of carbon and graphite products are based on properties that enable uses as terminal conductors for the conversion of electrical energy to other forms of energy. Electrolytic anodes of graphite are used in the conversion of energy from electrical to chemical; and electrothermic electrodes of graphite are used in converting electrical energy to heat.

The nuclear and aerospace uses of graphite are based on unique combinations of nuclear and physical properties, such as neutron moderation and high strength at high temperature.

Around 1800, Cruickshank discovered that a salt solution can be electrolyzed to form sodium and chlorine. About the same time, Davy demonstrated the electric arc between two carbon rods, forming a concentrated source of radiation for light or heat. These early experiments used primary batteries. From Faraday's discovery of the principles of electrical induction in 1831, the dynamo was developed in the 1860s.

With the advent of the dynamo, major industrial uses of electricity were soon developed. In the early 1870s, arc lamps were introduced for lighting. In 1878 to 1886, Siemens and Herroult invented electric arc furnaces which were soon adapted to metallurgical processes such as production of ferrous alloys and calcium carbide. In 1886 Hall invented the electrolytic process for producing aluminum. In 1890 alkali-chlorine plants were started. In the late 1880s, streetcars were developed that used electric motors, for which carbon brushes were found to be necessary.

The fabrication of carbon and graphite shapes for industrial uses is a comparatively recent invention. Because carbon has no distinct melting point at reasonable pressures, the usual metal-working techniques, such as casting or rolling, cannot be used. The graphite industry uses processes similar to those of the ceramics industry, but differing because of the thermoplastic binder and the need to protect the articles from slumping and oxidation while they are being baked.

The original physical experiments used small rods cut from charcoal or retort carbon. Formed rods were made later by pulverizing charcoal and mixing it with syrup, forming the rods, and baking them. In 1842, Bunsen made carbon electrodes for batteries. During the years 1846 to 1858, inventors developed processes for making carbon plates, using powdered coke and binders such as sugar or tar. In 1878, Brush first used the process of calcining petroleum coke as a preliminary step in the manufacture of arc carbons.

Acheson invented his process for graphitizing formed carbon shapes in 1895. Before this, the only graphite shapes available were clay-bonded natural graphite, whose properties were only adapted to such uses as crucibles and writing-pencil leads. The availability of Acheson graphite has enabled a major expansion of electric steel and chlorine production, as well as many uses of graphite in the metallurgical, chemical, electrical and mechanical industries.

Until World War II (and even thereafter), the higher volume of defense requirements reflected primarily a greater demand for industrial carbon and graphite products used in producing alloys, steels, chemicals and electricity for war production. Special new needs were generally met with standard processing methods, but using specially selected raw materials and additional purification or impregnation. A case in point was the development of high-purity graphite for reactors in 1942. Another was the use of ATJ graphite in missiles, although this was developed primarily for die applications in the metallurgical and metal-working industry.

The emphasis of the industry was mainly on the commercial markets. Commercial objectives were more easily defined, and the economics and timing of these markets permitted adjustable trade-offs. Wartime and subsequent defense requirements were not as easily or as well defined nor as flexible with respect to time. Defense work represented less than 2 percent of the industry's business, and this provided little incentive for the industry to invest heavily in scaled-up programs aimed solely at satisfying the DoD's needs. Fortunately, research activities aimed at improving commercial products and processes were equally applicable to defense uses.

Special Emerging Defense Needs

The first major use of graphite for missiles was for rudder vanes, which guide a missile during the firing period by direct action in the jet blast. The German V-2 rocket (at its stage of development in 1944) used rudder vanes of high-density graphite (1.8 grams per cubic centimeter).

Graphite nozzles were first used in 1942-45 for aircraft JATO (jet--assisted takeoff) rockets. Available industrial graphites performed satisfactorily in this application. The JATO nozzles were relatively small, about 2 inches in outside diameter. By about 1952, the outside diameter of nozzles had grown to 5 inches, and erosion conditions had reached the performance limits of industrial graphites.

A major problem facing both the users and the industry was their inability to write realistic, meaningful specifications which related measurable properties to performance characteristics. In a number of Defense programs, this had resulted in unnecessarily high scrap rates and a general lack of confidence in this class of materials, which offered so many unique possibilities for use in very high-temperature applications.

Between 1955 and 1957, several situations developed which were to have a long-range effect on graphite utilization for military missile applications in the ensuing decade. The development of higher energy solid propellants indicated the potential of solid systems for intercontinental ballistic missiles (ICBMs). This led to the establishment of two missile programs, the Navy's Polaris and the Air Force's Minuteman. Early development testing of the new propellants showed that available commercial graphites were only marginally acceptable. This jeopardized the inherent reliability and growth potential of both systems. During the same period, the Army, in developing the Redstone missile, was experiencing great difficulty in obtaining producible lots of graphite materials for jet vanes. The reason was that strict acceptance standards were being imposed on commercial graphite materials not developed for missile uses. About that time, the DoD transferred prime responsibility for land-based long-range missiles to the Air Force, so the development of adequate materials for the associated missile systems became the direct concern of that military department.

DEPARTMENT OF DEFENSE INVOLVEMENT

By virtue of its responsibilities in connection with work for the DoD, the Materials Advisory Board (MAB) sensed the impending emergence of new materials problems and opportunities. In 1956, Dr. J. R. Lane, an MAB staff scientist, recognized a potential problem in the graphite area and suggested to Mr. Verne Schnee, Executive Director of the MAB, that an MAB study of the graphite problems would be appropriate and potentially helpful to the DoD. Approached on this matter by Mr. Schnee, Mr. John Garrett, Staff Specialist, Office of the Assistant Secretary of Defense (Research and Engineering)[1], recognized the importance of such a study. Mr. Garrett then secured the approval of Mr. William Holaday, Deputy Assistant Secretary of Defense (Research and Engineering), for the study to proceed on 7 January 1957. Dr. Lane completed the MAB staff study and published a report on 9 May 1957. The report's conclusions are as follows:

> "1. Better graphite than is now available will be required as components of missiles now being designed.
>
> "2. While the uniformity of graphite now commercially available is considered satisfactory for power reactor applications and most civilian uses, a much higher level of uniformity is needed to satisfy certain reactor and missile structural applications. The adoption of realistic, meaningful specifications (including such as strength, density, grain size, etc.) for critical applications would mark a logical advance in its application. Improvements in nondestructive testing are needed to enable the routine production of grades to specification.
>
> "3. Manufacturers have significantly improved their product over the years, and it is to be assumed that such effort will continue. It may not be reasonable to expect that the present commercial process is capable of yielding a product of adequate uniformity and reproducibility for some future critical military applications. Other approaches to making graphite are known, but apparently are not being actively pursued. Commercial incentives for this work are small, and the government support would be required to achieve the rate of progress which weapon designs call for.

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[1] The Office of the Assistant Secretary of Defense (Research and Engineering) -OASD(R&E) - was the predecessor of the present Office of the Director of Defense Research and Engineering - ODDR&E.

"4. The development of superior grades of graphite for use in high temperature applications in such weapons as missiles will lag until performance requirements have been spelled out. This itemizing is clearly within the province of the military and weapon contractors. Involved are not only the accumulation of numerical data, but the determination of the special physical and mechanical properties which control performance.

"5. Specifications for pertinent grades of graphite need to be evolved by the concerted action of producers and users. Designers will be encouraged to specify graphite rather than possible alternate materials, if it can be produced to guaranteed narrow variations in limits on properties. It should be recognized that such practice would raise the cost.

"6. The ability to detect flaws and other undesirable characteristics in graphite is not highly developed. Sponsorship by appropriate agencies of research on nondestructive testing methods would enable the selection, with much more certainty than is now possible, of sound, strong specimens.

"7. By far the greater production of graphite is for grades (electrodes, anodes) inappropriate for use at high temperatures in weapons. Since the commercial incentive for the development of grades which might at some time be of interest to the Defense Department is small, it appears highly desirable to increase the support for research on basic studies and unique manufacturing methods. This should be done, if necessary, at the expense of sponsored research on modifications of the standard production procedure. [illegible] such as on oxidation - and erosion- [illegible] seems to be needed. Because of its characteristics, the use of graphite [illegible] couraged to the fullest extent commensurate with capabilities.

"8. In view of the extensive AEC [illegible] graphite for special reactor applications, [illegible] military programs on high temperature [illegible] require coordination with those of the Atomic Energy Commission."

The DoD Coordinating Committee on [illegible] study at its eleventh meeting, 26 July 1956, [illegible] study to producers in the graphite field [illegible] also set up an informal working group with [illegible] DoD staff to review the present government programs in graphite, in order that an [illegible] comments might be made.

Best Available Copy

The Working Group's review of government work and its study of replies from graphite companies led to the conclusion that lack of progress in obtaining graphite of proper quality for military application was due mainly to the inability of users to specify the properties needed. It also became clear that university-type research did not fulfill all requirements because properties of the relatively small pieces of graphite involved could not be extrapolated to larger pieces; and that there was a large source of know-how within the graphite industry-heretofore untapped by the DoD-that should be brought to bear on the general problem of obtaining better and more uniform graphite for Defense purposes.

Accordingly, the Working Group proposed to the Coordinating Committee on Materials that a tri-service program in graphite research and development be established, consisting of contracts with the companies manufacturing graphite. It was suggested that the program be managed by a single military department and that, if desired, an MAB technical panel could assist. The Working Group stood ready to establish the objectives of the program, to discuss with the graphite industry the feasibility of a cooperative effort, and to make recommendations to the Committee on the amount of effort required, including funding. The Working Group, in particular, proposed the establishment of an experimental facility for the pilot production of "missile grade graphite". The full report of the Working Group is included in Appendix A.

The Committee considered and approved this proposal at its thirteenth meeting, 6 December 1957, establishing, in place of the Working Group, a Steering Group for Tri-Service Program in Graphite Research and Development.

At a meeting on 12 December 1957, the Steering Group agreed with the suggestion of the Army member that an Army technologist make a survey of the user field in all three military services and report his findings to the group. Mr. E.J. Dunn, of the Ordnance Materials Research Office, was appointed by the Army member for this task. On 7 January 1958, Mr. Dunn outlined to the Steering Group his proposed action, which included submitting a questionnaire to graphite users. The proposal was approved by the Group. Subsequently, Mr. Dunn visited many plants in the user field and also, with members of the Steering Group, companies in the graphite industry.

Membership in the Steering Group shifted from time to time, but it was essentially as follows:

Mr. J.C. Barrett	OASD(R&E)
Mr. E.L. Hollady	Army Ordnance Corps
Mr. T.E. Hamill	Bureau of Naval Ordnance
Capt. I.K. Holdener	Air Force Materials Laboratory

Mr. Dunn's report, and recommendations arising from it, were discussed by the Steering Group at meetings in June and July 1958, at which time the report was accepted.

As a result of this policy decision and certain interservice decisions as well, the Air Force turned out to be the only military department with a direct interest in the recommended graphite program. In the Polaris program, the Navy selected refractory metal nozzles and laid primary developmental emphasis on pyrolytic graphite. Since its requirements for rocket nozzles were not severe owing to the shorter duration of their firing, the Army was more interested in the technology of solid-rocket-motor cases and devoted its resources to that area.

Already the Air Force Materials Laboratory had independently started to support several small programs related to many aspects of the recommended program. Subsequently, the Air Force continued to analyze the recommendations of the Steering Group to get a better understanding of the problems involved and the level of funding that would be required to carry out the program successfully. During routine management activities, a number of studies were completed. Among them were the following:

(1) the reassessment of DoD requirements and their relationship to Air Force needs,

(2) the solicitation of outside expert opinions,

(3) a reanalysis of industrial capabilities,

(4) an analysis of the effect of the graphite industry's proprietary attitudes on program goals,

(5) the determination of the goals' feasibility,

(6) the planning of a program approach, and

(7) an investigation of the availability of funds.

These studies were made during the year September 1958-1959. Final DoD approval and authority to proceed with negotiations for a nominally $12-million, 3-year program were granted early in October 1959. Concurrently, the need for such a program was reconfirmed by the Air Force's hardware, component and other laboratories.

In the September 1958-1959 period, there was considerable interplay within normal Air Force channels to DoD for program and funding approval. It involved the Air Force Materials Laboratory at Wright Air Development Center and the Manufacturing Methods Division of the Air Materiel Command (AMC), both of which had a technical desire to initiate the program. To sell the program as a candidate to start in FY 1960 required the support of three DoD organizations - the Air Research and Development Command (Major Krug) in Baltimore; Headquarters, U.S. Air Force (Colonel J. Hearn and Lt. Colonel J. Shipp);

and the OASD(R&E) (Mr. J. Barrett), both in Washington, D. C. This necessitated that Mr. Barrett secure the assignment of $2 million from the OSD (Office of the Secretary of Defense) Emergency Fund to the Air Force for use in the program.

As evidenced by the fact that the anticipated program cost was more than 10 times the total annual budget of the Air Force for exploratory development in ceramics and graphite, funding was a problem. It should be said here that the technical salesmanship of two highly interested Air Force Officers, Lieutenant Giancola and Captain Holdener, was fundamental to the DoD's acceptance of this program. Both were members of the Technical staff of the Air Force Materials Laboratory, Dayton, Ohio.

Funds were also obtained from a number of organizations in the Wright-Patterson Complex that recognized the need and unstintingly provided resources. The program was started with $3.5 million from the Air Materiel Command facilities people, $2 million from the OSD Emergency Fund, $500 thousand from the AMC's Manufacturing Methods Division, and $275 thousand from the Air Force Materials Laboratory. Further, because of the manufacturing technology aspects of the experimental facility, the AMC committed itself to an additional $1 million of support during the program. While the Materials Laboratory prepared to furnish from its normal budget the required balance, $4.6 million, to carry the 3-year program to its conclusion, this was done at the expense of other materials programs in the Laboratory.

After October 1959, the activities of primary interest involved negotiations concerning work areas, program costs, rights to data, special facility requirements, and the securing of deviations from normal Air Force contracting practice, particularly with respect to proprietary information and balance between government and company capital investments-all culminating in the DoD's award of a contract (effective 1 May 1960) to the National Carbon Company, Union Carbide Corporation, for the development of advanced graphite materials and the operation of an experimental facility for the Pilot Plant Production of Missile-Grade Graphite.

In summary, there was a recognition of need and opportunity by the Department of Defense; a decision to go ahead; funds and resources were obtained from a variety of sources; a contract was negotiated and a contractor selected to push ahead toward the development of high performance missile grade materials.

It should be pointed out that the use of National Carbon Company Trade Names, such as ATJ, ZTA, etc., to identify the products mentioned in this case history results simply from the role of National Carbon Company as the contractor under this particular development program. Use of these designations is not intended to imply that National Carbon Company products are the only graphite products suitable for missile or other DOD or nuclear applications. Other products of other producers have been tested successfully and are available.

HIGH-DENSITY GRAPHITES

Nature of the Problem:

Commercial graphites are manufactured by graphitizing carbon shapes made by baking the green shapes formed from mixtures of coke particles and pitch binder. Because coke particles are porous and about one-third of the binder is distilled off in the baking, industrial graphites generally have a porosity of 30 to 20 percent, with apparent densities of 1.6 to 1.75 grams per cubic centimeter (g per cc), as compared with the real density of single crystals-2.26 g per cc.

In characterizing graphites, apparent density is the simplest of properties to measure, but it is significant in itself only as a measure of carbon packing. For example, it is easy to mold blocks of 2.0 to 2.1 density with natural graphite or graphite precipitated from decomposition of carbides, but such graphite is so weak and soft as to be almost totally unsuitable as an engineering material. Thus, the achievement of high-density graphite is not significant unless accompanied by the improvement of other properties-strength, erosion resistance, thermal conductivity, permeability, etc.-needed for specific performance requirements.

For a graphite grade of given basic composition and processing, density may be associated to some degree with other properties that determine performance in specific applications. Therefore, it has been a long-standing objective of the industry to produce graphites of the highest practicable density. For example, in 1944 a basic objective of the National Carbon Company's research program on special applications was defined as "Study of manufacture of graphite of flawless, dense structure as near real density as possible". This objective was put into its simplest terms by setting as a target the development of graphite with a density over 2.0 g per cc.

Previous Alternatives:

During World War II, the postwar build-up and the Korean War (i.e., from about 1941 to 1953), graphite research and development (R&D) had to be focused primarily on specific needs for nuclear reactors, electrodes and anodes. Graphite-density requirements were met with available process technology, the two principal alternatives being pitch impregnation or the use of superfines in the mix.

In 1909 Acheson had developed the pitch-impregnation process to increase the density of graphite by filling the pores of the carbon blank with a carbonizable material, subsequently graphitized. For special needs, this process could be repeated to reach a graphite density of around 1.75 g per cc. Another method of making graphite of improved density is to incorporate superfines or furnace black in the mix to fill the voids between coke particles. With a combination of this mix and multiple pitch treatments, it is possible to make graphite with a density of about 1.85 g per cc.

Background:

The R&D program maintained by National Carbon since 1900 to improve and expand industrial uses of graphite has built an organization of people with interdisciplinary scientific and technical skills, equipped with the most modern scientific and special experimental facilities. Related to the management decision to adapt graphite to new uses, one of the general R&D objectives was higher density.

During 1944-47 and 1950-52 experimental studies were made on hot and cold pressing of purified natural graphite powders. This hot pressing used graphite tube furnaces for 4500°F to 5400°F, with carbon equipment for pressures to about 6000 pounds per square inch (psi). Though graphites up to about 2.0 density were produced, their engineering properties were not attractive.

In National Carbon's study of the triple point of carbon, small graphite boules of 2.0 density were made by recrystallization from the liquid phase of carbon in an arc furnace under 2000- to 3000-psi gas pressure. These boules had high strength as compared with natural graphite, and their electrical conductivity was about three times higher than that of good artificial graphite. This process, however, would not be practicable for producing engineering sizes of graphite.

The intensive development of the pressure molding-baking process that started in 1955, as a result of licensing the Cuban inventor's patent discussed previously,, provided a fund of engineering know-how and stimulated technical awareness of the possibilities in a high-temperature pressure process for carbon and graphite.

Recognition of the Need:

Entirely new levels of technical and economic considerations in the area of graphite were introduced in the early 1950's by major developments in missiles and aerospace vehicles. In this field, the technical requirements are much more critical than for industrial graphites, and the economic factors enable much wider latitude to achieve the technical goals.

During this initial period, about 1952-57, the National Carbon Company's specialists in engineering service to missile and aerospace builders improved the understanding of special technical requirements for graphite in these fields. It was evident that no available graphite would answer all needs; but, because its properties may be varied over such a wide spectrum, graphite represents a family of unique materials for space uses.

In 1957, National Carbon men visited the technical people of major contractors to get their thoughts about graphite-performance needs for current and future designs. This survey revealed great

interest in graphite with improved and more reliable high-temperature properties for services involving high degrees of strength, resistance to severe erosion, oxidation and thermal shock. There was also considerable interest in higher density, as possibly related to improvements in properties affecting performance of nozzles, cones, edges and reactors.

In view of this interest in higher density graphite, C.E. Larson, Vice-President for Research of National Carbon, asked V.C. Hamister, Associate Director and Senior Scientist, to study available technology and ideas and to carry out research-type experimental work to establish a principle suitable for development scale-up.

Hamister assigned this project to his engineering assistant, E.L. Piper. After consideration of the principles previously evaluated and the subsequent advances in pressure technology, Hamister recalled observations that he and his colleague, J.W. Gartland, had made in 1937 concerning the plastic flow of carbon beginning at 3100°F and of graphite at 4000°F. He suggested that Piper study the hot pressing of carbon preforms.

Key Findings:

Piper first made graphite of 2.06 density by hot pressing a piece of 1.56-density carbon (3/8 inch in diameter by 1 inch) at about 8500 psi at 4700°F in a tube furnace. This key experiment in 1957 demonstrated that hot pressing was a feasible method for producing high-density graphite.

The small size of the research piece did not allow the measurement of engineering properties, and it was realized that it would remain a lab curiosity until scaled up by a major development effort.

Development Scale-up of New Material:

The possibility of scaling up Piper's research finding was explored at National Carbon's Fostoria (Ohio) Development Laboratory, which had facilities and know-how for the molding-baking process to around 1800°F by resistance heating of the work piece. New tooling had to be developed to reach graphitizing temperatures in the experimental hot pressing of carbon or graphite preforms. It was found, however, that this process was not as practicable as an alternative developed at the Niagara (New York) Development Laboratory which had facilities and know-how for induction-heated processes. The development engineer there to whom this study was assigned, K.J. Zeitsch, built a small experimental unit to enable hot pressing to 5400°F.

National Carbon continued through 1959 with development work to establish engineering data on the hot-pressing processes for

producing high-density graphite. The first scale-up was to 2-inch-diameter blanks for subscale NERVA test nozzles, which were fir s delivered to Aerojet-General Corporation in March 1960. The next scale-ups were to diameters of 14 inches in September 1961 (on contract AF33(616)-6915) and to 30 inches in July 1963.

Although the principle of the process to make high-density graphite is quite simple, the engineering aspects are far from simple because of the extremes of temperature and pressure involved. Thus, major problems have been the development of materials and construction to enable practical and safe operation.

Testing and Uses of New Material:

Along with its effect on densification, the hot working of graphites results in a highly oriented recrystallized graphite with a crystal structure intermediate to premium and pyrolytic graphites and with characteristics that cannot otherwise be obtained. The process allows the use of a wide variety of base materials to make graphites with a broad spectrum of properties.

ZTA graphite is only one grade of this high-density type of material; its properties were selected for present service needs. With this hot-forming process,[2] it will be possible to develop other high-density graphites with optimum combinations of properties to meet specific needs of new weapon designs. Among the applications of ZTA graphite are the following:

(1) Approved by Aerojet-General Corporation for nozzles of both stages of the Skybolt missile.

(2) Approved by Atlantic Research Corporation for nozzle of the Redeye missile.

(3) Tested by Aerojet-General and Hercules Powder Company for second-stage nozzle of the Polaris A-3 missile. In the tests, its erosion rate was almost as low as that of pyrolytic graphite, but ZTA developed cracks that were due to design factors. For the stacked washer design, pyrolytic graphite was adopted. ZTA was not fully evaluated in the washer-type design.

(4) Approved and used by Westinghouse Astronuclear Division for structural components of NERVA nuclear propulsion reactors. Its properties and uniformity meet these particular service needs better than those of any other available graphites.

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[2] Wright Air Development Division, Technical Documentary Report No. WADD TR 61-72, Vol. VII and Supplement, "High Density Recrystallized Graphite by Hot Forming."

CASE HISTORY

ANALYSIS

This case study has selected three advances in graphite technology, Although their research origins were quite unrelated, they merged, during the exploitation stages. They were carried forward to use through a single Air Force contract which was established in 1960. The purpose of the contract was to start a broad program aimed at advancing graphite technology and to reduce the time from development to use. All three advances passed through similar stages and were interrelated. Only one evolved into commercial development. In all cases, the principle product was developed, evaluated or applied to a Defense application. The analysis of the REI stages in this summary was limited to "Erosion resistant, high density graphite". It is generally applicable to all three advances. This analysis includes both Research/Engineering Interactions and Engineering/Engineering Interactions.

Erosion Resistant High Density Graphite

Description of
Research-Engineering and Engineering-Engineering
Interactions (REI's)

a. Studies by Hamister and Gartland in 1937 were performed to gain a better insight into plastic flow of carbon and graphite. This was fundamental research aimed at improving the processing of carbon and graphite products.

b. Dr. J. Lane, a Materials Advisory Board Staff Scientist, published a report, during May 1957, which reviewed the state-of-the-art in graphite materials and recommended that the Department of Defense initiate a broad gauge attack on this class of materials.

c. It had been a long standing objective of the graphite industry to develop graphites as close to theoretical density as possible. Continuing effort in this area seemed to be the rule over long periods of time by National Carbon Company. As a result of the Lane Report and independent assessments of Defense Aerospace needs, a management decision was made to intensify efforts in the high density graphites. C. E. Larson, Vice President for Research asked V. C. Hamister, Associate Director and Senior Scientist of the Parma Laboratories to study existing technology and ideas for producing higher density graphite; develop a research program to be followed by development scale-up.

d. E. L. Piper carried out experiments based upon the 1937 observations of Hamister and Gartland. Piper first made 2.06 graphite by hot pressing 1.56 density carbon with about 8500 psi at 4700°F. This was the key experiment in 1957 which demonstrated that hot pressing was a feasible method for producing high density graphite.

e. Development scale-up of the process was first attempted in the Fostoria Development Laboratory, which had facilities and know-how for the molding-baking process using resistance heating. The project was later shifted by management to the Niagra Development Laboratory which had facilities and know-how for induction heated proces: K. J. Zeitsch, the Niagara Laboratory Development Engineer, built an experimental small unit to enable hot pressing. Process development work and property characterization was carried on until 1959.

f. Stroop and O'Denning of National Carbon arranged for a contract with Aerojet General Corporation for evaluation of the high density product in MERM test nozzles.

g. Overlapping the actions in f. above were a number of study groups established by OSD to examine weapon requirements for graphite materials and producer potentialities. During October 1959, the Air Force was given the authority to proceed with negotiations for a $12 million, three year program in Graphite Technology. Captain I.K. Holdner and Lt. J. Gianceola of the Air Force Materials Laboratory were the project officers. A contract was signed with National Carbo Company during May 1960. This resulted in the transfer of most of the process development, scale-up, and evaluation to the Lawrenceburg (Tenn.) Graphite Facility.

h. During and after further development and performance evaluation of these products close contact was maintained with the Aerospace Industry by both John Brannon, Manager of Applications and the Air Force project officers. The high density graphite was selected for (1) the Skybolt, second stage nozzle (weapon program subsequently cancelled), (2) Redeye Missile Nozzle, and (3) structural components of the NERVA nuclear propulsion reactors. It was also a candidate fo the Polaris A-3 second stage nozzle but was subsequently replaced by pyrolytic graphite.

STAGES AT WHICH REI'S OCCURRED

Stages **	Definition	REI
0	Scientific finding (knowledge)	a, d
1	Recognition of new material (process) possibility	b, c, g
2	Creation of useful material (process) form	e
3	Feasibility of using the material (process) in hardware	f
4	Possibility of using the hardware containing the material in a system	
5	Production of the system (product)	h*
6	Operation of the system (product)	

* In REI h, it is almost impossible to distinguish between stages 4 and 5.

** Stages were defined by the Committee for the purposes of this study.

FREQUENCY OF FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From its study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs. The statistical analysis of the frequency of these factors in this case is shown below.

Factor No.		REI								Total
		a	b	c	d	e	f	g	h	
1.	High educational level (advanced degree) of principal investigator	X			X					2/8
2.	Importance of management	X	X	X	X	X	X	X	X	8/8
3.	Importance of Government-sponsored research							X		1/8
4.	Importance of recognized need	X	X	X	X	X	X	X	X	8/8
5.	Requirement of flexibility to change direction during work and local control of funds (easily available resources)	X	X	X		X	X	X	X	7/8
6.	Industrial laboratory involved	X		X	X	X	X		X	6/8
7.	Basic research in the laboratory (for inst. or org.)	X			X					2/8
8.	Communications across organizations was important	X	X	X	X	X	X	X	X	8/8
9.	Technical problem was the principal obstacle	X			X	X			X	4/8
10.	Importance of a "champion"		X	X				X	X	4/8
11.	Freedom for individuals									0/8
12.	Broad spectrum of types of laboratories	X			X	X			X	4/8
13.	Geographic proximity									0/8
14.	Prior experience with innovation	X	X	X	X	X	X	X	X	8/8
15.	Organizational structure (barriers and bonds)		X			X	X	X	X	5/8

APPENDIX A

CMT 235/1

OFFICE OF THE ASSISTANT SECRETARY OF DEFENSE (R&E)
Washington 25, D.C.

5 September 1958

Report of Steering Group on Graphite
Research and Development

Background

On January 7, 1957, the OASD(R&E), recognizing the potential of graphite for high temperature applications but aware of its limitations, gave an assignment to the Materials Advisory Board to prepare a staff study on this material, considering the mechanical properties of graphite needed in weapons then being designed, and outlining any areas in which additional research would be necessary to achieve the desired properties.

This staff study (MAB-43-SM) was issued on May 9, 1957; some of the more pertinent conclusions, in brief, are:

Better and more uniform graphite is needed for high temperature structural applications.

Performance requirements need to be spelled out by weapons people; this would lead to the evolution of specifications for pertinent grades of graphite.

Since the commercial incentive for the development of grades for military use is small, it appears desirable to increase Government support for research on basic studies, unique manufacturing methods, coatings, and non-destructive testing methods.

The staff study was reviewed by the Coordinating Committee on Materials at its 11th meeting on July 26, 1957; it was decided to send the study to producers in the graphite field for comments and to set up an informal working group with the Services and DOD staff to review the present Government research and development programs in graphite, in order that an adequate study could be made of manufacturer's comments.

Activities of the Group

The Working Group's review of Government work and of replies from the graphite companies led to the conclusion that lack of progress in obtaining graphite of proper quality for military application lay mainly in the inability of users to specify the properties needed.

It also became clear that university type research, which involved relatively small pieces of graphite, did not fulfill all requirements because properties could not be extrapolated to larger pieces; and that there was a large untapped source of "know-how" within the graphite industry that should be brought to bear on the general problem of obtaining better and more uniform graphite.

Accordingly the Working Group proposed to the Coordinating Committee on Materials that a tri-service program in research and development of graphite be established, consisting of contracts with the companies manufacturing graphite. It was suggested that the program might be managed by a single Service and if desired an MAB technical panel could assist, as is presently done in the Titanium Sheet Rolling Program. The Working Group stood ready to establish the objectives of the program, to discuss with the graphite industry the feasibility of a cooperative effort, and to make recommendations to the Committee on the amount of effort required, including funding.

The Coordinating Committee on Materials considered this proposal at its 13th meeting on December 6, 1957, and approved it, establishing in place of the Working Group, a Steering Group for Tri-Service Program in Graphite Research and Development.

At a meeting on December 12, 1957, the Steering Group agreed with the suggestion of the Army member that an Army technologist make a survey of the user field in all three services and report his findings to the group. Mr. E. J. Dunn, of Ordnance Materials Research office, was appointed by the Army member for this task. On January 1958, Mr. Dunn gave to the group an outline of his proposed action which included a questionnaire to be submitted to users. The proposed action was approved by the Group, and subsequently Mr. Dunn visited many plants in the user field, and also, together with members of the Group, visited companies in the graphite industry.

Membership in the group shifted from time to time; the present membership is as follows:

Mr. J. C. Barrett	OASD(R&E)
Mr. E. L. Hollady	Army (Ord)
Mr. T. E. Hamill	Navy (BuOrd)
Capt. I. K. Holdener	Air Force (Materials Lab.)

Mr. Dunn's report, and recommendations arising therefrom, were discussed by the group at meetings held in June and July, 1958 at which time the report was accepted. Following is a summary based on answers to the questionnaire and comments of the group:

Question 1. Is there a pressing need for greater uniformity and standardization of properties and product? If so, bear this in mind in answering the subsequent questions.

a. There is a definite need for greater uniformity, as there are presently a large number of grades of graphite, and property variations are so great even with any one grade that successive samples of a grade often vary more than the average difference between grades.

Question 2. Considering those areas in which you currently have responsibility or in which you have knowledge and might plausibly expect to have responsibility in the foreseeable future, please describe the various defense applications with particular reference to structural, thermal and other high temperature uses wherein you feel graphite (if impregnated, coated, etc. state details), is or might be profitably employed, designating which, but omitting those for integral atomic reactor or nuclear use, or electrical uses. Please list the grade (and manufacturer), and salient properties required in each application emphasizing realistic minimum numerical values where possible.

a. Uses for graphite in the missile field include nozzles, jet vanes, jetavators, liners, nose cones, and injectors.

Question 3. Considering (2): (a) where a practical or probable increase in some property would greatly enhance this use, please state the use and the improvements (numerical values where possible) desired. (b) Please list any additional uses which might become profitable with a possible moderate improvement in properties of graphite and include some quantitative estimate of the property (ies) and improvement required.

a. Nozzle users are interested in higher strength, higher thermal shock resistance, and higher erosion resistance. Erosion resistance is particularly important because of the increasing specific impulse of solid rocket fuels, and the scouring action of metal additives. Jet vane users also need erosion resistance without a lessening of thermal shock resistance; also uniformity is very important, as the loss of part of a vane means loss of a missile. Coatings and impregnants have been used in attempts to improve oxidation resistance and erosion resistance with

limited success. Estimates of strength are given, but these vary with the application; it is the consensus, however, that higher strengths are needed.

Question 4. Do you have research or development work in progress or presently contemplated to develop material of the properties required in Par. 3, and if so, please give a sufficient description of the work so that its value to an over-all graphite R&D program might be determined, when it will be completed, where it is being done, and your comment as the adequacy of the effort considering the importance of the application.

a. While the Services are carrying out some work on graphite, the users in general are testing the commercial types of graphite, sometimes on pieces especially selected by the producers. Because no criteria for specifications exist, selection of pieces and grades by the producers is somewhat haphazard.

Question 5. Is the property information currently available sufficiently complete for design use for each grade for each specific application? If not please indicate specifically what is needed (include simple or direct property measurements if any listed in Par. 4 above and indicate whether that effort is sufficient).

a. Mechanical and physical property information is not adequate and available in all cases, in part due to the nature of graphite and to variations in graphite. Needed are more reliable property data, particularly at temperatures above 3000°F, and criteria for evaluating and comparing thermal shock resistance, mechanical shock resistance and erosion resistance. It is noted that National Carbon is working on a comprehensive handbook on graphite, which should be of some help, even though it deals only with present commercial grade graphites.

Question 6. Considering (2) and (3), as a measure of industry importance please estimate the foreseeable poundage per year probably required for each item (list for items 2, 3a and 3b separately) under mobilization conditions. In many cases obviously the poundage figure bears no relation to the importance of the item to the Defense effort; therefore, additionally please

include any other parameter you care to for such items, i.e. if the proper or desirable functioning of some large missile, missile system, or other important item is prevented or limited by some specific property of a small piece of graphite, poundage figures have no meaning as to the effort worthwhile to effect improvement, but consider alternative design or materials when indicating this importance.

a. Poundage figures were not forthcoming, but it was the consensus that graphite is important to missiles and that it should take a priority ahead of ceramics and cermets. This is so because graphite is the only material known to increase in strength as the temperatures is raised (with a peak at about 4500°F).

Question 7. If you believe there is a need for increased effort other than as indicated above, please state specifically what is needed and why; please give any general comments pertinent to this questionnaire and its subject.

a. It is agreed that need for increased effort exists, and suggestions for the direction of this effort follow:

Properties obtained from destructive and non-destructive tests should be correlated with end use results. DOD control through a consulting committee with personnel from the missile and graphite industries should be maintained.

A new manufacturing process or processes are needed to produce uniform missile grade graphites, with the manufacturing facilities set apart from existing plants.

Better starting raw materials are needed. Specifications should be established to control uniformity of raw material character in order to achieve processing control and uniform end product.

Work should be carried out on pressure baking, controlled porosity (for thermal shock resistance), graphite "whiskers", pyrolytic graphite, melting of graphite, crystal structure, and the control of anisotropy.

Some general comments in Mr. Dunn's report are also summarized:

The three graphite companies which were visited - Great Lakes Carbon Corporation, National Carbon Company, and Speer Carbon Company - were very cooperative in stating their problems and offering suggestions to improve graphite. All have research facilities; National Carbon, which is the largest company, has a well established and well staffed facility involved in a surprising amount of basic research on carbon and graphite.

Unrealistic factors of safety must be used in designing for graphite because of the lack of available design information.

This relates primarily to the fact that at present no graphite specimen is precisely like any other graphite specimen, no successive lots are identical even in average properties, and that each graphite is influenced by a large number of independent and interdependent factors associated with its composition, fabrication and thermal history. It is felt that efforts to obtain precise numerical values for physical properties will largely be ineffective until a better understanding of the relation between these properties and the factors influencing them is obtained. It is felt that more work should be sponsored by the defense agencies, and that a careful effort be made to coordinate and disseminate the results. This effort will largely be wasted unless it is accompanied by an opportunity for close and effective cooperation among the contractors, the carbon companies, those presently responsible for space vehicle design, and the military agencies.

It is noted that there apparently will be no one grade of graphite capable of handling the gamut of missile uses. Increasing density (by reducing porosity) or increasing strength which, at present, invariably results in a reduction of thermal shock resistance, is not the panacea first thought; this is proven by a study of the Chrysler-ABMA vane work wherein a relatively poor extruded graphite is successful whereas a premium higher strength one fails by thermal shock.

There is a definite "size factor" in graphite technology. Properties of small size pieces cannot be translated to larger sizes, so that what proves to be successful in laboratory investigations might be wholly inadequate when full size components are involved. Because of this differential, tests must generally be conducted on pieces of somewhat the same size as the end item in question.

It is pointed out that the starting materials in the manufacture of graphite are oil refinery coke and coal tar pitch. These are complex organic compounds which vary in chemical composition and physical properties from one batch to another. Processing variables such as baking temperature, graphitizing temperature and section size all influence the character of the graphite and the resulting properties. Because of this complexity, it is not surprising that reliable property values as related to end uses are practically unknown.

The report was accepted, and agreed recommendations were evolved, based on suggestions in the report.

Recommendations of the Steering Group for R&D Program on Graphite

Short Range	Total Estimated Funding (thousands of dollars)
1. That a contract be created to develop experimentally and to produce in required sizes for typical applications, suitable missile grade graphites, and to measure all of their pertinent properties. The contractor should be in a position to exercise control over the qualities and properties of the raw material, and must have adequate facilities and experience with research, development and production of special types of graphite. The new process of "pressure baking", which results in a more uniform product and which cuts lead time drastically, should be included in this program.	1500 (over 3 years) (exsluding new facilities which eventually may be necessary, and which will cost about $3 million).
2. That a coordinated program of end item evaluation by the users be established, to tie in with Recommendation #1, and to come into being after Recommendation #1 is implemented. Users should include Government laboratories and missile development contractors. Testing of both full size components and smaller standardized specimens should be undertaken.	1500 (over 3 years)
3. That the present laboratory efforts sponsored by the Services in which attempts are being made to accomplish on a small scale generally what is proposed in Recommendation #1, be continued, and that these efforts be coordinated with, provide auxiliary input to, and act partially as an unbiased check on the effort in Recommendation #1. These efforts might also be directly applicable to small size pieces. Sponsorship of contracts for new processes, and acquisition of information from private sources on such processes, should be encouraged.	150

Short Range (continued)	Total Estimated Funding (thousands of dollars)
4. That a contract be given to an independent research organization for the purpose of surveying the current work in the fields of coatings, gaseous deposits, and impregnants. The end product of the survey should be an evaluation of the adequacy of the present effort and recommendations for further work.	50
5. That a program to evaluate the advantages of extruding and molding to shape be created; comparison of the undisturbed surface with that of a machined surface could be made, as it is suspected that machining may be detrimental. This effort should be correlated with, or might form part of the programs cited in Recommendations #1 and #2.	100

Recommendations of the Steering Group for R&D Program on Graphite

Long Range	Total Estimated Funding (thousands of dollars)
(Note: the following recommendations refer only to missile-grade graphites such as will be forthcoming from the program outlined in Recommendation #1; commercial grade graphites are not considered.)	
6. That the present program on improvement of erosion and oxidation resistance through additives to the graphite mix be expanded to consider all avenues of approach.	200
7. That research work on high strength graphite "whiskers" be expanded to determine their potentialities; an investigation should also be made to determine whether these whiskers can be formed into aggregates.	100
8. That a contract be established for further research in differential heat flow graphites and determination of their properties.	50
9. That a fundamental study of the crystal structure of graphite be made, including allotropic forms (other than diamond) which may exist at high temperatures.	50
10. That an investigation be made of possible methods for controlling the shape, size, and amount of porosity in graphite, and to determine if such control leads to graphite of better thermal shock resistance.	100
11. That methods of control of anisotropy in graphites cast from a molten condition be investigated and developed, to determine if usable products will ensue; hot work of such graphites and also conventional graphite could be an adjunct to this work.	100

Establishment of an Experimental Plant for Missile Grade Graphite.

The survey report leads one to conclude that immediate consideration should be given to the establishment of a facility to produce missile grade graphite, as opposed to present commercial grades. The non-uniformity of the present grades, the reluctance of the industry to put its own money into developing a small tonnage product with little or no profit, and the problem of predicting properties of large pieces of graphite from results on small pieces are all obstacles to the development of the high quality graphites needed for missile applications. Recommendation #1 is designed to fill this need, and if it is not filled many of the other recommended steps might not be worthwhile.

Recognizing that this concept is of highest priority, the Steering Group took preliminary action in this area prior to full consideration of the other recommendations, and instructed the OASD(R&E) staff member to prepare a letter to the graphite producers, asking them to comment on the feasibility of setting up a pilot or experimental plant, which would be divorced from their other facilities, and which would be run on an R&D rather than production basis. A copy of this letter, and copies of the replies from five of the graphite producers, are attached to this report. Perusal of the replies indicates that the graphite companies, on the whole, are in full accord with the concept and would like to enter into a program of this type.

The Steering Group feels that this program should be implemented as soon as possible. It is felt, moreover, that National Carbon Company should be awarded the contract, because of its preeminent position in research and development within the industry (corroborated by committee visits to the producers) because of its more positive program as outlined in its reply to our query, and because it recently has developed a "pressure baking" process which should aid in the development of graphites with reproducible properties. It is probable that the work can be initiated with the company's present facilities; if the demand is great enough and there is need for further refinements in processing, new facilities may have to be built. In that event and particularly if production of reasonably large quantities is involved, coordination can be effected with facilities and production personnel in the Services.

Previous Alternatives: The low- and medium -priced specialty graphites were developed from the electrode type, with gradual improvements in quality from general advances in graphite technology. These graphites are satisfactory for the majority of industrial uses.

The premium-priced ATJ specialty graphite was developed to meet the need for highest quality and finest grain in critical uses such as dies for continuous casting of metals and nuclear-reactor parts. The ATJ process could not be practicably extended to pieces beyond about 17 inches in diameter.

For larger sizes of specialty graphite 30 to 50 inches in diameter, it was necessary to use the ATL type of medium-grain structure, which has a lower strength.

Background: As part of the management decision to adapt graphite to new uses, a general R&D objective was to develop graphite of maximum homogeneity and uniformity of properties. In 1950-54 studies of thermosetting binder systems were extended to new resins and sulphur-modified pitches. The expanding development of the pressure molding-baking process (started in 1955) stimulated thinking toward the possibility of using pressure processes in the production of graphites with greater structural homogeneity.

Recognition of the Need: New levels of technical and economic factors associated with graphite were introduced in the early 1950s by missile uses, which emphasized the need for graphites of improved reliability with properties of the highest possible level. About 1955 similar needs were indicated for nuclear reactors that called for large pieces of graphite impermeable to molten metals.

During mid-1955, in view of these product needs and the already promising development of the pressure molding-baking process, C.A. Odening, Director of Development, National Carbon Company, authorized a group of development engineers, led by R.C. Stroup, to experiment with pressure curing of the thermosetting resin binder systems studied in the early 1950s.

Key Findings: The first experiments with pressure curing used a resin binder for test pieces 3 inches in diameter. Although these pieces could be cured, they could not be baked. In 1956 the work shifted to pitch binders with sufficient sulphur to effect thermosetting at around 600°F to 700°F. After successful trials with 4-inch pieces, equipment was improvised to make graphite pieces 26½ inches in diameter by 13 inches.

This experiment showed that the principle of pressure curing could be used for developing a process to make a homogeneous carbon article at around 700°F, which then could be baked and graphitized. The advantage indicated was the ability to process relatively large pieces of fine-grain structure with bond levels optimized for physical properties of the graphite.

APPENDIX B

Related Graphite Advances

Improved Large-Diameter, Fine-Grain Graphites

Nature of the Problem: Flexibilities in graphite fabrication enable to a considerable degree the optimization of properties to meet specific performance needs. For example, graphite for furnace electrodes is designed for maximum resistance to extreme thermal shock, high-temperature strength and electrical conductivity. Similarly, graphite for chlorine anodes is designed for maximum resistance to chemical-reaction conditions and electrical conductivity. The numerous other specialty applications of graphite require a wide range of characteristics in structure and properties; for many of these uses, the technical requirements allow the use of relatively normal grades, whereas other applications are sufficiently critical to justify the use of premium types of graphite.

Graphite processing becomes more difficult as the size of the product increases. Thus the size of the piece needed for an application is a critical factor in the production of a graphite article whose structure and properties meet performance requirements.

Commercial graphites for specialty uses have been developed in three general types:

Low-priced (e.g., AGSR, AGSX)	Medium-grain structure to 12 inches in diameter; coarse-grain in 14-to 35-inch diameters. May have minor internal voids and laminations. Has good thermal and electrical properties. As size increases, grain becomes coarser, with a reduction in strength.
Medium-priced (e.g., CS, ATL)	Medium-grain structure in 30- to 50- inch diameters. Has better structural quality and strength in larger sizes.
Premium-priced (e.g., ATJ)	Extremely fine-grain structure to 17 inches in diameter. Structure is essentially free of flaws. Has high strength. Can be machined to very close limits and sharp detail.

In adapting graphite for the most critical applications, the real need is for structural homogeneity and the absence of fissures or localized areas of lower density, strength, etc. Thus, it is a perennial objective of the R&D program to find means for improving structural homogeneity and texture for a larger size range and at a cost consistent with the economics of the material's end use.

Previous Alternatives: The low- and medium -priced specialty graphites were developed from the electrode type, with gradual improvements in quality from general advances in graphite technology. These graphites are satisfactory for the majority of industrial uses.

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For larger sizes of specialty graphite 30 to 50 inches in diameter, it was necessary to use the ATL type of medium-grain structure, which has a lower strength.

Background: As part of the management decision to adapt graphite to new uses, a general R&D objective was to develop graphite of maximum homogeneity and uniformity of properties. In 1950-54 studies of thermosetting binder systems were extended to new resins and sulphur-modified pitches. The expanding development of the pressure molding-baking process (started in 1955) stimulated thinking toward the possibility of using pressure processes in the production of graphites with greater structural homogeneity.

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This experiment showed that the principle of pressure curing could be used for developing a process to make a homogeneous carbon article at around 700°F, which then could be baked and graphitized. The advantage indicated was the ability to process relatively large pieces of fine-grain structure with bond levels optimized for physical properties of the graphite.

Development Scale-up of New Material: As an initial step toward scaling up the pressure-curing process, National Carbon set up an experimental facility at its plant in Columbia, Tennessee, to do trial work on 17- and 40-inch-diameter test pieces for the Babcock & Wilcox LMFR program. During 1957-1959, this work showed that the process had a potential capability of producing graphite of excellent structure and improved uniformity-if optimum control of the process could be developed, particularly to avoid gradients that caused cracking.

Thus, the National Carbon-supported development of pressure curing, together with precursor work on pressure baking and thermo-setting-binder systems, made it possible to undertake a specific development project aimed at the goal established by contract AF 33(616)-6915, "...fabrication of large size pieces of graphite which are equal or superior to ATJ grade and have approximately one-third the standard deviation of the properties of strength and bulk density of ATJ."

For this contract, the development work on improved process equipment, materials and techniques produced RVA graphite in sizes up to 30 inches in diameter by 40 inches in length that had (1) average physical properties close to those of ATJ and (2) standard deviations in strength and density not more than one-third those of ATJ. Under contract AF 33(657)-11304, RVA has been scaled up to a diameter of 58 inches.

This process was also used to develop an even finer grained graphite, grade RVD, for improved resistance to erosion.

Another graphite developed with this process is grade RVC, whose thermal expansion characteristics closely match those of silicon carbide to around 2000°F. Thus, RVC is an excellent substrate for silicon-carbide coatings to protect against oxidation.

Testing and Uses of New Materials[3]:

(1) RVA was approved by Aerojet-General to be used in nozzles for Algol motors used on the Little Joe and Scout programs.

(2) CFZ(RVA with impregnation) is Aerojet-General's leading candidate material for the first-stage nozzle of Poseidon.

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[3] Ibid., Vol. XII and Supplement, "Development of an Improved Large-Diameter, Fine-Grain Graphite for Aerospace Applications" (RVA); Vol. XIII and Supplement, "Development of a Fine-Grain Isotropic Graphite for Structural and Substrate Applications" (RVC); Vol. XXXVIII and Supplement, "Development of an Improved Large-Diameter Ultrafine-Grain Graphite" (RVD).

(3) RVD, an all-flour RVA, was tried once unsuccessfully by Thiokol Corporation and Picatinny Arsenal for Minuteman's first-stage nozzle. The failure was due to a misunderstanding in the initial production of RVD, which was not representative of present RVD graphite.

(4) RVC, a high-thermal-expansion form of RVA, was developed as a machining substrate for silicon-carbide coatings. It was used successfully for the Dynasoar nose by Ling Temco Vought.

The RV series now makes available large monolithic articles of graphites with fine-grain structure and much more uniform physical properties than previous graphites had. The process is flexible and enables the development of graphite grades with new combinations of physical properties as required to meet new service needs.

Oxidation-Resistant Graphite-Base Composites

Nature of the Problem: Graphite has excellent properties for uses requiring high-temperature strength, thermal-shock resistance, electrical or thermal conductivity, machinability, etc. These properties are particularly valuable for applications such as furnace electrodes, metallurgical process equipment, nuclear reactors and rocket components.

A characteristic restricting some uses of graphite is oxidation, beginning at temperatures over about 700°F. In many uses, such as electrodes, the rate of oxidation even up to 3000°F is not prohibitive, considering all other factors of use. However, there are applications for which oxidation and erosion conditions are extreme, e.g., for rocket nozzles or other high-temperature uses in which structural integrity and strength must be maintained within critical limits. The development of increased resistance to oxidation, therefore, is a natural consideration in the R&D program for expanding the uses of graphite.

Previous Alternatives: Many approaches have been studied for the development of oxidation-protective barriers on the surface of graphite. The first attempts, from about the 1930s to 1951, investigated mainly coatings, such as boric oxide and other ceramic materials.

Beginning in the early 1950s, the need for rocket-nozzle materials greatly intensified the search for protective coatings. During 1953-1957, much work was done on many types of coatings, impregnating or infiltrating graphite with metals to form coatings such as carbides, oxides, nitrides or silicides. The major difficulty with coatings is in getting an adherent and oxygen-impermeable coating which is really effective and mechanically practical. Only a few of these coatings showed a limited usefulness, for example, silicon carbide and silicon nitride.

Background: In its general R&D program, National Carbon has studied the mechanism of carbon oxidation and possible controls.

For example, in 1924 protective oxide coatings for arc carbons were studied; in 1935 metal coatings for electrodes; and in 1943 boric-oxide coating for metallurgical molds. In 1948, coatings were classified with respect to their end-use requirements and whether they were solid, plastic or liquid in the operating temperature range. This recognized the value of self-healing for the coating. Studies were made of the oxidation rates of graphites as affected by composition and processing. Fire-proofing impregnations, such as the phosphoric-acid type, were investigated. In 1951, under contract, Armour Research Foundation developed a technique for spraying fused oxides on the surface of graphite, but the oxide films were too permeable. In 1952, a carbon brick composite with boric oxide and silica was developed which formed a self-healing glaze when the brick oxidized. In 1955, under contract, Stanford Research Institute studies zirconium/zirconium-oxide coatings for graphite.

Since the late 1950s, an extensive R&D program has been maintained for the study of properties and the fabrication of high-temperature refractory compounds such as boron nitride, titanium diboride and zirconium diboride. In 1957-58, as the result of progress with the pressure molding-baking process, and the jet torch nozzle test, conventionally processed composites of graphite with titanium carbide, zirconium carbide and boron carbide were studied for possible use as rocket-nozzle materials. Silicon-carbide and silicon-nitride coatings were developed.

Recognition of the Need: The key action leading to the recognition of the possibility of developing the new graphite-base composites was the 1957 decision to study high-density graphite, which led to development of the hot-forming process.

By 1959, the hot-pressing process was making high-density graphite blanks 2 inches in diameter for MERM nozzle tests.

Key Findings: In 1960, K.J. Zeitsch, the development engineer working with the hot-pressing process, was trying to make 2-inch-diameter graphite over 2.0 g per cc in density, starting with coke flour. He was able to make pieces of about 2.0 density, but most of them had a conchoidal fracture. To strengthen the graphite, he added metal compounds, which melted during the hot pressing and were squeezed into the pores of the plastically compressed carbon matrix to produce a semialloyed graphite-base composite.

Zeitsch first tried boron carbide as an additive. Physical-property testing showed the first pieces of this composite to have remarkably low permeability. Previous tests with the National Carbon jet torch and MERM nozzle tests with Aerojet-General had indicated some correlation between permeability of the graphite nozzle throat and resistance to flame erosion. In view of the low permeability of the composites, Zeitsch tested them for oxidation and found outstanding resistance to oxidation in terms of weight loss. With this promising finding, further investigation was undertaken as part of

one of the goals of contract AF 33(616)-6915, described as "...investigation of impregnants, coatings, carbides, fibers, unique processes and unusual carbon base composites."

Development Scale-up of New Materials. Working with 2-inch-diameter pieces, Zeitsch carried out tests with a wide variety of additive materials, proportions, and processing conditions to establish general guiding principles for selecting materials to give optimum properties for various operating temperature ranges. In general, the additives can be borides, carbides and silicides of refractory metals. The carbon content of the graphite composites generally exceeds 70 percent by volume, in order to keep the basic properties of graphite.

Special test equipment was developed so that effects of high-temperature oxidation on properties of the graphite composites could be measured. Weight loss by arc image and levitation furnace tests, flexural strength, thermal expansion and thermal and electrical conductivities were measured at exposures up to around 4500°F.

As a basis for size scale-up, a graphite/zirconium-diboride/silicon composition was selected as representing a reasonable balance of properties for present uses. The first scale-up was to 5 inches in diameter to enable initial hardware evaluations. Scaleup to 14 inches in diameter has now been accomplished.

These graphite-base composites are a unique type of high-temperature material that is homogeneous and intrinsically resistant to oxidation. When these composites are exposed to oxidizing conditions, they form a glazelike surface of highly refractory solid solutions of oxides which protects against further oxidation; this surface is self-renewing if damaged. Since the composites are homogeneous, they can be machined without destroying their oxidation resistance. It is possible to mold articles roughly to final shape. These composites have excellent physical properties at high temperatures.

Testing and Uses of New Materials[4]: The JTA graphite-refractory composite is used by Rocketdyne in attitude control motors for Gemini and Apollo. These motors must maintain controlled thrust in start-and-stop pulse-type operation over many cycles of varying duration. The hypergolic fuel is so highly oxidizing that conventional graphites do not stand up. JTA is an oxidation-resistant form of graphite which is used in motors with flame temperatures as high as 5000°F with suitable heat-dissipation designs.

JTA has been successfully tested for Surveyor by Space Technology Laboratories. This composite is now being tested by several organizations for hypersonic reentry and other high-performance requirements. JTA has been scaled up to 14 inches in diameter, which is adequate for nozzles and leading edge sections.

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[4]Ibid., Vol. XXX, "Oxidation-Resistant Graphite-Base Composites."

Best Available Copy

JTA represents only one grade of these graphite-refractory composites; its composition and properties were developed as the best overall balance for present service needs. With this hot-forming process and the great compositional flexibility and with further study of basic mechanisms, it will be possible to develop other graphite-refractory composites with properties adapted to meet specific needs of new uses requiring such types of high-temperature structural materials.

A CASE HISTORY OF THE EARLY WORK LEADING TO THE INVENTION OF LODEX® PERMANENT MAGNETS

Prepared by
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A CASE HISTORY OF THE EARLY WORK LEADING TO THE INVENTION OF LODEX® PERMANENT MAGNETS

NARRATIVE

Introduction

This is a story of materials synthesis; the deliberate construction, piece by piece, of a complex material composite using scientific principles as a base to produce a product with prescribed properties. It is tempting, in retrospect, to describe the process by which this orderly synthesis was achieved in terms of deliberate rational steps. This will be resisted here, however, for one of the important points which this model example of materials synthesis emphasizes is the role of the unexpected, the accident, the chance observation by prepared minds, in bringing about technical advance.

Lodex® Permanent Magnets consist of fine particles of magnetic iron or iron cobalt, with each particle surrounded by a protective coating of non-magnetic material (e.g. tin, aluminum, or zinc), and imbedded in a matrix of non-magnetic material such as lead or plastic.

The outstanding permanent magnet properties of this material stem from the fact that the fine magnetic particles are made in the shape of rods a few hundred angstroms in diameter and several times this dimension in length. The experimental verification of the existence of shape anisotropy, the specific discovery at the General Electric Company of materials made from such elongated magnetic particles, the electro deposition processes by which the particles are made and the technique for protecting and assembling these particles into commercially competitive magnets form the subject of this case.

Scientific Background

From the earliest times magnetic phenomena have excited man's imagination. Up until about 1200 A.D., however, the only magnetic material known and exploited was lodestone, a naturally occurring magnetite. At this time the first artificial magnet was made from iron. Iron and plain carbon steel were then used as a permanent magnet material principally for applications such as a mariner's compass until the discovery in 1917 of the 35% cobalt K. S. magnet steel.

This material had over five times the coercive force of previous alloys and considerably widened application possibilities.

The next significant development in permanent magnets came in the 1930's with the rapid discovery and exploitation of a whole series of precipitation hardened and order hardened alloys with coercive forces two to three times higher than cobalt steel. The most significant of these was a family of nickel aluminum iron precipitation alloys, with coercive forces up to 700 oersteds, which were to become known as the Alnico magnet alloys. In spite of the extreme brittleness and high cost of these materials, they nonetheless had gained a well established position in industry by 1940 due to the combination of high coercive force and high induction that they exhibited.

The theory of magnetic phenomena and the behavior of magnetic materials progressed steadily throughout the world after about 1900. Nonetheless, permanent magnet material development had remained largely an empirical art through the 1930's. Each alloy was developed by a mix and measure procedure and its properties optimized by trial and error casting and heat treating practices. The Alni alloys were developed in this way. Although the theory of magnetic behavior advanced considerably during this period, no widely accepted explanation of the magnetic properties of this alloy were forthcoming until the mid-1950's.

Work on magnet development continued at a considerable rate during the decade of 1940 due to a combination of factors. The outstanding magnetic materials then known were not only very brittle and hard to make in precise shapes but also contained nickel and cobalt, both strategic materials during the World War II and Korean conflicts and both expensive materials in peacetime. In addition, the theory of permanent magnet behavior was rapidly advancing, drawing additional experimenters to the field to verify and exploit the advances in understanding.

By 1940, it had been firmly established and broadly recognized that magnetic materials contained many magnetic regions or domains, each magnetized to saturation along any one of the easy magnetic axes in the material. Each of these separately directed regions had been shown by Bloch in 1932 to be separated by a transition zone, or Bloch wall, several hundred angstroms thick,

in which the magnetism gradually changed direction. The magnetization process had further been shown to consist of the motion of these walls, allowing those domains oriented in the direction of the applied field to grow at the expense of others.

On this background it had then been hypothesized that permanent magnet materials derived their properties from one of two possible sources. Either fine non-magnetic particles or other obstructions could be put into a magnetic material to inhibit the motion of domain boundaries, or the magnetic material could be sub-divided so fine that it could no longer contain a domain boundary.

The permanent magnet properties of fine particles had been demonstrated but not recognized as early as 1896 by Nagaoka in Japan who achieved a coercive force of 370 oersteds in iron electrodeposited in Mercury. However, no satisfactory method of compaction of fine iron particles was demonstrated until Honda in Japan in 1937 produced a compact of fine iron particles from the low temperature reduction of iron oxylate. Finally, in 1941, Dean and Davis[1] were granted a patent which was assigned to the Chicago Development Company on a magnet compacted from fine particles of iron electrodeposited in Mercury.

Each of these processes produced particles of substantially round shape. The coercive force was thus determined by the ease with which the magnetisation could be rotated out of the preferred crystal directions. This magnetic crystal anisotropy for iron is not very large and so the utility of magnets made in this way was limited. Nonetheless, a fine iron particle magnet was developed by Neél and others in France during World War II and was commercially produced by the Societe de Electro-chemie, d'Electro-Metallurgie et des acieries Electrigue d'Ugine in France and later by Salford Electric Instruments Ltd. in England.

During the early 1940's, three developments occurred which greatly influenced the course of magnet development. The first of these was the positive demonstration by Guillaud in France in 1943 that the origin of the coercive force of fine round particles was the crystal anisotropy of the particle and that this could be made very large by the selection of the proper material for the particle. He worked principally with manganese bismuth and achieved a coercive force of 12,000 oersteds. Unfortunately, the high temperature coefficient of this material and the high price of bismuth make it of chiefly academic interest.

The second advance was made simultaneously by Neel, Stoner and Wolfarth, and Guillaud in 1947. They theoretically predicted that a fine magnetic particle would have a coercive force which was dependent on its shape. Stoner and Wolfarth calculated that the maximum coercive force of an elongated particle could be as high as one half of the saturation induction of the material, giving approximately 10,000 oersteds as a possible coercive force for iron.

The third advance, that of the development of the electron microscope by which very fine particles could be seen and their nature verified, came from work apart from magnetism and demonstrates the strong interaction between scientific fields.

This was the world science stage upon which the development of Lodex® Permanent Magnets was set. Considerable activity existed throughout the world in attempts to understand and improve empirically developed properties of Alnico and other alloy magnets, and to find materials with high crystal anisotropy to develop magnets of the kind demonstrated by Guillaud in France. Little effort was being directed toward the development of elongated single domain particle magnets for three reasons. First, the theoretical concept of shape anisotropy was new and not universally accepted. Second, no method had been demonstrated to produce elongated fine magnetic particles of any kind to test the theoretical predictions. Third, since techniques were not readily available for seeing such fine particles, shape was not an observable variable.

Industrial Background

During the period of the 1940's the General Electric Company, a manufacturer of a broad range of electrical and related equipment, was situated in a large number of separate plant locations. Each location concentrated on a different set of product lines and each operated semi-independently of the other but connected through the Company headquarters. In addition to these product departments, the Company maintained several central service organizations, one of which was the General Electric Research Laboratory.

Although much of the more advanced scientific research of the Company was carried out in the central laboratory, each department maintained its own staff to carry on advanced technical work of direct and immediate interest to its

product functions. Since the technology underlying the products of various departments overlapped, a series of technical committees (consisting of members from each interested department and the central laboratories) had been developed to maintain effective communication between groups and to coordinate similar activities.

Of the several departments in General Electric with an interest in permanent magnet materials at that time, the Meter and Instrument Department in West Lynn, Massachusetts had assumed a leadership role. The engineering design and competitive performance of most of the products (in particular the electric watt-hour meter and the then growing line of aircraft instruments) of this department depended critically upon the magnetic properties and costs of available permanent magnet materials. As a consequence, the department had for some time maintained a development program in permanent magnetism and manufactured magnets for its own use. Its technical personnel had made a number of inventions in the processing of cobalt steel, silmanal, vectolite, Cunico, Cunife, Alnico and other alloys that the department manufactured.

During the 1940's the manager of engineering in the Meter Department was I. F. Kinnard, who also held the position of chairman of the Magnetic Committee. The head of the metallurgy group in the Research Laboratory during this same period was W. Ruder, who was chairman of the Magnetic Research and Development Subcommittee.

I. F. Kinnard was an outspoken man of strong will and sound technical judgment, who had hired most of the engineers in his organization personally, principally during the 1930's. Although the group engaged in advanced technical work was no larger than a few men, they made a considerable contribution to the economic development of permanent magnet materials from the early 1930's through World War II.

The tone of the Meter Department effort was set by Kinnard. He had an abiding faith in the value of advanced technical work, in particular in materials. He saw in materials advance the principal area of both engineering and manufacturing innovation opportunity for his products and he focused much of his attention on it.

His own creative imagination, technical judgment and analytical ability were sound and he exercised them constantly in dealing with his advanced technical people. He insisted that each person set challenging technical goals and review his work periodically in the presence of his associates and technical peers and insisted upon a convincing technical justification for the work and the direction that it was taking. Once convinced of the merit of a project, he became a stout champion and often chided the younger technical man with "If you are really convinced of the value of the work, why should you be concerned about me?"

In the 1940's the advanced technical work became formally organized in a Measurements Laboratory and later a new facility was built to house the organization. Although a laboratory manager was in place between Kinnard and the laboratory staff, his personal interest and technical judgment continued to be a predominant factor in the atmosphere and conduct of the research and development work.

Work Leading to Elongated Fine Particles

In the later part of the 1940's, H. T. Faus, a particularly inventive engineer of the Meter Department Laboratory began investigations into the Dean and Davis patent and the Nedl process, trying by purely empirical means to duplicate and improve on the fine particle results of Dean's work. He was joined by L. I. Mendelsohn and later by W. Meikeljohn. All three of these workers tried various methods including electrodeposition of iron in mercury and decomposition of iron salts, off and on to improve upon the fine particle magnets then known. All of these attempts were based purely upon empirical reasoning. In time this work was abandoned for lack of promise and it became evident that if any substantial progress was to be made in magnetic materials at the Meter Department, it would be necessary to obtain additional scientific, Ph.D level personnel with a more sophisticated knowledge of the recent theoretical advances in the field of magnetic materials.

The head of the metallurgical activity had been sent by Kinnard earlier to the Research Laboratory for a year prior to his coming to the Meter Department with what was considered good effect. It was therefore decided to

proceed to recruit a Ph.D metallurgist and similarly have him spend a year at the Research Laboratory familiarizing himself with the field of magnetism.

In late 1949, T. O. Paine, a Ph.D metallurgist, graduate of Brown and Stanford, was hired and placed at the central Research Laboratory. There he was introduced to a variety of new ideas being generated throughout the scientific community concerning the role of crystal defects in controlling the properties of solids. This included, of course, an introduction to the field of magnetism including discussions of magnetic domain boundaries, the effect of their absence in fine particles and the concept of crystal anisotropy and in particular the promise of shape anisotropy in the improvement of permanent magnets.

Paine began almost at once to attempt to produce fine elongated particles of iron. Initial attempts were made by repeatedly drawing bundles of iron wire clad in other metals, principally copper and silver. This approach was not successful in producing shaped particles of fine enough dimensions by the end of 1950.

When Paine transferred to the Meter Department at the beginning of 1951, he was encouraged by financial support of the Magnetics Research Subcommittee headed by Ruder of the Research Laboratory to undertake a program to develop superior permanent magnets from fine particles. Having abandoned the approach of drawing fine wires, Paine turned with Mendelsohn to the possibility of obtaining fine elongated particles by chemical means. In addition, work was begun on the preparation of fine particles of materials with high magneto-crystalline anisotropy.

It was recognized from the beginning that there would be considerable difficulty in finding a process that would provide a fine particle of iron with the surface energy needed to allow it to assume an elongated shape. Nonetheless, the promise of outstanding permanent magnet properties was judged equally large. Thus, according to Paine, it was decided to pursue a fine particle magnet development program aimed at discovering an economically practical, high saturation-high crystal anisotropy material, while at the same time trying every method conceivable to produce elongated single domain particles of iron.

In October of 1951, Paine became manager of Materials and Process Development in the Meter Department Laboratory (called the Measurements Laboratory) which helped assure support for the fine particle magnet program locally, and continued technical direction to the work. For a while the work progressed with enthusiasm but without specific encouraging results.

In the spring of 1952, L. I. Mendelsohn was engaged in attempts to obtain elongated particles by electrodeposition of iron into mercury. He reasoned that the eventual ability to grow elongated particles and produce a superior fine particle magnet was dependent on the understanding and control of the processes occurring at the mercury electrolyte interface, and those occurring at or near the growing particle surface. In order to be able to expand this line of attack and to provide additional understanding in the chemistry of the process he asked for a chemist to assist him. During the summer of 1952, a chemist was assigned to this effort.

There then ensued, in series, an oversight and then an accident which pointed the direction for the subsequent work, leading to the invention and development of the Lodex® magnet.

It was natural that Mendelsohn and his chemist associate wanted to set up their own electroplating experiments and to explore different areas of the process. When the second electroplating bath was constructed there was not a spare stirring machine immediately available to stir the electrolyte during plating. Now it was well known in the plating art that undesirable ion concentrations would develop in the electrolyte if the solution was not continually stirred, and this was considered to be a distinct handicap in the work. Nonetheless, some experiments were begun.

One of the approaches being tried was to use different cathode materials at a variety of temperatures. One of these was a molten mixture of lead, bismuth, and mercury. After the plating experiment, the molten cathode was hot pressed in order to extract the iron particles. Unfortunately, on one occasion the pressing was made from the material from the unstirred plating bath prior to the time the cathode had melted in the press and some of the solid extruded out past the piston of the pressing fixture. When magnetic

measurements were made on this extruded material, a small magnetic anisotropy was discovered indicating an alignment of slightly elongated particles in the direction of extrusion.

After numerous attempts to duplicate this result which was only barely above experimental error, it was recognized that positive results were achieved from only one of the plating baths regardless of the plating conditions. Finally, it was decided by Mendelsohn that there was no difference left between the baths except the oversight of the stirrer. When this was taken from the unsuccessful bath and placed in the successful one, the difference was discovered. A quiescent interface between the electrolyte and the electrode was thus determined to be an important factor in obtaining elongated particles.

The invention of a magnet composite that would have utility still lay ahead. The properties of the initial particles indicated only slightly elongated shape. Means had to be found to produce larger, more controlled elongations and to protect the particles from oxidation, to align the particles to take advantage of the elongation and to insert them in a suitable matrix.

Meanwhile, a continuing effort was being made to improve the general scientific competence of the Department Laboratory. During this period, Dr. F. Luborsky was added to the staff, and after about a year at the Research Laboratory, joined the research group with Mendelsohn under Paine in the Measurements Laboratory of the Meter and Instrument Department. He very soon became interested in the fine particle work. There then ensued an extended period of concentrated effort before the process and a satisfactory product were invented. Additional research was required by Luborsky on the fundamentals of electrodeposition of iron in mercury and by the Corporate Research Laboratory staff on the magnetic properties of irregularly shaped fine particles as well as the development of means of separating and coating fine particles and compacting magnets before technical success could be achieved. Finally, in 1955, patents were filed for an elongated fine particle magnet by Paine, Mendelsohn, and Luborsky.[2]

Conclusion

The above story is an account of the work only up to that point where nature provides an experimental clue that an invention is possible. The

difficult, expensive stages of the research and development effort were still ahead. An additional five years would be needed, in which a number of setbacks and seemingly insurmountable barriers, tried the faith of those connected with the effort.

By this time, however, most of the elements of ultimate success were in place. A continuing strong economic need existed. A history existed of successful efforts to develop a business through technological advance in materials. A specific direction toward a solution had been demonstrated possibl A dedicated, convinced, and competent technical group was in place, strongly connected to the product needs through the local business organizations and to world advances in science through the Research Laboratory. Paine soon became Manager of the Department Laboratory ar as such provided strong support for the program from a position of authority. Because of the overall business success of the department, risk capital was available for innovative work. Even so, the development was nearly terminated on a number of occasions when lack of progress and the priorities of other problems raised serious doubts as to the merit of the program. On these occasions, the steady continuing optimism and intense interest of those engaged in the work was critical to the continuation of the development. Had any of these factors been removed during work, the development and application of this science area would most certainly have been delayed for at least another decade.

(1) R. S. Dean and C. W. Davis - U.S.P. 2,239,144

(2) R. O. Paine, L. I. Mendelsohn, F. E. Luborsky - U.S.P. 2,974,104

APPENDIX
TO
CASE HISTORY
ON
THE EARLY WORK LEADING TO THE INVENTION
OF LODEX® PERMANENT MAGNETS

The General Electric Company

The General Electric Company, while primarily a manufacturer of electrical goods, produces over 200,000 different products for home, industry, and defense. They range from toasters to turbines and from miniature lamps to engines for jet aircraft and atomic submarines. It has approximately 260,000 employees and the number of its share owners is more than 516,000. Its products are made by nearly 100 operating departments, in plants in about 115 cities throughout the United States. Its annual sales billed have totalled over $4 billion for each year since 1956.

Born on the threshold of an economic revolution and growing up as a vigorous pioneer in the expansion of our economic frontiers, General Electric has become the acknowledged leader in a great industry. This leadership has its roots in a record of achievement dating back to the earliest days of electrical development.

By 1940, General Electric employed about 76,000 workers and had 34 plants throughout the country. And with the advent of World War II, General Electric took over the job of supplying a large portion of the equipment for the biggest arms program in the nation's history up to that time.

From General Electric production lines flowed thousands of electrically-operated aircraft gun turrets and jet engines, propulsion units for three-quarters of the Navy ships of war, radar and radio equipment, electrically-heated flying suits, searchlights, naval gun directors, howitzers, bazookas, fuses, and scores of other weapons. From the laboratories came new systems for the detection of enemy aircraft and ships, and a new smoke generator, far more effective than previous ones, for screening troop movements.

During the years immediately following World War II, General Electric carried out an extensive program of expansion and decentralization. In the earlier days of its history, the Company's efforts were directed toward

consolidation, integration, and centralization of a number of previously separate organizations. But, as its business expanded, as the number of its geographical locations grew, as the number of separate products multiplied, and as the sales volume of each of the products increased, the need for a more decentralized organization became increasingly apparent.

Not only did the growth of the Company make it necessary to decentralize operations in the form of relatively small, autonomous product departments, but in addition, geographical decentralization helped in meeting its marketing objectives. Thus General Electric tries to avoid undue concentration of manufacturing facilities in individual communities and thus is able to spread employment into more areas from which it obtains consumer and industrial business

Emphasis on research and development has continued to characterize the Company. In the decade 1950 through 1959, General Electric spent 1.37 billion of Company funds and also performed $1.5 billion worth of research and development work for the Government. During this period, scientific research was carried out in the Research Laboratory, The General Engineering Laboratory, and a large number of laboratories connected to the decentralized operations of the Company. Such a laboratory was the Measurements Laboratory of the Meter and Instrument Department.

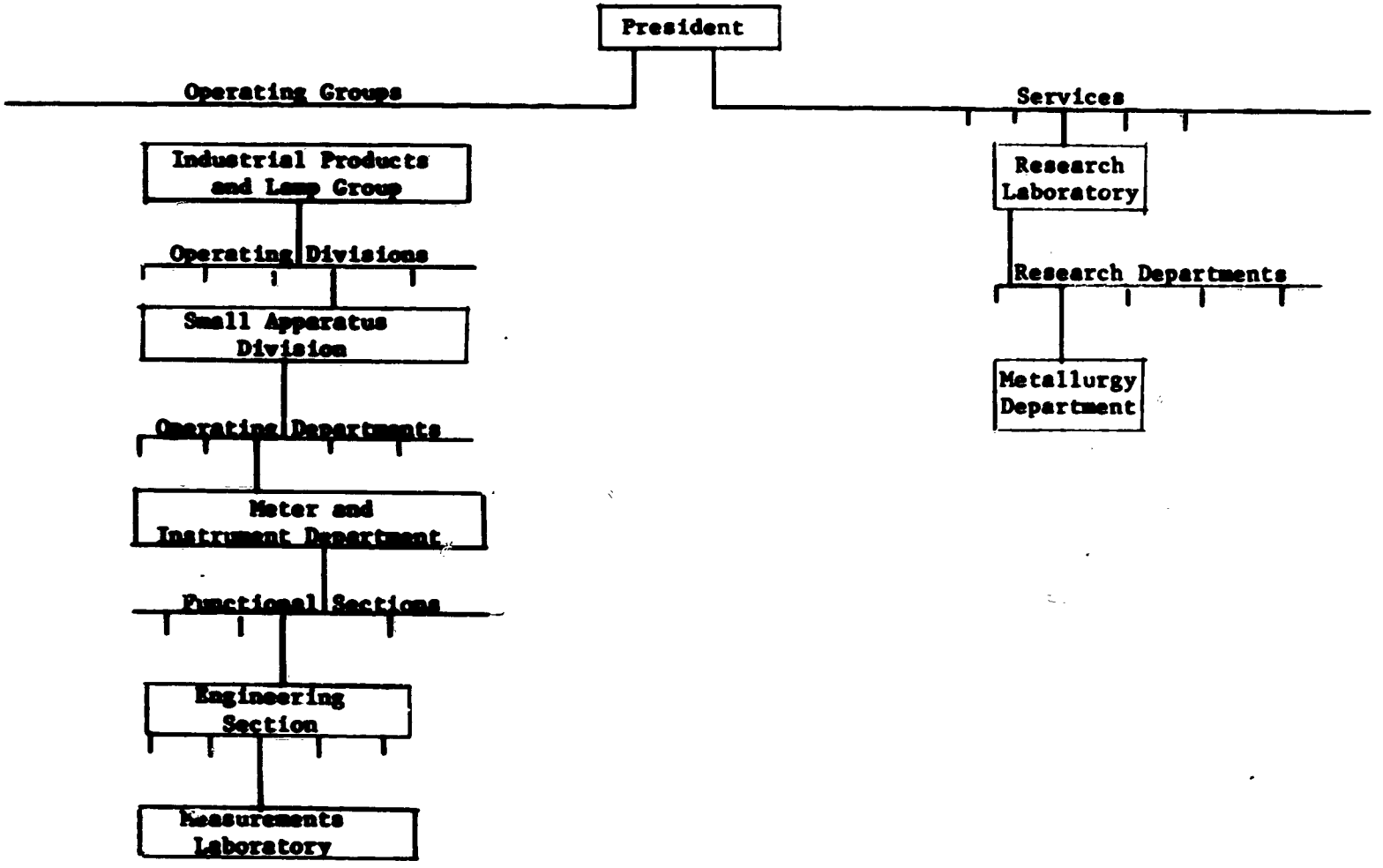
General Electric business can be broken down into four broad classifications as follows:

1. Heavy capital goods, including turbine-generators, atomic power reactors large electric motors, transformers, and switchgear.

2. Components and materials supplied primarily to industrial customers, including such equipment as small electric motors, electric control devices, mete and instruments, plastics, special metals, electrical construction materials, and computers, and other electronic equipment for industrial applications.

3. Consumer goods, including household appliances, radio and television receivers, small electric housewares, air conditioning equipment, and lamps.

4. Products for national defense, including defense electronic equipment, aircraft gas turbines, and development of aerospace systems.



GENERAL ELECTRIC COMPANY SKELETON ORGANIZATION STRUCTURE
RELEVANT TO THE CASE HISTORY
(circa 1951)

ANALYSIS

DESCRIPTION OF THE CRITICAL RESEARCH ENGINEERING INTERACTIONS

REI

a Paine, hired by GE Meter Department - told of problems and opportunities concerning commercial magnets - sent to Corporate Research Laboratory to become familiar with science area and there stimulated by excitement over advances in elongated fine particle theory. From these interactions, Paine and Mendelsohn formulated applied research program.

b Paine returns to GE Meter Department, Measurements Laboratory where he joined Mendelsohn. They both were subjected to constant business pressure to develop better magnets, and had continuing interaction with laboratory personnel on magnet theory and testing techniques, as well as rapidly advancing electron microscope techniques for seeing small particles. These interactions were essential to the first discovery of fine elongated iron particles.

c Need to develop and optimize a fine elongated particle magnet process caused additional fundamental research in understanding of kinetics of iron electrodeposition in mercury to be done in the Measurements Laboratory and theory of coercive force of irregular shaped fine particles to be undertaken in the Research Laboratory.

d Results of research initiated in (c) above and engineering information concerning types of magnets needed were crucial to development and optimization of elongated fine particle magnet process.

e Continuing and close interaction required from development stage through Pilot Plant to production engineering between marketing, engineering, research, and development personnel. For example, market requirements on magnet stability stimulated research to understand oxidation protection of fine particles and the effects of oxidation on magnetic behavior, etc. These continuing interactions were essential to the success of a commercial product.

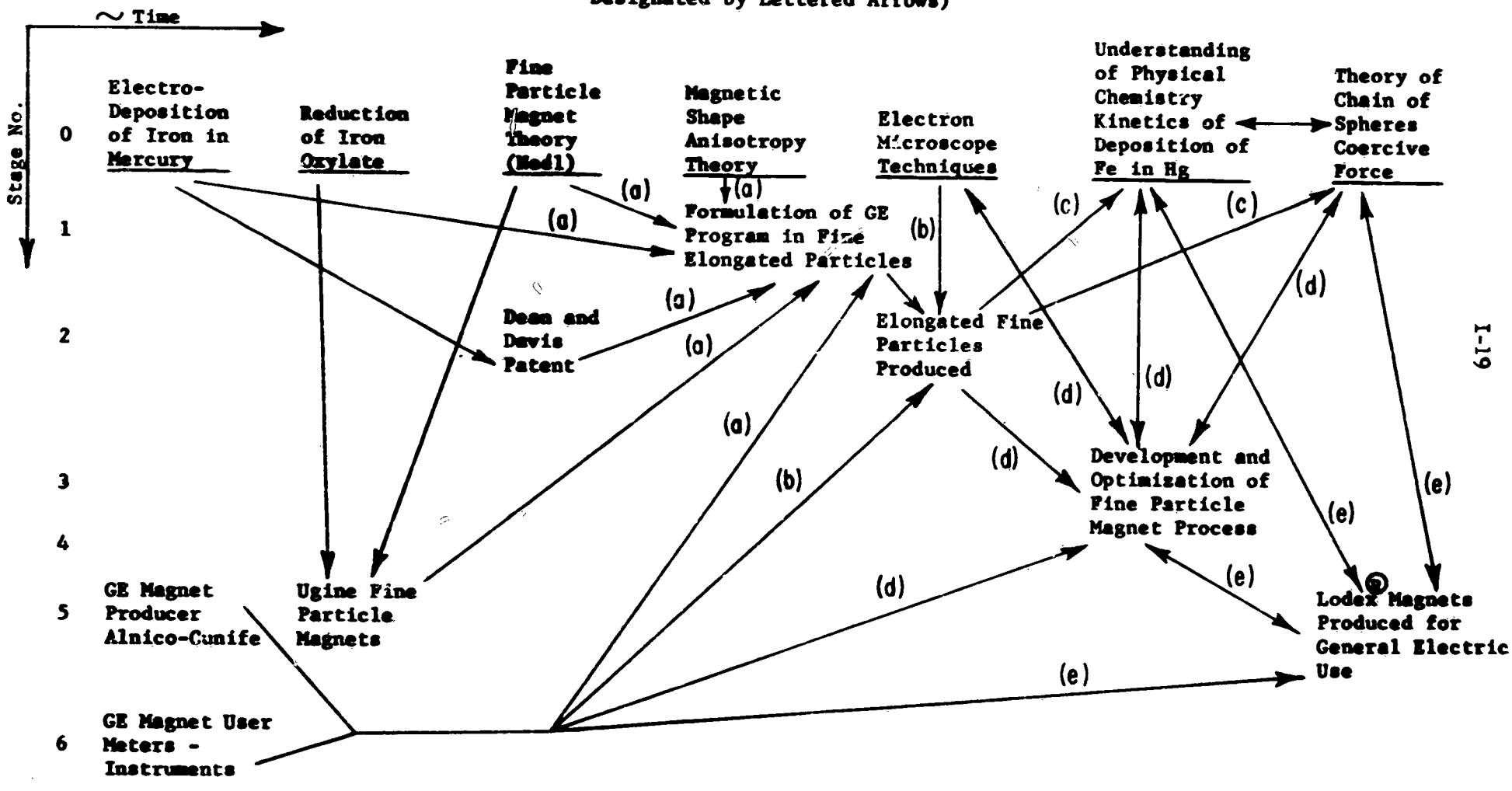
DEFINITION OF REI STAGES

(See Chart I)

No.	Definition
0	Scientific finding (knowledge)
1	Recognition of new material (process) possibility
2	Creation of useful material (process) form
3	Feasibility of using the material (process) in hardware
4	Possibility of using the hardware containing the material in a system
5	Production of the system (product)
6	Operation of the system (product)

Chart

KEY STAGES AT WHICH CRITICAL REIs OCCURRED
(With Research-Engineering Interactions Designated by Lettered Arrows)



FACTORS CONSIDERED IN ANALYZING EVENTS OF REIs

From its study of all the cases, the Committee selected a number of the more prominent factors which seemed to be operating with some frequency in the identified REIs. The statistical analysis of the frequency of these factors in this case is shown below.

FREQUENCY OF FACTORS IN REIs

(Statistical Analysis)

Factor No.		REI a	b	c	d	e	Freq.
1.	High educational level (advanced degree) of principal investigator	X	X	X	X	X	1
2.	Importance of management	X	X	X	X	X	1
3.	Importance of Government-sponsored research	0	0	0	0	0	0
4.	Importance of recognized need	X	X	X	X	X	1
5.	Requirement of flexibility to change direction during work and local control of funds (easily available resources)	X	X	X	X	X	1
6.	Industrial laboratory involved	X	X	X	X	X	1
7.	Basic research in the laboratory (for inst. or org.)	X	X	X	X	X	1
8.	Communications across organizations was important	X	0	X	X	X	4/5
9.	Technical problem was the principal obstacle	X	X	X	X	X	1
10.	Importance of a "champion"	X	X	X	X	X	1
11.	Freedom for individuals	X	X	X	X	X	1
12.	Broad spectrum of types of laboratories	X	0	X	X	X	4/5
13.	Geographic proximity	0	X	0	0	0	1/5
14.	Prior experience with innovation	X	X	X	X	X	1
15.	Organisational structure (barriers and bonds)	X	X	X	X	X	1

A CASE HISTORY OF THE DISCOVERY OF MATERIALS FOR THE CONSTRUCTION OF SUPERCONDUCTING HIGH MAGNETIC FIELD SOLENOIDS

Prepared by
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THE DISCOVERY OF MATERIALS FOR THE CONSTRUCTION OF SUPERCONDUCTING HIGH MAGNETIC FIELD SOLENOIDS

A Case History Prepared by
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Discovery of Superconductivity and Early Considerations of Superconducting Solenoids

The phenomenon of superconductivity was discovered by H. Kammerlingh Onnes at the University of Leiden in 1911.[1] Onnes was performing experiments to test a hypothesis that the resistance of pure metals would decrease gradually as they were cooled, approaching zero resistance as the temperature approached absolute zero. He discovered unexpectedly that the resistance of pure mercury dropped discontinuously to an unmeasurably low value at approximately 4°K. This abrupt decrease in resistivity well above absolute zero was completely unexpected and was named "superconductivity."

The discovery of the possibility of electrical conductors of zero resistance led immediately to speculation about the practical applications of these materials. Onnes's records show that one of the earliest possibilities that occurred to him was the use of these materials in the form of solenoids to produce large magnetic fields.

Magnetic fields up to about 25,000 oersteds are readily produced by taking advantage of the magnetic properties of certain materials, notably alloys of iron, nickel and cobalt. However, metal core magnets are generally limited to fields of about 25,000 oersteds. In order to produce more

intense magnetic fields, it is necessary to resort to air core electromagnet and such magnets consume very large quantities of power because of the finite resistance of the electrical conductors from which they are fabricated Such magnets are not only expensive to operate but are expensive to build because of the power and cooling equipment which is required. These facts were appreciated by Onnes. He realized that the possibility of using a conductor with zero resistance could well outweigh the difficulties of cooling th solenoid to very low temperatures. The technical values of using more intense magnetic fields in rotating electrical machinery and the value of having laboratory electromagnets which could produce very intense magneti fields for scientific investigation were equally appreciated. Thus, Onnes a his colleagues soon set about to investigate these possibilities. Almost imm diately they discovered a new phenomenon which seemed destined to destroy these hopes.

It was discovered that superconductivity in the materials with which the worked disappeared abruptly if the current flowing through the superconduct was increased beyond certain limits. Soon after, it was discovered that an external magnetic field would also cause the transition from the supercondu ing to the normal state. Indeed, in the materials which Onnes and his group investigated, the transition occurred at magnetic fields of a few hundred oersteds. These facts thwarted the early hopes for using superconductors to make electromagnets.

The problem remained dormant for many years while the group at the University of Leiden, and investigators in a few other laboratories around the world, continued a broad fundamental investigation of the phenomenon of superconductivity in an attempt to understand its origins and define the phenomenon in detail. One early result of these studies was the postulate of a relationship between the critical current which would quench superconductivity and the critical magnetic field which would also destroy the effect. This relationship, postulated by Silsbee in 1916,[2] suggested that the effect of a current in destroying superconductivity might be due simply to the magnetic field which that current produced and thus the phenomenon of a critical current and a critical magnetic field might be identical. This relationship was verified in detail for several pure elemental superconductors. This hypothesis was very important to the possibility of making superconducting solenoids, for it suggested that if a material could be found with high enough critical field then it should be able to carry the current required to produce a magnetic field of that value in a solenoid.

However, as new superconducting materials were found, the hopes for producing large magnetic fields with superconducting solenoids grew dimmer. In each new superconducting material the critical magnetic field was of the order of a few hundred to a few thousand oersteds. The discovery of superconductivity in the element niobium, with its transition temperature of 9.25°K, one of the highest transition temperatures of any element, was

accompanied by the discovery that even in this material the critical field was apparently below three thousand oersteds. Thus it appeared that eve as new superconductors, with increasingly high transition temperatures, were discovered, the hope was dim for getting into the interesting magnet field range which begins at about 25,000 oersteds.

An Opportunity That Did Not Mature

There was a brief flash of encouragement in 1930, when DeHaas and Voogd[3] reported a critical magnetic field of over 20,000 oersteds in an alloy of bismuth and lead. However, this hope was short-lived, as measu: ments showed that this alloy did not obey Silsbee's hypothesis, and that an unexpectedly low value of current would destroy superconductivity in this material. This discovery discouraged the further study of this alloy as a possible material for superconducting solenoids. In an article by W. H. Keesom,[4] published in Physica in 1935, it is stated:

> "The fact that some alloys have a very high magnetic threshold value of the disturbance of supraconductivity has on several occasions given rise to the idea that it should be possible to devise a coil of supraconductive alloy that would be able to carry a strong current and so develop an intense magnetic field.
>
> "An attempt to realize that idea by experiment, however, did not lead to success. As a matter of fact, it appeared that an alloy, which according to previous investigation, should have a

high magnetic threshold value possesses only a moderate current threshold value; viz., a current threshold value of the same order of magnitude as that of a pure metal."

Recently it has been shown[5] that if the bismuth-lead alloys had been studied more intensively using only techniques and materials which were readily available in the laboratories of the 1930's, alloys could have been developed which could be used to make superconducting solenoids that would produce magnetic fields in the range of 20,000 oersteds. However, the work was not pursued in the 1930's and for the next three decades the notion persisted that superconducting solenoids to produce magnetic fields of more than a few thousand oersteds could not be constructed.

During the next thirty years the technical literature is essentially barren of any consideration of high magnetic field superconducting solenoids. The next quoted reference[6] appears in 1955 in an abstract of a short talk given at a meeting of the American Physical Society. This work was by Yntema at Cornell, who built an iron core electromagnet with niobium windings which produced a field of 7,100 oersteds at liquid helium temperatures. The magnet was constructed in the course of his research and was recommended as a useful way to produce moderate magnetic fields for low temperature research. Of course, much of the observed field strength was obtained from the magnetic induction of the iron core so that this particular experiment did not obviously reveal any new information about the critical field properties of niobium.

Pertinent Events in Parallel Areas

In the meantime, scientific and technological developments in contiguous areas were proceeding in directions which were soon to affect investigations of high magnetic field superconductors.

Shortly after World War II the A. D. Little Company announced the commercial availability of the Collins Cryostat. This commercial helium liquifier soon made low temperatures accessible to a much larger number of laboratories and stimulated considerably the investigation of phenomena at very low temperatures.

In other areas the need for producing magnetic fields at low temperatures was increasing. Experiments in nuclear magnetic resonance and electron spin resonance which began just before World War II and grew in popularity after the war required magnetic fields of a few thousand oersteds with samples which were frequently cooled to liquid helium temperatures. In general, the magnetic fields were supplied by conventional magnets operating at room temperature while the samples were immersed in a cryostat at the desired temperature.

During the early 1950's great interest and activity were created by the proposals for generating power by nuclear fusion. The only attractive method for containing the ultrahigh temperature gases required both for experimentation and in any final practical embodiment, appeared to be a magnetic field with a required intensity in the neighborhood of 50,000 oersteds. This was well beyond the capabilities of metal core electromagnets

and was a serious deterent, both to experimentation and to the hopes of a final practical embodiment. The high efficiency theoretically attainable in a superconducting solenoid would be very attractive for this application and there is evidence that these possibilities were discussed by the workers in this field. However, there is no evidence that there was any serious or intensive attempt to reopen the investigations.

In the period of 1955 to 1956 a new electronic device was announced, the microwave maser. The first embodiment of this device used ammonia gas in an electrostatic field. However, soon thereafter a solid state microwave maser was conceived and built which employed a magnetic field for tuning. The solid state devices were operated at liquid helium temperatures to optimize their properties, and this then created another practical application for a device to produce a magnetic field at low temperatures. Here again the first devices were operated using conventional magnets at room temperature to surround the active medium of the solid state maser which was itself located in a cryostat near liquid helium temperatures. However, these structures were quite bulky and also very sensitive to stray magnetic fields.

Events Leading to the Discovery of High Field Superconductivity

The possibility of using superconducting solenoids in conjunction with solid state masers seems to have been first appreciated by S. H. Autler[7] at the Lincoln Laboratory. Autler had become interested in solid state microwave masers shortly after their invention had been announced. He

had participated in some of the early experiments on these devices at Lincoln Laboratory.

During this period Autler also became interested in the rapidly developing field of radio astronomy realizing that his experience with microwave masers might be very useful in radio astronomical investigations. He began to search out an opportunity to become involved with an active group in this field. He soon made contact with a group at the Signal Corps' Laboratories in New Jersey and after some general discussion with them it was agreed that Autler would begin development of a microwave maser to operate at the frequency of the hydrogen line (1420 mcps) which would be used in conjunction with antennae and other equipment at the Signal Corps' Laboratories in their radio astronomy program.

In his early considerations of an appropriate maser structure, Autler decided to try to develop a maser that would require only a very low field of a few hundred oersteds in order to get around the difficulty of the large bulky magnet structure that was conventionally used. He first thought of using a simple copper solenoid which he would operate at room temperature in order to give him the required field of a few hundred oersteds. However, he also thought of the possibility of using a superconducting solenoid since the fields that he expected to require were quite low. Indeed, he actually constructed a small solenoid using lead wire which he operated at a few hundred oersteds.

He soon discovered, however, that he was unable to obtain the maser characteristics which he desired at these low magnetic fields and that, indeed, he would require a magnetic field of the order of a few thousand oersteds in order to obtain a useful device.

It was clear that it would be impractical to use a simple copper solenoid to produce a field of this magnitude, and he also expected because of the published properties of the critical field of superconductors, that he would be unable to use a simple superconducting coil. However, it did occur to him that he might use a superconducting coil in order to drive an iron core electromagnet. This approach was very similar to Yntema's work but Autler was unaware of that work and arrived at his proposal independently. At that time he expected that he could easily get to a field of the order of 15,000 oersteds which is within the range of the magnetic saturation of iron. Early in 1959 he tested an iron core electromagnet using lead wire as the exciting winding and achieved a field of about 1,000 oersteds.

Autler states that at this time the Signal Corps' interest in a cooperative program on radio astronomy had decreased greatly. However, he decided to continue in order to prove the feasibility of a maser operating in the field of a superconducting magnet. He had little prior experience with superconductors and began to acquaint himself with what was then known about superconductors.

It was during this period that he began to consider the possibility that niobium would be a considerable improvement over lead because of the

reported higher critical field of niobium. In June of 1959 Autler made his first small solenoid with annealed niobium wire and obtained a field of 2,200 oersteds. He was excited and surprised by this result because this field was significantly greater than he had expected from the published properties of pure niobium. These results were reported in the July 15, 1959 Lincoln Laboratory Quarterly Progress Report on Solid State Research (issued September 15, 1959 and distributed shortly thereafter). This report receives a rather broad distribution to government laboratories and to industrial laboratories which are engaged in government supported research and development.

During the next month he built several iron core magnets using niobium wire as the exciting coil and reached fields as high as 7,100 oersteds. It was also during this period that he realized from literature references that the critical field of hard worked, unannealed niobium wire was considerably greater than that of the annealed wire with which he had been working. He immediately set about to build a coil from unannealed wire and by the middle of July had built a small air core solenoid which produced a field of 5,100 oersteds. By the end of August, he combined a larger superconducting solenoid using unannealed niobium wire with a maser structure and produced the operating device which had been the goal of his original program. These results were reported in the October 15, 1959, Lincoln Laboratory Quarterly Progress Report on Solid State Research (issued in January, 1960 and distributed shortly thereafter).

In addition to this publication, Autler presented a short paper at the 1959 Thanksgiving meeting of the American Physical Society (Nov. 27-28, 1959). He also described his work at one of the press conferences which the American Physical Society normally arranges for this purpose at their meetings and a description of his results was published shortly thereafter by several newspapers (Cleveland Plain Dealer, New York Times, Boston Herald). In spite of this publicity, this work seems to have stirred very little immediate action outside of Lincoln Laboratory.*

Dr. R. Kompfner, of the Bell Telephone Laboratories, learned of Autler's experiments during a visit to the Lincoln Laboratory in December of 1959. This visit was a part of an informal series of reciprocal visits between the Lincoln Laboratory and the Bell Telephone Laboratories at each other's establishments over the period of a few years. Kompfner and his colleagues at Bell Laboratories had had a continuing interest in microwave masers. They were involved in some of the first work at Bell Laboratories in this field and had also been involved in the first use of the microwave maser in the Bell Laboratories experiments with the Echo satellite. During the visit, Kompfner saw a demonstration of the work which Autler had been

*There are other indications that there was general, if perhaps passive, knowledge of Autler's work during 1960. He received several requests for reprints of his Physical Society talk. His early results were published in more complete form in the April 1960 issue of Reviews of Scientific Instruments. He received over 200 requests for reprints of this article and also several direct letters asking for specific advice on how to build niobium superconducting magnets. In one case, he actually supplied a magnet to a university group for their experimental studies.

doing with superconducting magnets as an integral part of the solid state microwave maser structure. Kompfner was quite impressed by this demonstration not only because of the large reduction in size which the superconducting magnet permitted, but especially by the stability of the field and by the ability of the superconducting solenoid operating on a persistent current to shield the maser from stray magnetic fields.

After returning from this visit, Kompfner described the work which he had seen at one of the regular meetings of the Research Area staff. At lunch following that meeting he suggested that an attempt should be made to extend this work. Kompfner had been very close to Matthias' work on superconductors at Bell Laboratories. Indeed, he and Matthias had in the past discussed the possibility of superconducting magnets. Kompfner had attempted some experiments at Matthias' suggestion using Nb_3Sn for this purpose. This compound had been discovered by Matthias[8] and had the highest transition temperature of any known material. However, these early experiments had been discouraged because of the great difficulty in fabricating this inherently brittle material into a suitable form. It seemed apparent that many of the problems involved in pursuing this work would be metallurgical problems and Kompfner suggested at this luncheon that the support of the Metallurgical Research Laboratories would be very important. E. E. Schumacher, Director of the Metallurgical Research Laboratories, who was also at the table, agreed that this should be considered.

As a result of this discussion, a meeting was held which included Kompfner, Schumacher, Matthias, S. Millman, T. H. Geballe, J. H. Scaff, J. H. Wernick and M. Tanenbaum. During this meeting Kompfner described the work he had seen and Matthias suggested several materials which he felt might be considerably superior to niobium. Attention was focused on ductile metal alloys, in particular the molybdenum-rhenium system where superconductivity had been discovered by J. K. Hulm.[9] However, other materials were mentioned including alloys of niobium as well as the brittle beta-tungsten superconductors such as Nb_3Sn. The possibility of producing a niobium wire with a surface layer of Nb_3Sn was also discussed. At the end of this meeting it was agreed that the Metallurgical Research Laboratories would begin a program to prepare and study the properties of niobium and of some of the ductile superconducting alloys suggested by Matthias, in particular the molybdenum-rhenium alloys.

Following the meeting J. E. Kunzler, a member of the technical staff of the Metallurgical Research Laboratories, was told about the work that Kompfner had seen at Lincoln Laboratory and of Matthias' suggestions concerning the ductile alloys in the molybdenum-rhenium system. Kunzler had been interested in the transport properties of metals and had established a comprehensive experimental facility for detailed measurement of the electrical properties of metals at liquid helium temperatures. He was intrigued by Autler's experiments, both because of their possible technological significance and because he himself was interested in producing high

magnetic fields for his own experimental work. About one year earlier, the Bell Laboratories had installed an 88,000 oersted magnetic field facil using a conventional air-core solenoid. Kunzler had been making measu ments in this facility, but it was much in demand and experiments had to scheduled well ahead of time. Although at this time there was no real ho of using superconductors to produce fields equivalent to those available in this magnet, nevertheless, Kunzler was intrigued by the possibility of ev much lower fields for his own experimental purposes.

Thus, Kunzler decided to participate in the study of superconducting materials and began studying the properties of molybdenum-rhenium alloy It was arranged that E. Buehler and C. V. Wahl, who were also members of the technical staff of the Metallurgical Research Laboratories, would pr pare the alloys, and Kunzler would make the measurements and provide ge eral guidance. The very first experiments on these alloys indicated that their properties were much superior to elemental niobium, and this greatl increased the interest in looking further. As a result of further discussion between Kunzler and Matthias, Matthias suggested several other ductile superconducting alloys. A number of these were prepared and evaluated by Kunzler and his colleagues. Some of the materials were not very promisin but among the suggestions were alloys of niobium with zirconium which proved to have properties far superior to the original molybdenum-rhenium alloys. Indeed, the niobium-zirconium system has become one of the most popular materials for use in solenoids for operation at magnetic fields in the range between 50,000 and 80,000 oersteds.

Meanwhile, Kunzler proceeded to extend the conductivity measurements to the highest possible fields in order to obtain a complete evaluation of this unusual superconductor. Using the 88,000 oersted air-solenoid facility, he and his colleagues found that the ingots of Nb_3Sn remained superconducting at fields of 88,000 oersteds and that, furthermore, the critical current of these cast ingots at the highest fields was 3,000 amperes/cm^2. This value of critical current at these very high fields was completely unexpected. Furthermore, extrapolation of the results indicated that the limiting critical field of Nb_3Sn was well above 100,000 oersteds.

Shortly after the very first measurements on Nb_3Sn indicated a critical field of greater than 20,000 oersteds, Kunzler and his colleague, E. Buehler began a serious consideration of how one might circumvent the brittleness of this material in order to make a solenoid from it. By the time the high field measurements were made they were well on their way to developing a satisfactory technique. The process which they developed takes advantage of the fact that the components of the compound, niobium metal and tin metal are quite ductile, and that a mixture of fine powders of these metals containe in a niobium tube can be worked by conventional metallurgical processes into a fine ductile wire. After this ductile wire is wound onto a spool, it is heat treated at about 1000°C, allowing the metal powders to react and form the intermetallic compound which although brittle is now in the desired solenoidal form. They soon discovered that the compound prepared this way had a critical current density fifty times greater than that of the cast ingot. At

4.2°K the critical current of some of the earlier samples of this wire was 150,000 amperes per square centimeter at an applied external magnetic field of 88,000 oersteds.

The properties of Nb_3Sn were announced on February 1, 1961.[11] The properties of the ductile niobium-zirconium alloys were announced at the Washington meeting of the American Physical Society (April 25-28, 1961).[12]

First Commercial Applications

The unexpected and exceptional properties of Nb_3Sn and the niobium-zirconium alloys immediately stimulated a broad program of investigation in a large number of laboratories of the fundamental properties of these materials and of their possible technological applications. Other forms of Nb_3Sn have become available including vapor deposited tapes[13] that do not have to be heat treated after the solenoid is wound. At the present time there are several suppliers of the various forms of the various materials and of magnets made from them. The first commercial applications have been in simple solenoids to produce magnetic fields for laboratory investigations and in instruments such as spin resonance spectrometers and microwave masers.

The first application of large volume, uniform field superconducting magnets in operating systems, was to provide the magnetic field for microwave masers that were used in military radars and in the American Telephone & Telegraph ground station at Andover, Maine, in conjunction with the Telstar satellite communication system. These magnets were designed at Bell Telephone Laboratories and were conceived by P. P. Cioffi.[14] Cioffi had

been a leader of magnet design efforts at the Bell Laboratories for many years. At the time of Kunzler's early measurements, Cioffi was deeply involved in the design of permanent magnets for microwave masers that were being developed to work with military radars. In one particular application, in order to develop a field of 4,000 gauss across a 3 inch air gap, with a uniformity of plus or minus one gauss over the 6 inch leng of the traveling wave ruby maser, the final magnet weighed 750 pounds. This fact was particularly disturbing to Cioffi since he realized that the efficiency of the magnet was extremely low because of flux leakage and fringing fields. Indeed, he calculated that the magnetic efficiency of the best structure which he could design was only about 3%. He realized that one reason for this inefficiency was that the magnet structure was separa from the ruby maser crystal by the walls of a dewar which was required t contain the liquid helium to cool the maser crystal. However, he calculated that even if he could put the permanent magnet structure inside the liquid helium dewar, the magnet would still weigh approximately 100 poun and would require excessive quantities of liquid helium in order to cool it.

The thought of putting the magnet inside the dewar stimulated Cioffi to think about an idea which he had had several years earlier. He had been aware that superconductors were perfect diamagnetic materials with zero permeability. They could, therefore, be used as magnetic insulators to shield magnetic structures against leakage and fringing flux and thereby raise the efficiency of the magnetic circuit to nearly 100%. The idea was

discarded at that time because the critical field of superconductors was too low and because their application to ordinary magnetic circuits was not practical. However, the necessity of operating the ruby maser in liquid helium and the prospect of a large reduction in magnet weight through the use of high critical field superconductors as magnetic shields made the operation of the magnetic circuit with the maser in liquid helium feasible and practical.

Cioffi had designed the 88,000 gauss conventional electromagnet that was in use at Bell Laboratories for solid state physics investigations and which was the facility that Kunzler used for his measurements on Nb_3Sn. Cioffi was frequently called in consultation on problems in magnetics and was especially conversant with the various users of the electromagnet. Among these was T. H. Geballe, who was a colleague and collaborator of B. T. Matthias. Indeed, Cioffi's laboratory was next door to T. H. Geballe. Through this very close association, Cioffi was familiar with Kunzler's early measurements essentially as they happened. He, thus, made a very quick connection between his maser magnet problems, his much earlier idea on the use of superconductors as diamagnetic shields and Kunzler's new results. He suggested the use of superconductors to solve the maser magnet problem and was strongly encouraged by E. D. Reed, who was responsible for the maser development, to pursue these ideas.

After discussion with Kunzler, it was decided that lead bismuth alloys, because of their great ductility and moderately high critical field, would

provide a good starting material for this application. Cioffi first built a small model which he tested at liquid helium temperature with and without a lead bismuth shield. His results agreed almost exactly with his predictions. With this encouragement, he then proceeded to build a maser magnet. Since leakage and fringing flux did not have to be provided for in the design, a weight reduction of nearly two orders of magnitude was possible from the original 750 pound magnet. After confirming by magnetic measurements that the required level of field intensity and degree of uniformity had been achieved, the magnet was turned over to W. G. Nilsen[15] who used it with an operating laboratory traveling wave ruby maser and demonstrated conclusively the feasibility of Cioffi's proposal and that his original expectations were completely achieved.

At about the same time, a second Bell Laboratories' development group at the Allentown laboratory began the design of a fully engineered, persistent current superconducting magnet using diamagnetic shielding for use in the Bell System's Earth Station at Andover, Maine, as an integral part of the Telstar communications satellite system. This structure was incorporated in a closed cycle liquid helium refrigerator and was demonstrated early in 1962.[16] It was placed in operation at Andover early in 1964. During this period there was a continuing evolution and improvement in the magnet design. One important aspect of this was the substitution of niobium-zirconium alloys for the original lead bismuth alloys with significant improvement in the operation and stability of the resulting structure.

In addition, a new design approach was originated which does not require a superconducting shield. Present magnet designs weigh only a few pounds resulting in an overall weight saving of approximately one hundredfold and a comparable saving in volume.[17]

Succeeding Development in Theory and Application

The fundamental investigation of the properties of superconductors in high magnetic fields has also been greatly stimulated by the experimental discovery of high critical field materials. Here again, it is interesting that the fundamental theoretical background of the phenomenon had been established for several years before Kunzler's measurements. It was implicit in the Ginzburg-Landau[18] theory published in 1950 that superconductors could be divided into two kinds. These considerations were explicitly amplified by Abrikosov (1952, 1957)[19] and Gorkov (1959)[20] who showed that for one kind of superconductor (called Type II) there would be two critical fields. The lower critical field is the thermodynamic field of a few hundred to a few thousand oersteds which had classically been thought to limit the fields that could be produced by superconducting solenoids. However, the theory proposed that superconductivity may continue to exist in a sample above this first critical field until a second critical field is reached. It is significant that these theoretical considerations did not suggest how large this second field could be and apparently no one suspected that these effects would be as significant as they are now known to be. Indeed, it was after the report of Kunzler's measurements that Goodman

(1961)[21] and others pointed out that prior theory could account for the observations.

During the years from 1961 to the present, as magnets of increasing strength were built using superconductors, new phenomena were discovered which have influenced the commercial development of high field superconducting magnets. Two of the most significant of these are the "training" effect and the phenomenon of flux "creep" and flux instability.

The training effect was observed as soon as the first magnets of niobium-zirconium were produced and measured. The effect was reported in the literature by M. A. R. LeBlanc,[22] at Stanford University.

The standard procedure for evaluating a batch of niobium-zirconium wire before producing a magnet is to take a short piece of the wire and measure the critical current as a function of magnetic field. From these measurements it is possible to predict how large a magnetic field can be produced by a solenoid made from this particular batch of wire. It was generally observed, however, that when the solenoid was wound and tested the maximum field that it would produce before the transition to the non-superconducting state was significantly smaller than the field that was predicted by the measurement on short lengths of wire. Furthermore, it was also observed that the solenoid could be "trained" to produce higher magnetic fields which more closely approximated the short wire prediction. For example, suppose that the solenoid was cooled to liquid helium temperature, the current increased until the solenoid suddenly became non-

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superconducting and the current was then turned off. If the solenoid was permitted to cool back down to the bath temperature and the current was then slowly increased again, a higher current value and higher magnetic field would be obtained. Furthermore, this process could often be repeated many times and each time a slightly higher magnetic field was obtained before the normal (non-superconducting) state was produced.

This training effect has not yet been quantitatively explained. One widely accepted explanation of the training effect was proposed by D. B. Montgomery at the National Magnet Laboratory and is based upon the generation of trapped eddy currents in the solenoid structure.[23] As the current in the solenoid is increased, it is postulated that eddy currents are produced which tend to oppose the field generated by the primary current. The pattern of these eddy currents is quite complex and must depend in detail upon the geometrical configuration of superconducting and non-superconducting regions in the mixed state of the Type II superconductors. By driving the solenoid normal several times, the configuration of the eddy currents can be rearranged so that their undesirable contribution to the overall magnetic field is decreased. Similarly, it has been observed that if the windings of the superconducting material are separated somewhat within the solenoid structure, either by air or by a non-superconducting material

such as copper*, then the field values obtained in the solenoid more closely correspond to the values predicted by measurements on short pieces of wire. In the more loosely wound configuration, the eddy currents generated in one part of the structure will have a weaker effect upon the adjacent windings in the solenoid. The "training" effect is quite troublesome in designing and building high field solenoids, since its elimination requires that the packing factor of the superconducting material be reduced. Therefore, the overall structure must be larger than would otherwise be necessary. However, by proper design the apparent degradation in the properties of the superconducting material can be largely overcome.

Flux "creep" appears to be a more basic phenomenon in determining the properties of high field superconductors. The phenomenon of flux creep was observed by Y. B. Kim, C. F. Hempstead and A. R. Strnad[24] at Bell Laboratories. The theory of flux creep was proposed by P. W. Anderson[25] of Bell Laboratories. Hempstead is a physicist and a member of Kompfner's research group. Shortly after Kunzler and Matthias' early results on molybdenum-rhenium alloys, and at Kompfner's

*It is interesting that magnets were being made routinely with such non-superconducting insulation. In the original construction of the Nb_3Sn "wire" the outer tube of niobium served as such an insulation. Also, much of the early niobium-zirconium wire was sheathed with copper or similar metal to aid in wire drawing. This layer was often left in place, principally to absorb the energy dissipated if the structure was driven to the normal state.

suggestion, Hempstead and Strnad began experimenting with magnet structures to determine how adaptable they might be for experimentation and application of high magnetic fields. They were soon joined in their study by Kim who was on a year's leave of absence from the University of Washington. He arrived just at the time that the first results on high field superconductors were being obtained and was attracted to this new and exciting field.

While making some of their early measurements on superconducting solenoids and on tubes of superconducting alloys such as niobium-zirconium, they observed minute instabilities in these structures. In particular, they observed that the magnetic flux in the center of the superconducting solenoid or superconducting tube might change discontinuously in very small steps as an external magnetic field was applied. These observations came to the attention of P. W. Anderson, who had long been interested in superconductivity and had been an important contributor to the theoretical understanding of the field. Anderson proposed that these instabilities might result from the nature of the flux distribution in a Type II superconductor.

The Ginzburg-Landau-Abrikosov-Gorkov (G. L. A. G.) theory of Type II superconductors postulates that in the high field region, a Type II superconductor is composed of a mixed state where the magnetic field is described by a lattice-like structure of quantized flux lines. Anderson pointed out that a current flowing through the superconductor will produce

a Lorenz force on the flux lines. As the flux lines move, they dissipate energy and thus produce an effective resistance in the superconductor which is undesirable. Thus, in an ideal Type II superconductor, where the flux lines are completely free to move, one would expect that the superconductor could not sustain a very large current without an appreciable energy dissipation and heating of the material. Fortunately, defects in the superconductor structure apparently act as pinning points which retard the motion of the flux lines. It has been postulated that this is the principal effect of the metallurgical structure in improving the critical current carrying capacity of Type II superconductors. Anderson proposed that the small flux jumps that Kim, Hempstead and Strnad observed might be produced by the thermally activated motion of bundles of quantized flux lines past pinning points as a result of the Lorenz force on these lines caused by the current flowing through the superconductor.

This theory has been further substantiated by detailed measurement and provides an important mechanism for dissipation in superconducting magnets. Indeed, the theory suggests that there will always be some dissipation in a Type II superconducting magnet at fields in excess of the thermodynamic critical field. However, if there is a sufficient concentration of pinning points, this dissipation can be negligibly low until the magnetic field closely approaches the upper critical field defined by the G. L. A. G. theory.

The motion of bundles of flux lines also provides new insight into the instabilities that are often observed in high field superconducting coils. If a large bundle of flux lines is suddenly freed from a pinning point, the motion of this bundle can create a local hot spot in the solenoid. This, in turn, can produce the motion of surrounding flux bundles leading to a catastrophic process which can cause the rapid transition of the superconducting solenoid to the normal state dissipating large quantities of stored energy in a very short time. In the design of practical solenoids this condition is alleviated by imbedding the superconducting material in a normal metal such as copper. The excellent electrical conductivity and heat diffusivity of the copper tends to smooth out the hot spots that moving bundles of flux lines might otherwise produce and thereby can help prevent a catastrophic transition. Thus, the same technique that helps reduce training effects can also stabilize the solenoid against catastrophic failure.

Conclusion

Thus the history of the discovery and use of high field superconductivity is a history of a possibility that lay dormant for some 50 years. Today's superconducting solenoids are the realization of a possibility that was clearly recognized by Kamerlingh Onnes in 1911. In the 1930's with the discovery of the unusual properties of bismuth-lead alloys, the possibility of superconducting solenoids almost ripened into reality, but somehow the opportunity was missed. It seems likely that if this system had been thoroughly investigated and 20,000 oersted solenoids had been

constructed, this might well have stimulated a more intensive and continuing investigation of each new superconducting material as it was discovered, and today's high field superconducting solenoids might have been available many years sooner.

It is also interesting to observe that the eventual discovery was closely associated with a well-defined practical application of the phenomenon, namely, the need to produce magnetic fields for use with low temperature, solid state microwave masers. The final discovery took place at Bell Telephone Laboratories in an environment where this need was clearly appreciated and where, also, the original work on some of the key materials had been performed. Here again, however, the realization of the well-defined need in this environment appears to have been a critical part of the stimulation of the final discovery.

ACKNOWLEDGEMENTS

The preparation of this history has been possible only through the generous help and cooperation of many people and organizations. Several of the individuals mentioned in this history have contributed time and effort both in supplying details of the developments and in reviewing the final document. The author is indebted to all of these individuals and organizations as well as others not directly mentioned in the case history but who contributed importantly in the final results.

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APPENDIX A

THE LINCOLN LABORATORY

The following statements have been selected from published sources which describe the Laboratory's organization and mission.

"The Lincoln Laboratory was established by the Massachusetts Institute of Technology in 1951 at the request of the United States Army, Navy and Air Force. A Federally financed research center operated by a university, its primary area of interest is advanced electronics with special emphasis on applications to National Defense and space exploration.

. . . . . .

"Consistent with its original purpose, Lincoln Laboratory continues its efforts toward advancing National Defense capabilities combining research and technological development.

"Lincoln Laboratory research extends from fundamental investigations in science to technological development of devices and components to the design and development of complex systems.

"There is a growing awareness that much significant work at the boundaries of current knowledge requires the resources and equipment, manpower or organization that only a large research center can provide. Conversely, technological applications directed toward the solutions of problems of national security require a foundation of research concentrated in selected technical areas.

"Accordingly, the work of the Lincoln Laboratory consists of programs undertaken in response to requests of Government Agencies whose needs coincide with the Laboratory's areas of competence as well as a program of general research.

. . . . . .

"General research comprises basic studies in fields of advanced electronics underlying the Laboratory's overall research and development. The areas included are solid state physics, chemistry, and metallurgy; information processing; communications; control systems; radar; radio physics and astronomy; and space surveillance. The continuing program of general research provides not only a background of experience and ideas for research and development in specific program areas but also a source of scientific and technological advances.

The association of Lincoln Laboratory with M. I. T. has always been a very important factor in the Laboratory's operation within the eyes of its leaders. This is expressed by Carl F. J. Overhage, who was director of the Lincoln Laboratory during the period of the work described in this case history.

". . . . . the crucial factors in the future of Lincoln Laboratory are the quality and the versatility of the technical staff. . . . if Lincoln Laboratory, as it grows older, succeeds in keeping a staff capable of the performance demonstrated in its first ten years we can

be confident of the future of the organization. And a key to continued vitality and excellence in the staff is the closeness of the Laboratory's interaction with M. I. T. With that interaction there will always be new ideas and young men to match tomorrow's challenges, and Lincoln Laboratory will go forward with M. I. T. as a useful and respected member of that great community."(2)

During the period around 1960 when the work described in this case history was performed, the Lincoln Laboratory had approximately 500 professional staff members with about twice that number of supporting personnel. Again in the words used in descriptive literature from Lincoln Laboratory:

". . . . The training and background of the professional staff includes many disciplines. Despite Lincoln's role in the development of military systems and equipment, much of the work at the Laboratory is not covered by any security classification. Staff members publish most of their work in established journals and participate freely in meetings of professional societies."(1)

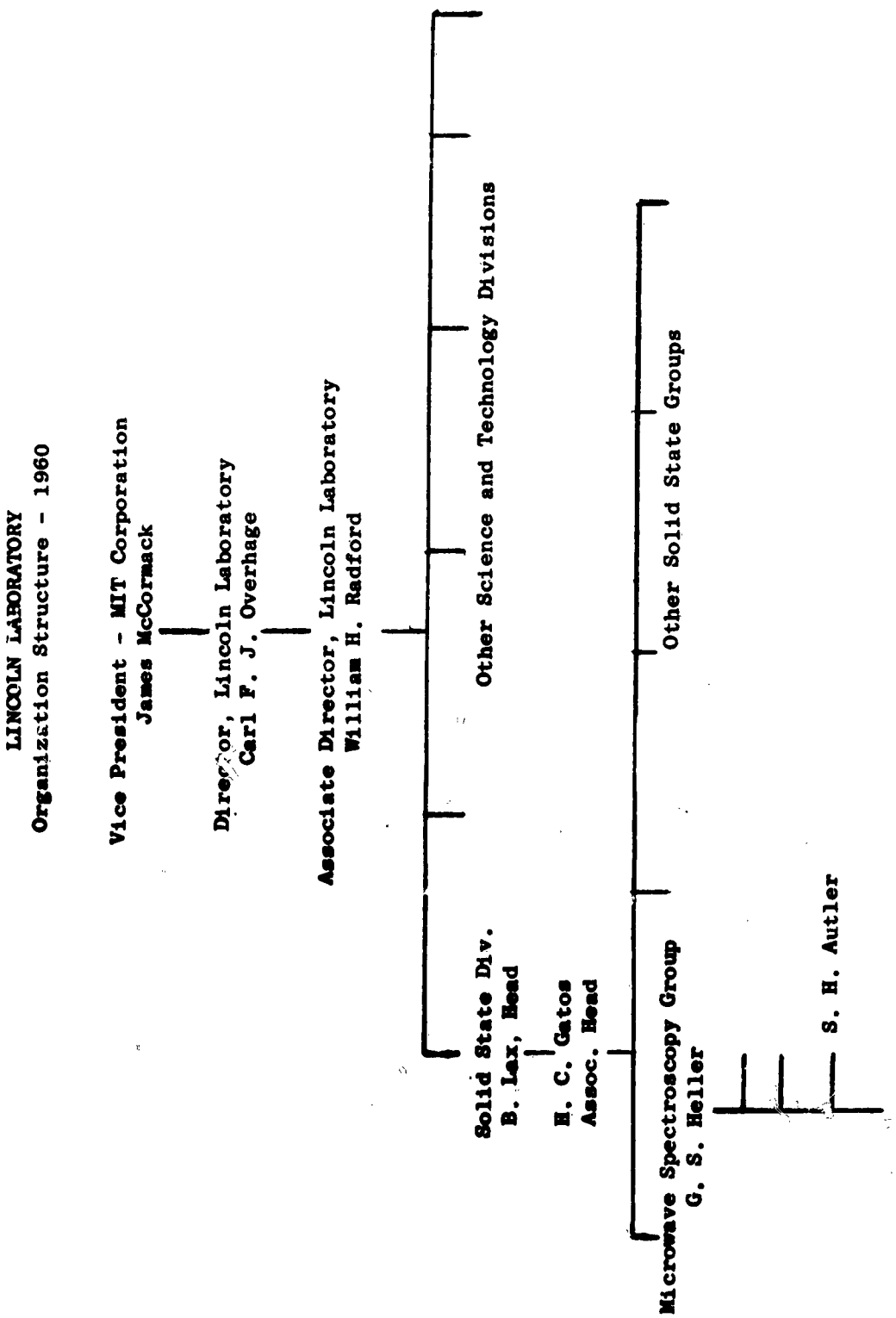
The Lincoln Laboratory is especially well-known for its work in solid state physics and solid state devices. From a fundamental viewpoint the Laboratory has been especially distinguished by its work on the spectroscopy of solids, including both magnetic materials and semiconductors. The magneto-optic properties of semiconductors has been an

area of special contribution. In solid state devices the Laboratory is distinguished for the invention of the cryotron, for its early pioneering work on magnetic thin film memories, and for its independent discovery of laser effects in semiconductor diodes.

The work of Autler on superconducting magnets was also performed in the solid state division. The organization of that division at the time of this work as well as the position of that division in the overall structure of the Lincoln Laboratory is shown on the attached chart.

(1) "Lincoln Laboratory, Massachusetts Institute of Technology," produced for the M. I. T. Office of Publications by T. O. Metcalf Company April 1963.

(2) "Lincoln Laboratory and the Greater M. I. T. Community," Carl F. J. Overhage, Technology Review, January 1962.


LINCOLN LABORATORY
Organization Structure - 1960
Vice President - MIT Corporation
James McCormack
Director, Lincoln Laboratory
Carl F. J. Overhage
Associate Director, Lincoln Laboratory
William H. Radford
Other Science and Technology Divisions
Solid State Div.
B. Lax, Head
H. C. Gatos
Assoc. Head
Other Solid State Groups
Microwave Spectroscopy Group
G. S. Heller
S. H. Autler

APPENDIX B

THE BELL TELEPHONE LABORATORIES

The Bell Telephone Laboratories is responsible for the design and specification of the telephone and communications equipment and systems used by the Bell System to provide communications services. At the time the work described in this paper was performed, the Bell Laboratories consisted of approximately 12, 000 employees, including about 4, 000 professional members of the technical staff. The work described in this case history was performed entirely within the research area. This comprised approximately 500 professional scientists and engineers engaged in fundamental and applied research in the physical sciences, communications sciences and mathematics. The attached chart shows the general organizational structure in which the principals involved in this case history were located.

Several aspects of the history, organization, responsibilities and philosophies of the Bell Telephone Laboratories are discussed in a statement delivered to the Sub-committee on Science, Research and Development (Committee on Science and Astronautics, House of Representatives) on December 11, 1963, by Dr. James B. Fisk, President of the Bell Laboratories. The following are excerpts from that statement beginning with comments concerning the Bell Laboratories responsibilities in the Bell System.

"As the research and development organization of the Bell System, our work begins at the forefront of science and extends across the entire scope of creative technology through research, development, design and engineering. Its end products are the specifications and designs for manufacture of the technical facilities it has created and the engineering practices to be followed in their operation and maintenance.

"Western Electric Company is the manufacturing branch of the Bell System and supplies the major portion of the System's technical facilities. The Bell System is thus unique among organizations providing service in that it assumes responsibility through Bell Laboratories and Western Electric both for its own technology and for the manufacture of its technical equipment."

In describing the underlying principles of the Bell Laboratories' work and organization, Dr. Fisk quotes a statement made in 1925 by Mr. H. Thayer, of the A. T. & T. Company, and selects a few aspects of that statement for special emphasis. At one point Dr. Fisk says:

"Another idea which appears very strongly in the quotation is that of close cooperation among scientists, designers, shop people, manufacturing engineers and the like in pursuing the final objective. This concept of the complete technological process as one involving close integration of a number of phases, from scientific research to

final design for production, has been applied in amplified and developed form at Bell Laboratories ever since."

Continuing the discussion of principles, Dr. Fisk describes some of the "enduring themes" of the Laboratories' work. In introducing this discussion he says:

".....Aside from broad principles of operation, nothing perhaps controls the destiny of a research laboratory quite so much as the definition of the subject area in which it will work. One cannot choose an area that is too extensive; even the best laboratories cannot excel across the board. One cannot choose too narrow a one either, since this does not give the professional staff reasonable elbow room in which to work. With the increasing scale and the increasing competitiveness of science and technology, the choice of the right field, and of the right aspect of that field, is becoming increasingly more difficult. It calls for the most perceptive scientific judgment I can think of, and even the best scientists may frequently go wrong.

"In general, the most satisfactory subject matter is that which is vitally related to the objectives of the enterprise and has technical qualities of enduring interest and enduring potential for growth....."

Dr. Fisk describes the organizational arrangement in terms of research and development as follows:

"As we use the terms, research and associated fundamental development are our unprogrammed and unscheduled areas of work.

They provide the reservoir of new knowledge and new understanding which is essential for new communications systems and facilities. The work includes all sectors of science that appear likely to contribute to the advancement of the art of communications and is carried out in enough volume to ensure a minimum reasonable time lag in our realization of the potential significance of a scientific advance. In contrast, specific development and design (which constitutes the bulk of our development activities) is always carefully programmed and there may be several well-ordered steps in its performance. It is the activity which leads directly to new systems and facilities."

Dr. Fisk describes research at the Bell Laboratories in some detail:

"It is convenient to begin the discussion of research by considering the meanings of the terms 'unprogrammed' and 'unscheduled' with reference to this area. As compared with procedures necessary in the development area, research is indeed unprogrammed and unscheduled. This, however, does not relieve the management of a research laboratory of the responsibility of making the hard basic decisions concerning subject matter, scale and 'enduring themes' to which I referred earlier. Actually, in BTL, the vice president for research and I give continuous thought to the total amount of research appropriate to meeting Bell Laboratories' responsibilities. We are also concerned with the division of this total amongst the various

research disciplines so that a proper balance is maintained in the pursuit of new knowledge in these different areas. In collaboration with the directors of the individual research groups, we try to outguess the future, to determine which unexplored areas of science may yield discoveries of value to our industry.

. . . . . .

"A research department has two important frontiers. One borders on the outside world of science, primarily in the universities but also including other industrial laboratories, government laboratories, etc. In areas of importance to us, we attempt to participate fully and actively in this general world. There are two reasons for this. One is a matter of simple give-and-take; we try to contribute to areas from which we expect a great deal. The other is that it is very difficult to understand a field fully unless you are doing research in it yourself. Thus, it is important for us to participate in major fields which may have particular significance for our long term missions.

"Inspired and productive research in industry requires men of the same high quality as is required for doing pure research in our universities. We attempt to give our research men freedoms that are equivalent to those of the research man in a university, and they participate in the research world on a natural and informal basis. It is important for us that the total level of research, which must

in the long run be conditioned largely by activities in universities, be kept high, so that there will be a large and fruitful reservoir of new understanding to draw upon.

"The other important frontier of a research department is internal. It is, in other words, primarily an interface with development areas. One of our thoughtful research administrators of recent years, Dr. Ralph Bown, in reflecting upon the issues underlying this relationship, saw that it was important to specify two freedoms for a productive research organization. One is the freedom to resist pressures from other departments to work on their specific problems. The other is the freedom occasionally to carry ideas experimentally into the applicational stage to a point where merit can be demonstrated, when the researcher considers that this merit has not been recognized or has been overshadowed by development schedule pressures. The wise researcher will know that these freedoms have to be merited and that they impose obligations. The first freedom cannot ignore the occasional emergency where all available skill must be enlisted to solve a serious fundamental problem. The second cannot extend to stubborn clinging to a favorite scheme when wisdom would call for new approaches or a new activity."

After a discussion of the development organization and systems engineering and the description of several examples chosen to exemplify the relations between research, development and systems engineering,

Dr. Fisk then concludes the statement to the Committee with the following paragraphs:

"I would like now to sum up in just a few words. What I have been trying to describe, largely by a series of examples, is a sort of 'philosophy of research' under which Bell Laboratories operates. The philosophy may be of interest to you because it has developed gradually over a long period of time and thus represents a great deal of experience. It may also be of interest because, as I suggested at the outset, it represents private industry using its own economic resources and operating under ordinary business constraints. Thus, it exhibits at every point a kind of complex interplay among economic and technological factors which is not an obvious feature of many of the country's R&D activities.

"On the other hand, I am quite aware that our approach may not fit all situations. It emphasizes extremely long range planning and the patient accumulation of technological resources until the groundwork for a new major development is well established. This works for us and does not prevent us from taking quick decisive action when necessary, as the radar and Telstar satellite examples show. Other laboratories meeting different problems, on the other hand, might find a somewhat different approach more satisfactory. Whatever the approach, however, I believe it is important to recognize that both science and technology have deep roots and a great deal of

long term continuity. Major advances seldom occur without elaborate prior preparation of the ground. Progress is much more likely to resemble the flow of a stream than a series of lightning bolts.

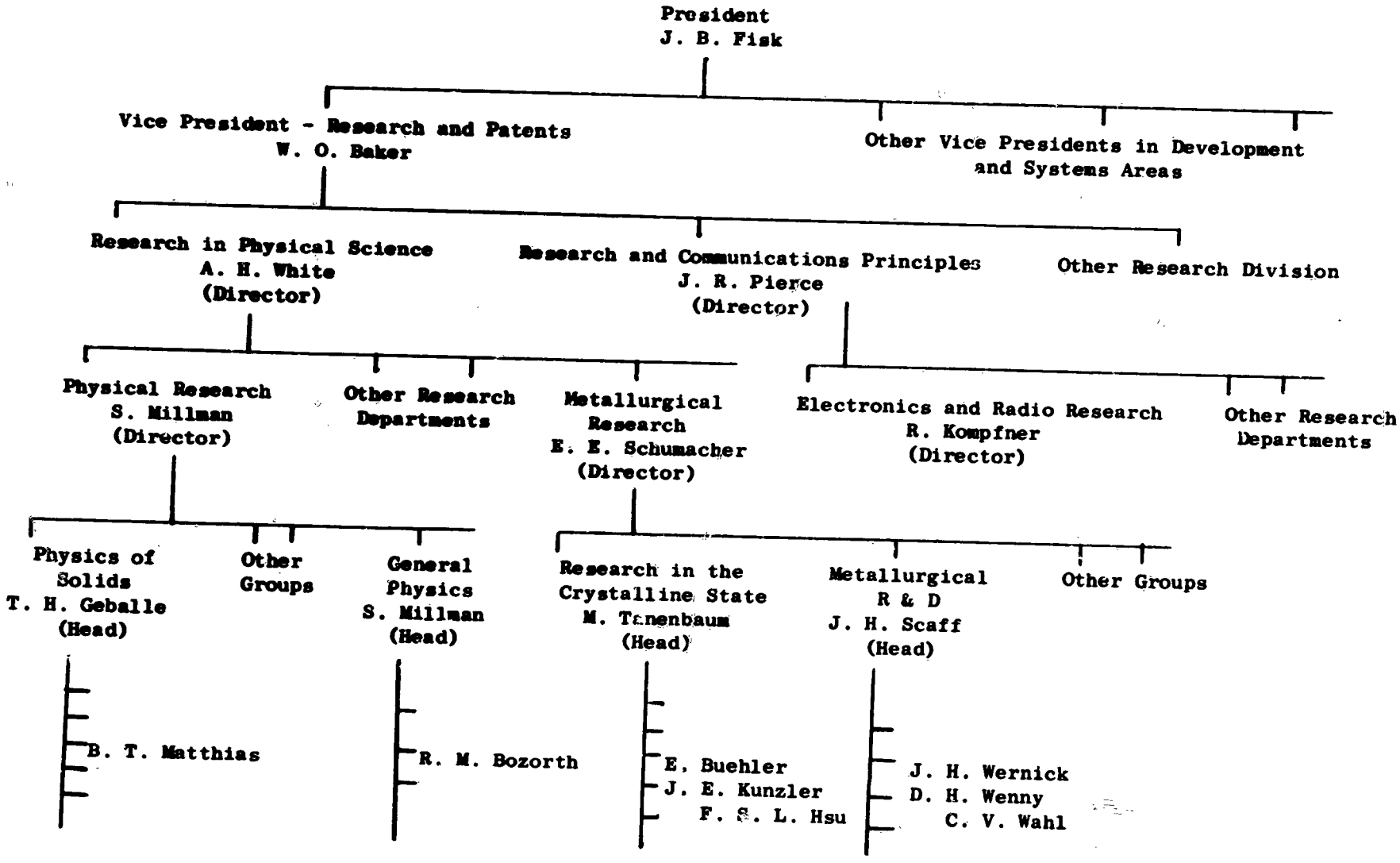
"Our experience, in any case, seems to have turned up no easy roads to success in R&D. Certainly, risk-taking is always inherent in decision-making. Our philosophy contains no magic formulas. Instead, it almost reduces to a mundane exhortation to do the best possible job in all the elements of the complete technological process, from research through systems engineering and development to production and service. Attention to all these areas does indeed seem to be important. They need to be properly staffed, properly chartered, and the interfaces between them need to be defined with care.

"If there is any one aspect of the subject which deserves particular prominence, I believe it is that of choosing the right definition of mission for an R&D enterprise. To make the right choice, and then to adhere to it, may not be as easy as it sounds. For example, one may have to decide rather frequently whether entrance into a new field is, in fact, compatible with the long term objectives of the organization. We have occasionally in the past had the even more wrenching experience of withdrawing from promising areas in which we were already well established because they threatened to lead us too far away from our primary objective of providing ever better communication service. However, such mission definition is necessary

if the organization is to develop the 'enduring themes' and flow of technology which I have described. In the long run, it is the best means of giving the organization continuing purpose and vitality."

Bell Telephone Laboratories

Organizational Structure - 1960



THE DISCOVERY OF MATERIALS FOR THE CONSTRUCTION OF SUPERCONDUCTING HIGH MAGNETIC FIELD SOLENOIDS

CASE ANALYSIS

This case has been analyzed by two complementary methods.

First, the research-engineering interactions are identified and assigned to the various stages described in the report summary. A factor analysis is also included.

Second, a chart has been prepared which provides a kind of chronology of the research-engineering interactions.

DESCRIPTION OF IDENTIFIED RESEARCH-ENGINEERING INTERACTIONS

a) Discovery of superconductivity. This was a serendipitous event. The discovery occurred during a fundamental investigation of the properties of metals at very low temperatures. The work was conceived and directed by a physics professor in a university laboratory in Europe before World War I.

b) Proposal of superconducting magnets. This idea apparently occurred almost immediately to the discoverer of superconductivity and the suggestion appears in his early notebooks.

c) Use of a superconducting magnet in a microwave maser and the construction of a niobium air core magnet which produced a field of greater than 4,000 oersteds. This work was performed by a Ph.D. physicist in a research laboratory completely funded by the federal government and managed by a private university. The investigator was working essentially independently and his principal original objective was to produce a microwave maser suitable for radio astronomy.

d) Discovery of the high critical field of Nb_3Sn, NbZr alloys and other materials. The discovery was made by a Ph.D. physical chemist and his colleagues working in an industrial laboratory supported entirely by private funds. The work was triggered by a technical

visit with the laboratory in REI-c and was carried out in an atmosphere of strong interaction with fundamental investigations of superconductivity, materials scientists and engineers, and communications scientists and engineers who were interested in the application of high field magnets.

Invention of a technique for producing Nb_3Sn magnets. This work followed immediately upon the discovery of the high field properties of Nb_3Sn. The inventors of the techniques were key figures in the original discovery of the physical properties of Nb_3Sn. (This refers to only the first of several techniques which now exist for making Nb_3Sn magnets. Others are referred to in the case but have not been searched and documented in this study.)

Invention of a superconductor shielded magnet. This device structure was invented by an applied physicist working in the same industrial laboratory where the original discovery of high field superconductivity was made. He was designing magnet structures for microwave masers and a portion of the work was stimulated by military needs. The inventor was also physically located near some of the participants in the fundamental studies of superconductivity and participating with them in the design of apparatus for fundamental research.

Discovery and explanation of training and flux creep effects. Important aspects of the studies of training effects were carried out in two

private university laboratories and supported by federal funds. They resulted from fundamental interests in high field superconductivity and also as a result of efforts to design magnets. The flux creep studies were performed in the same industrial laboratory as REI-d and supported entirely by private funds. Here also the studies were a result of both a fundamental investigation and the desire to design and build magnets for experimental use.

h) Use of superconducting magnets in Telstar and military systems. The specific events described here represent only a few of the possible examples of further development, manufacture and commercial use of superconducting magnets. These specific examples were carried out in the laboratories of REI-d and involved developments in both geographically proximate and distant groups and were a direct follow on to REI-f. They involved both private (Telstar) and federal (military) funding. They included strong interaction with the fundamental physics and materials studies and required additional invention for their successful completion.

ASSIGNMENT OF RESEARCH-ENGINEERING INTERACTIONS TO STAGES

STAGE	REI
0	a, g
I	b, d
II	e
III	f, c
IV, V, VI	h

Stages were defined by the Committee for purposes of this study, ollows:

STAGES

Definition

Scientific finding (knowledge)

Recognition of new material (process) possibility

Creation of useful material (process) form

Feasibility of using the material (process) in hardware

Possibility of using the hardware containing the material in a system

Production of the system (product)

Operation of the system (product)

LIST OF FACTORS CONSIDERED IN ANALYSIS

1. High educational level (advanced degree) of principal investigator.
2. Importance of management.
3. Importance of Government-sponsored research.
4. Importance of recognized need.
5. Requirement of flexibility to change direction during work and local control of funds (easily available resources).
6. Industrial laboratory involved.
7. Basic research in the laboratory (or institution or organization).
8. Communications across organizations was important.
9. Technical problem was the principal obstacle.
10. Importance of a "champion."
11. Freedom for individuals.
12. Broad spectrum of types of laboratories.
13. Geographic proximity.
14. Prior experience with innovation.
15. Organizational structure (barriers and bonds).

FACTOR ANALYSIS OF RESEARCH-ENGINEERING INTERACTIONS

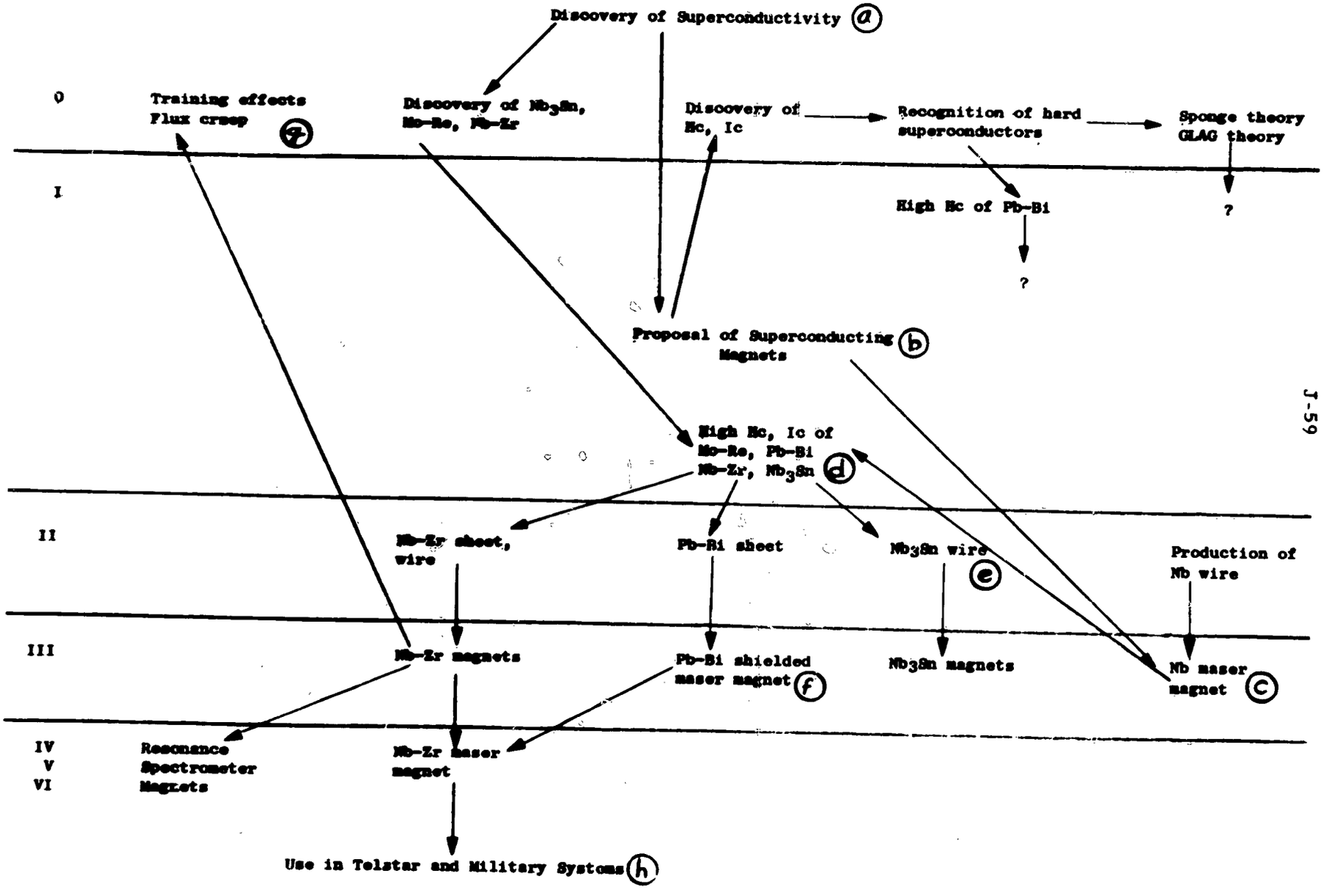
actor	REI								Frequency
	a	b	c	d	e	f	g	h	
1	x	x	x	x	x		x		6/8
2			x	x	x	x	x	x	6/8
3			x			x	x	x	4/8
4		x	x	x	x	x	x	x	7/8
5			x	x	x	x	x	x	6/8
6				x	x	x	x	x	5/8
7	x	x	x	x	x	x	x	x	8/8
8			x	x	x	x	x	x	6/8
9			x	x	x	x	x	x	6/8
0									0/8
1	x	x	x	x	x	x	x	x	8/8
2			x	x	x	x	x	x	6/8
3	x	x		x	x	x	x		6/8
4	x	x	x	x	x	x	x	x	8/8
5			x	x	x	x	x	x	6/8

CHART OF RELATIVE CHRONOLOGY OF RESEARCH-ENGINEERING INTERACTIONS

Events attendant to the case are placed on this chart with arrows between them. The arrows indicate a kind of chronology which is not exact but which provides some logical sequence through the events. For example, in some cases, two separate arrows will emanate from a given event indicating two chains of activity which may or may not have started simultaneously.

When an arrow crosses between levels on the chart, a research-engineering interaction may have taken place. The eight specific research-engineering interactions which are especially identified are designated by the letters a through h.

In some cases, an arrow terminates in a question mark. This indicates that a significant chain of events might have begun here, but did not.


Discovery of Superconductivity (a)
0
Training effects
Flux creep (g)
Discovery of Nb3Sn, Mo-Re, Pb-Zr
Discovery of Hc, Ic
Recognition of hard superconductors
Sponge theory
GLAG theory
I
High Hc of Pb-Bi
?
?
Proposal of Superconducting Magnets (b)
High Hc, Ic of Mo-Re, Pb-Bi Nb-Zr, Nb3Sn (d)
II
Nb-Zr sheet, wire
Pb-Bi sheet
Nb3Sn wire (e)
Production of Nb wire
III
Nb-Zr magnets
Pb-Bi shielded maser magnet (f)
Nb3Sn magnets
Nb maser magnet (c)
IV
V
VI
Resonance Spectrometer Magnets
Nb-Zr maser magnet
Use in Telstar and Military Systems (h)

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R&D

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Qualified requesters may obtain copies of this report from the Defense Documentation Center.

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None	Assistant Director (Materials), ODDR&E, The Pentagon, Washington, D. C.

13. ABSTRACT

Ten separate material developments were investigated and case histories are presented. A technique of analysis was developed and applied to the case histories to identify common elements and patterns which might be used as guides by the Department of Defense to stimulate research-engineering interactions in the solution of materials problems. The analysis identified several elements which were prominent in many of the cases. Among these are: (1) Flexibility for the individual investigators to make major changes in direction and goals was frequently required; (2) Close and frequent communications between organizationally independent groups were often essential; (3) Key individuals played essential roles in bridging the geographical, organizational, and functional barriers between groups; (4) The recognition of an important need was most frequently the principal factor in stimulating research-engineering interactions; and (5) Often technical approaches were available and lay dormant for some time before their pertinence to a specific need was recognized.

It is recommended that these findings be considered in future materials research and engineering efforts of the Department of Defense. In addition, the value of the case history approach as an educational tool is emphasized and suggested for further consideration. A series of questions is developed to aid further self study by research and development organizations. Finally, the need for more effective tools of case history analysis is identified.

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Unclassified

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Management of research and development						
Coupling research and development						
Materials research and technology						
Technological innovation						
Case histories in technology						
Motivation						
Communications between groups						
Bridging barriers to innovation						

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