

Dental Materials Research

Proceedings of the 50th Anniversary Symposium
Held at the National Bureau of Standards
Gaithersburg, Md., October 6–8, 1969,
in Recognition of Fifty Years of Dental Research at NBS

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Abstract

A Symposium on Dental Materials Research was held at the National Bureau of Standards, October 6-8, 1969, on the occasion of the fiftieth anniversary of the dental research program at NBS. The Symposium brought together outstanding researchers in the dental materials field from throughout the world for a comprehensive examination of the present state of research and a look at future dental needs and expectations. The program covered the broad dental materials field—from an examination of the oral environment to a consideration of future needs from the viewpoints of dental practice, dental education, dental industry, and basic science. Invited papers covered metals research, new developments in nonmetallic restorative materials, dynamic methods for determining the mechanical properties of dental materials, and problems of evaluating dental materials and making such evaluations useful to clinical dentistry through the development of specifications.

Key words: Adhesives; composite restorative materials; dental materials research; dental restorative materials; future dental needs; laboratory testing and clinical research; mechanical properties; metals research; specifications.

Foreword

The Dental Research Section, a unit within the Polymers Division of the Institute for Materials Research, National Bureau of Standards, renders a unique assistance to efforts to improve dental health. The research program is a cooperative effort both in personnel and funding involving several agencies of government and a major professional health association. The specific aim is to bring physical science expertise and instrumentation to bear on those aspects of dental research which may yield only to this approach.

The current collaborative dental research program at NBS is conducted in cooperation with the Council on Dental Research of the American Dental Association; the National Institute for Dental Research; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, U.S.A.F.; and the Veterans Administration.

Dental research was begun at the National Bureau of Standards in 1919 in response to a request from the War Department for assistance in evaluating dental materials purchased by the Government. From 1919–1922 the research staff consisted of Dr. Wilmer Souder, in whose honor the present symposium has been dedicated. From 1922–1928, the Weinstein Research Laboratory supported Research Associates as assistants to Dr. Souder. In 1928, the American Dental Association established its Research Associate Program and this continuing collaboration has encouraged close rapport among this physical science laboratory, dental manufacturers, and practicing dentists.

The achievements of the Dental Research Section during the past 50 years have transformed the practice of dentistry in many ways. Early accomplishments included the development of precision casting techniques for gold alloys. Later innovations included a high-speed contra-angle turbine drill, a panoramic dental x-ray machine, spherical particle amalgam alloy, and composite restorative materials. Current efforts are directed toward a better understanding of the fundamental properties of tooth structure, the physical and chemical mechanisms relating to initiation and development of caries, and toward the development of new and improved materials and instrumentation.

It is particularly important, in paying tribute to a half century of dental research, that opportunity be provided in this symposium to see not only where we have been but where we need to go. The response of dental materials experts from around the world in meeting the challenge of delineating the research needs for the future is especially exhilarating.

J. D. Hoffman, Director
Institute for Materials Research
National Bureau of Standards

Preface

This book is the formal report of the proceedings of the 50th Anniversary Symposium on Dental Materials Research sponsored by the National Bureau of Standards and the American Dental Association with the cooperation of Johnson and Johnson, Kerr Manufacturing Company, and Surgident, Ltd. The Symposium brought together many outstanding researchers for a comprehensive examination of the present state of research and a look at future dental needs and expectations.

The papers included herein encompass the broad dental materials field—from an examination of the oral environment to a consideration of future needs from the viewpoint of dental practice, dental education, dental industry, and basic science. Invited papers cover metals research, new developments in nonmetallic restorative materials, dynamic methods for determining the mechanical properties of dental materials, and problems of evaluating dental materials and making such evaluations useful to clinical dentistry through the development of specifications.

The symposium offered an opportunity to pay tribute to the founder and for many years guiding inspiration of the dental research program at NBS, Dr. Wilmer Souder. It also recognized the outstanding leadership of Dr. Irl C. Schoonover in the development of a unique organization for dental research which has directly involved a government laboratory, the National Bureau of Standards, and a private professional society, the American Dental Association, in a cooperative program supported and participated in by the National Institute of Dental Research, the Armed Services and the Veterans Administration Dental Corps.

Members of the Symposium Committee wish to express their appreciation to the authors and to all participants who contributed toward making the symposium a truly memorable event. Thanks are also given to Mrs. Marion Kumpula of the ADA Research Unit at NBS and to Mrs. Ruth Davenport for their attention to the many details involved prior, during, and immediately after the symposium. The NBS Office of Technical Information and Publications under the direction of W. R. Tilley, with special help from Robert T. Cook, gave invaluable assistance in many phases of the effort. Particularly appreciated is the assistance of Johnson and Johnson, Kerr Manufacturing Company, and Surgident Ltd. in contributing to the funding of the Symposium.

Committee for the 50th Anniversary
Symposium on Dental Materials Research

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Identification of some commercial materials and equipment has been necessary in this book. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

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I. Introductory Session

Dental Research at the National Bureau of Standards—Reminiscences

Wilmer Souder*

Chief, Dental Research Section, NBS, 1919-1945

In 1918 dental amalgams had a high rate of failure and few data on their physical properties were available. Using the interferometer for determination of the dimensional changes of amalgam and scientific test methods for other properties, NBS began to obtain information on the physical properties of dental materials. The specification for dental amalgam developed in the early days with numerical limits for physical and clinical properties and details of test methods has served as a model for specifications for dental materials for over 40 years. Although the early results were challenged and the program opposed by some, the dental profession soon recognized the value of the work and requested its expansion. In time schools, dental associations, and manufacturers joined in commending the research program.

Key words: Amalgam, dental; American Dental Association; dental materials; Dental Research Section, NBS; interferometer, dental; specifications, dental.

1. Reminiscences

Thank you, Mr. Chairman, for the kind invitation to attend and the liberty to address this symposium. More than ten years ago the Bureau said "Good Bye and Best Wishes". No attempt has been made to have succeeding leaders change their programs. I had my opportunity and am pleased with the results. The future opportunities and prospects are bright. Your request for reminiscences is dangerous. It means looking back. One of our former directors, Dr. Lyman J. Briggs, had a motto: "Never look back; something might be gaining on you". Any attempt to brag on the achievements would flavor of conceit. To criticize would be dangerous in the presence of this audience. So what is left? There are some personal errors, then some confrontations and a rapprochement of all interested parties. It seems proper to document these, as they were encountered.

No honest comment on the research can be made without an acknowledgement of the aid given by loyal assistants. Among the first of these were, Peters, Coleman, Hidnert, Sweeney, Swanger, Taylor, Isaacs, and Berger; and later Caul, Dickson, Paffenbarger, Lynch, Brauer, Jordon, Schoonover, and Richardson. Others are named in various publications and may be mentioned by those who follow on this program.

2. A Dental Research Considered

A preliminary review of the dental situation in 1918 revealed a high degree of failures in dental restorations made from silver amalgams. Claims and endorsements were available and techniques were numerous and elaborate but not in technical

terms. Tests to substantiate these claims in terms of physical, chemical, and engineering properties (necessary in restoring the needed functioning of a tooth) were not found. The pioneer who first pointed out this defect was Dr. G. V. Black. He had a clear understanding of the needs and methods for establishing the quality of an amalgam. His heroic efforts to create a micrometer sensitive enough to document, with definite accuracy, the length and volume changes in amalgams, and their dependence on chemical compositions and operational practices, were not entirely satisfactory. His micrometer was dependent on levers and gears which introduced friction in pivots plus hysteresis lags. This preliminary search pointed to the necessity of a more sensitive micrometer. The interferometer, having a normal sensitivity of one millionth of an inch, is such an instrument.

3. Precision Data

Mr. C. G. Peters, of the Bureau's optical laboratory, had an interferometer and gladly consented to measure the length changes in amalgam specimens which I condensed. These tests established, in definite terms, the changes and defects which Black had suspected. It is doubted that any dental college, dentist, or manufacturer had an instrument approaching the precision of the interferometer. Peters and I published our findings in the *Physical Review* [1].¹ Our data established a difference of three to one for the thermal expansions of amalgam to dentin; the amalgam having the higher value. This established the necessity for a positive setting expansion of all amalgams to cancel any separation between the amalgam and the tooth

¹ Figures in brackets indicate the literature references at the end of this paper.

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when exposed to cold foods or drinks. Several brands gave setting shrinkages. The dentist is called upon to create a restoration surpassing the perfection of the natural tooth which has failed. Furthermore he must completely exclude germs, acids, and all other hazards; always ready to destroy his restoration. No immediate response came from this publication. I decided to create an interest by dentists, manufacturers, and the public by writing a news item for release by the Bureau containing, among other information, a statement: "The public could better avoid the dentist who drills out a cavity and fills it with a shrinking amalgam". The news item was sent to the Department for approval. The item was returned with a statement (essentially) as follows: "There is no question on the accuracy of the tests; however, it is not considered wise to create a situation such as this would create unless, at the same time, a remedy is offered." So died the attempt to awaken the public.

4. Sparrings

Unfortunately or otherwise, a metallurgist, interested in amalgam alloys, made some disparaging remarks about our budding efforts and pointed out unimportant variations in our results when he made a report on his own tests. These were printed in a metallurgical journal. Peters and I set up a reply criticizing his results which revealed greater variations than any of ours. Also we referred to his great emphasis upon a transformation in amalgams when heated to 80 degrees Centigrade; a condition not compatible with dental health. We were careful to make no reference to our connections with the Bureau and paid for the publication of our reply. We were elated at the neatness of our reply—until a few days after the appearance of the journal. We were asked to come to the office of the Director at our convenience. We were anticipating the approval of Director George K. Burgess, a metallurgist of the first water. He inquired about our work. Then he showed us a copy of the magazine containing our reply and asked what we knew about it. We said we prepared it and paid for its printing and purposely avoided any reference to the Bureau. Then the sky fell in. He chewed us out as they say in the Army. He reminded us we had stooped to put our abilities on a level of the one we had attempted to expose. He said the Bureau does not encourage scraps. It looked like the last day for two career Civil Service employees. Then his attitude changed. He said "You have abilities, you can develop positive approaches. Go back to your laboratories and prove it". From that day we kept within the traces, absorbing most criticisms.

5. Specifications

A request from the Army in 1918 asking for assistance in awarding contracts for dental amalgam alloys gave the Bureau its first opportunity to

give service in this field. About twelve samples were submitted with the request. There were numerous claims for superiority and endorsements printed on the cartons, but not one numerical datum to support the claims. After making tests of setting expansion, compressive strength, and ease of amalgamation, it was possible to rate most of the samples as defective or inferior. The Army was advised which of the remaining alloys should give satisfaction. This experience pointed to a need for a real specification. Accordingly a study was inaugurated and a specification [2] was set up. This specification was modeled on the pattern of the American Medical Association's Pharmacopoeia specifications. It gives numerical limits for physical and chemical tests and refers to instruments and techniques for making the tests. These two are musts for any intelligible test. Otherwise quibblings are sure to erupt. I claim credit for this theft or appropriation of the American Medical Association's pattern. The limiting numbers may be changed as qualities are improved by the manufacturers. This type of specification for various dental materials has survived forty years and is basic for the Certification Plan adopted later by the American Dental Association.

6. Questioned Progress

The service to the Army Dental Corps was the first signal of a serious interest in the Bureau's work in the selection of dental materials. As might be expected, some manufacturers (whose products might not meet a specification) were not enthusiastic about the plan. Deans, prominent lecturers, and dentists whose personal endorsements were ignored in the specifications were in a clouded area. We were disappointed when the Journal of the American Dental Association in 1920 could not find it possible to print our first extensive (32 page) report, "Physical Properties of Dental Materials". However, another agency was quite willing to print the report [3] with a volunteered commending editorial. Later, consideration of the refusal was understandable. With certain members of the Association lukewarm and several manufacturers suspicious of the outcome of the Bureau's work, they can be excused for the decisions to wait for more assurance of the purposes. When convinced of the ability and integrity of the Bureau, the American Dental Association became one of our loyal supporters.

7. Genuine Interest

After the publication of the first extensive report, interest developed rapidly. Correspondence with dentists, schools, and associations requesting lectures and clinics piled up. The Director approved many of these requests. (The Bureau position, relating to such requests assumed that the Bureau official would be reimbursed for travel and

subsistence costs and that no honorarium would be accepted.) Requests for an extension of the program to include a study of dental gold alloys, cements, and accessory materials came to the Bureau. The Bureau felt that after having set up a pattern for research in the field, it should not assume the responsibility and expense for extensions. However, it did ask for advice [4] on the problem. Dr. Louis J. Weinstein, Director of the Weinstein Research Laboratory in New York, expressed a genuine interest in seeing the research continued.

8. The Research Associate Plan

Dr. Weinstein's request was simple and direct: "I want to see data on dental gold alloys and accessories which will stand up when presented before schools and private groups and not be confused by data in present day texts and glaring advertisements." The Bureau Research Associate plan was explained to him whereby qualified scientists may work at the Bureau on problems of public interest. The Bureau directs and supervises the work and publishes the results. The sponsor pays the salary of the associate. Dr. Weinstein accepted the opportunity and supported the program for six years (1922-1928).

9. Organized Opposition

The first comprehensive report [5, 6, 7] on the Weinstein Research Associate's achievements was given at the Dallas meeting of the American Dental Association. It was quite evident at this meeting and in other happenings that a fission between vested interests and the research associates was developing. These interests wanted to crush the research. They appealed to the Secretary of Commerce, insisting that the reports were creating confusion among the dentists and in the schools and requested that the work be stopped. The Bureau was asked for a statement on the claims. The Director explained to the Assistant Secretary that the research was a public operation and all findings were announced promptly. Furthermore, he stated that the program was a health-saving research needed by every citizen of the United States. No cease or desist order was issued. By some means the dentists across the Nation become aware of what was about to happen and were preparing for a fight. Had this developed, with the support of 90,000 dentists across the Nation, it would have made the Bureau's later AD-X2 confrontation look like child's play.

10. American Dental Association

Meanwhile, the American Dental Association had expressed an interest in and a desire to cooperate formally and actively in the program. The details for this cooperation were completed in

1927 and the cooperative program has continued unbroken from 1928 to date. In 1942 Dr. M. D. Huff, Chairman of the Research Commission, expressed the feelings of the American Dental Association in the following words [8]: "It was a fortunate day when Doctors Barber, Brown, and Volland of the Research Commission went to the National Bureau of Standards in 1927 to complete the details of the cooperative research which has become so valuable to the dental profession. . . . Our associates have been wholeheartedly welcomed by the Bureau. . . . The supervision of the work, the assumption of responsibility for the data, and the complete publication of all findings by the Bureau, have given us an authoritative position seldom possible in such fields of research."

11. World War II

During World II the Bureau found it necessary to curtail activity on many programs as it devoted about 90 percent of its work to problems of defense. It was declared a Restricted Area under the supervision of the Departments of War and Navy. The American Dental Association sent a prompt and patriotic request to the Bureau authorizing it to feel free to transfer its dental associates to Bureau military work as needed, salaries to be continued by the Association. Both, Bureau and Association scientists, filled assigned military positions with distinction. Dental research was restored to its full-time activity at the close of the war.

12. Rapprochements

Within 10 years after the previously mentioned oppositions were met, all dissenters had disappeared. The schools, societies, and manufacturers were joining in their commendations of the work. New and better materials and techniques have been discovered. Perhaps the comment of one manufacturer can be used as a summary: "The research and specifications are our only effective protections against competitors trying to exploit inferior materials by glaring advertisements and personal endorsements".

13. An Unfinished Research

One project on the possible "Remineralization of Dentin", started by Schoonover and Souder, was dropped by reason of the more important war needs. The illustrations in the preliminary report [9] show a deposit of some material in the hardness indentations; the length of the indentation mark is shortened after exposure to a fluoride solution. The body's ability to repair a broken bone suggested the possibility of some such attempt to repair injury to dentin, under favorable conditions. Dr. von Buest of the University of Louisville Dental School was the only one to give us encouragement on the idea. Quotes from recent re-

ports on the effects of fluoride are given below: Bierman, M.D. [10] "the (cancerous) bone becomes harder and more durable". Hoffman, NDRI [11] "topical fluoride can reverse the dental caries process and may even heal incipient caries". A research [12] "... into the molecular basis of disease" has been announced. Even a TV puppet declares that fluoride makes a tooth stronger. Perhaps some budding researcher may decide to make an independent evaluation of these reports.

14. Fare Thee Well

With these scattered reminiscences my part in this program must close. These are no feelings of resentment toward anyone. Rewards and gestures of appreciation have been excessive. My response is, Thank You and Best Wishes for the Future.

15. References

- [1] Peters, C. G., and Souder, W. H., Some physical properties of dental materials, *Phys. Rev. NS* **13**, 302 (April 1919).
- [2] Souder, Wilmer, Measurement and application of certain physical properties of dental amalgam. *J. Dental Res.* **7**:173 (June 1927).
- [3] Souder, Wilmer H., and Peters, Chauncey G., An investigation of the physical properties of dental materials. *Dental Cosmos* **62**:305 (March 1920).
- [4] Burgess, George K., Dental research by Department of Commerce. *J. Am. Dental Assoc.* **11**:249 (March 1924).
- [5] Coleman, R. L., Physical properties of dental materials (wrought gold alloys). *J. Am. Dental Assoc.* **12**:520 (May 1925).
- [6] Coleman, R. L., Physical properties of dental materials (III) Progress Report of research on the dental casting process. *Dental Cosmos* **68**:743 (August 1926).
- [7] Coleman, R. L., Physical properties of dental materials (gold alloys and accessory materials) *BS J. Research* **1**, 867 (1928) RP32.
- [8] Souder, Wilmer, and Paffenbarger, George C., Physical Properties of Dental Materials, NBS Circ. 433, 222 pages (1942), Foreword.
- [9] Souder, Wilmer, and Schoonover, Irl C., Experimental remineralization of dentin. *J. Am. Dental Assoc.* **31**:1579 (December 1944).
- [10] *J. Am. Med. Assoc.* **208**:(No 6) 953, May 12, 1969.
- [11] *Am. Dental Assoc. News Letter* **22**:(No 7) March 31, 1969.
- [12] *Physics Today (We Hear That)* June 1969, p. 97.

Dental Research at the National Bureau of Standards—History and Individuals

W. T. Sweeney*

Chief, Dental Research Section, NBS, 1953–1968

Dental research at NBS was initiated in 1919 by Dr. Wilmer Souder with work on dental amalgams. Dr. Souder built the Section on the principle of cooperation between research laboratories, manufacturers and the dental profession. In the 1920's research associates, first from the Weinstein Research Laboratory and later from the American Dental Association were added to the NBS dental research staff. Dr. N. O. Taylor and Dr. George C. Paffenbarger were the first ADA Research Associates. In 1945 while Dr. Irl C. Schoonover was Chief of the Section, the laboratory staff was further enlarged by the addition of Guest Workers from the Armed Services. Among the many important areas of research were precision casting, dental cements, polymers for dentures bases, composite restorative materials, high speed turbine handpieces, panoramic X-ray equipment, studies of natural tooth structure and development of standards and specifications.

Key words: Amalgam, dental; American Dental Association; casting, dental; dental research; Dental Research Section, NBS; guest workers; Paffenbarger, George C.; Schoonover, Irl C.; Souder, Wilmer; specifications, dental.

1. Introduction

The objective of this paper is to give a brief and concise report of the most outstanding events, personnel, and accomplishments of the dental research program at the National Bureau of Standards in order to set the stage for the symposium honoring the 50th Anniversary of the program. Only a few of the many persons and events can be discussed or even mentioned in the limited time allowed.

The name of Dr. Wilmer Souder is the most outstanding of all the scientific staff because he is responsible for setting the character and ideals of the program and was chief of the Section for the first half of its life. The merit of bringing good scientific measurements into the health field as an adjunct to better dental health care for the public was thereby established. He also realized that a cooperative effort was essential between the three groups, dental profession, manufacturers, and general public as represented by the government. While this sounds trite, looking back today, it was not a very popular idea when he first started in 1919, as there were very few who had the long-range vision to see the advantages of such cooperation.

2. Early or Formative Period, 1919–22

This period was the most important as it is the germ from which the Section grew. The original request from the War Department to the National Bureau of Standards for assistance in evaluating

dental products purchased for the Federal services was referred to Dr. Souder for a routine reply. Amalgam was the material of interest. Souder, as a young physicist fresh from his Ph.D. studies at the University of Chicago, naturally looked at the problem scientifically. The more he examined the basis for selection of dental materials, the more he was convinced that the science of measurement could make a contribution to the dental profession and the dental treatment of the public. He, in short, visioned the substitution of quantitative measurements of properties for the art of personal skill and personal recommendations. He had the zeal and forethought to advocate and demonstrate that physical science had a great many things to offer the health professions.

A few people, notably G. V. Black, a dentist, had carried out some very basic investigations but the precision of a physicist was almost unknown to the science of materials used by the dentist. Souder first turned his attention to dental amalgams and in 1919 published his report on the measurement of such properties as dimensional setting changes, strength, and flow. His results and methods are good today even after 50 years and have led to much improvement of alloys and techniques for dental application. He held the theory that the best way to evaluate any material is to measure the properties that are important for its application. He meant to obtain numerical evaluations by measurement and then delineate his procedures so that any competent scientist could repeat and check his results. This was a unique point of view in the field of dental materials. He was told that it was impossible to

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determine the elements in certain alloys, as the analytical methods were too crude. As a matter of fact this was correct, in some cases at least, but he answered this by saying that if we obtained a scientifically trained staff, we could overcome this and he certainly proved it.

Souder, realizing in this early period that a working together of the research laboratories, manufacturers, and profession was required if the public were to receive maximum dental service, tried to interest the dental profession through their national organization to join in a cooperative program. While certain individuals gave moral support to the idea, the organization was not yet willing to put financial support into the research program. When this failed he was fortunate to secure financial assistance from Weinstein Research Laboratories, who provided substantial support from 1922 to 1928.

3. Expansion of the Program Via Research Associates, 1922-28

This period was most productive as it represents the first expansion of the dental work by the addition of research associates to the group. The research associates were directed by NBS and supported by the Weinstein Research Laboratory. The first research associate, R. L. Coleman, an engineer, was selected from the NBS Staff, a member of the Weights and Measures Division. His work on measurements of properties of gold alloys and precision casting techniques is classical in that it set the standard for precision casting, not only in the dental field but later in industry, such as in the casting of blades for turbines. During this period the first dental specification for amalgam alloys was promulgated, based on the original work of Souder; and the properties of accessory materials used in dental casting, such as waxes, investments, and orthodontic wires were studied, and standard measuring techniques were developed so that specifications could be written later.

The chemical analysis of alloys of gold and the platinum group metals by the joint efforts of Raleigh Gilchrist, an NBS chemist, and William Swanger, a research associate, was an example of how the cooperative effort produced worthwhile scientific results. Their reports justify Souder's prediction that well trained chemists could determine accurately the composition of dental alloys. After these reports, it was obvious that secret formulas would be secret only until someone was willing to spend the time and money to do precision chemical analysis. This work created many controversial problems for NBS on the policy of publication of analyses of trade brand alloys or materials. These problems have not yet completely disappeared because it is a moot question as to how far a tax-supported institution should go in publishing trade secrets that individual companies have spent much in developing. In general, the

dental profession argued that it should know exactly what it uses and the manufacturer thought he needed protection because he spent a lot of money to advance his product. The principle has been to use trade names in publications if they are necessary for understanding by the reader. Details of methods of analysis were given in scientific reports so anyone competent could evaluate properties versus composition.

Verbal reports and many articles by the staff of the Section during this period created such a demand by the dental profession for more scientific evaluations that by 1928 the profession was willing to support the research program and give official recognition to it by formal agreement between the American Dental Association and NBS. This arrangement made for a much broader base of operation and the liaison has proven most profitable to all concerned.

4. Cooperative Program With American Dental Association, 1928-45

In April 1928 the cooperative program between the American Dental Association and the National Bureau of Standards was initiated. The first ADA research associate was Dr. N. O. Taylor, a chemist, who was followed in 1929 by Dr. George C. Paffenbarger, the first dentist to work full time in the Section. The period of the late 1920's and 1930's witnessed a great expansion of the research program through the addition of both NBS and ADA personnel. Basic research on the physical and chemical reactions of many materials was undertaken. This period was productive and an improved understanding was obtained of the properties of practically all the materials used in restorative dentistry from amalgam alloys to denture resins. The approach was basically the same for all materials. First a study was made of the properties of the available materials and how they were affected by composition and by techniques used in practice. Typical examples were studies of the effect of heat treatment on gold alloys and how the mechanical properties were changed by cooling rates in the dental laboratory; how the method of mixing cements could drastically change the useful properties of the material; and how exposure to light affected the color stability of pink denture base resins.

Many special methods were developed for measuring properties of these different materials. The fact that dentistry uses small specimens in comparison to those commonly employed in industry makes it necessary to use unique test methods. Special tests were developed to more closely simulate dental use. The fact that the oral cavity has a varied atmosphere with a variety of temperatures and humidity, makes it necessary that materials be evaluated under conditions which are found in clinical use. Biological requirements put many restrictions on otherwise suitable materials.

The specification program was a major development as it made the results of research useful to the general dentist and the public. The history of the research program during this period followed a consistent pattern of sufficient research on a type of material to understand the basic reactions and properties of dental significance followed by a survey of the existing materials to ascertain what could be reasonably supplied and to determine the range of properties of the satisfactory materials. A specification was then written using the information obtained to place numerical limits on the properties thought to be important. This was reviewed by a Specification Committee consisting of representatives from the profession, the manufacturers, and the government (representing the public). Following the recommendation of this Committee the specification was adopted as an official specification of the American Dental Association. Producers were asked to voluntarily guarantee their products to comply by signing a formal document of agreement. Specimens were purchased on the open market and tested for compliance at NBS by the ADA research associates. Materials which complied were listed in the ADA journal.

Specifications developed for the Federal Government and advice provided in writing purchase descriptions are among the many benefits of the Section's program to the government.

The series of reports on dental casting and accessory materials by Taylor, Paffenbarger, and Sweeney made it routinely possible to make clinically acceptable castings. This is in contrast to an early investigation where only 2 of 25 leading dentists were able to make an inlay casting that would fit even reasonably well a standard die furnished them by NBS.

The very excellent work on analytical methods for dental materials by Caul and Schoonover added new and precise information to the scientific literature on such a wide variety of materials as chrome-cobalt alloy, mercury-containing alloys, resins, denture rubber, impression materials, etc. and made it possible for manufacturers to improve and better control their production. These methods are used also to define composition limits of elements in many modern specifications such as those for amalgam alloy, and gold alloys.

5. Expansion of the Research Program to Include Guest Workers From Federal Dental Services and Foreign Countries, 1945-69

The period immediately following the end of World War II saw a major expansion in the program. As a result of the large scale procurement and utilization of dental materials by the Armed Services, persons directly knowledgeable in dental materials research and clinical practice had first hand experiences which emphasized the great need

for more technical information. This made it possible for a very valuable liaison to be initiated.

Schoonover, with the help of Fischer (USAF) and Paffenbarger (USN), cooperated to set up working arrangements with the Federal dental services that added great strength to the Section by increasing both personnel and funds. This made it possible for NBS to equip a clinical unit and correlate many laboratory findings with clinical practices. These arrangements also made it possible for personnel from the Federal dental services to work in the NBS Dental Research Section as Guest Workers for periods of one to several years. The guest workers included not only dentists with much clinical experience but also scientifically trained enlisted personnel (chemists, physicists, engineers, etc.). In addition to the research accomplished, this program resulted in providing the services a number of dental officers trained in materials research. Also to the benefit of NBS, several of the enlisted guest workers remained after their tours of duty in service to become permanent members of the NBS staff.

It has been the policy to draw no sharp distinction between NBS staff members, ADA research associates and guest workers in the operation of the Section. A spirit of cooperation has prevailed with the result that many are the reports co-authored by representatives of each of the three groups. Guest workers have been encouraged to take advanced study and frequently the research carried out in connection with such studies involved collaboration with a Bureau senior scientist.

This period was characterized by many sharp contrasts of opinions on the relative amount of effort that should be put on basic in contrast to applied research. It is my strong conviction that in an area such as dental materials and clinical dentistry the most return will be obtained by conducting, as we have at NBS, the two side by side. Each is an asset and a source of strength to the other.

In 1950 a very thorough review and bibliography was published by Schoonover and Souder¹ to which the reader is referred for many details about the Section's work up to that time.

6. Summary—Résumé of History and Individuals

One cannot help but be impressed by reviewing, such as I have, the programs since my first contact on August 3, 1922. At that time the Section consisted of three scientists, Dr. Souder, Dr. Hidnert, and Mr. Coleman. This is in contrast with today's staff of thirty-five. About 175 individuals have been associated with the Section during the past 50 years.

Space to even mention all the major projects is not available but items that come to my mind as being specially noteworthy will be recorded with

¹ NBS Circ. 497, 14 (1950).

the individuals connected with them. In doing this it is realized that others may have different ideas but it is certain that these items have been an influence on dental practice.

1. The development of standards for dental materials based on measurements of properties of dental significance. This is probably the most used and productive effort of the Section. It covered many types of materials, in fact, most of the materials widely used in dentistry. The adoption of specifications and the publication of a list of certified products by trade names added to the practical usefulness of the program. The combination of professional approval and the scientific integrity of NBS combined to make a most reliable buyers' guide for dentistry. Also, the specification program served the manufacturers well, as it made available a standard to compare the quality of products without any reference to selling price. The success of this program has spread to many countries of the world and standards developed here are used as models for others.

A survey a few years ago showed that only 0.1 percent of the items on the published certified lists did not in fact meet all the requirements. This is proof that the production control by American manufacturers is very good. These results are based on tests of materials bought in the open market.

2. One item which is not usually emphasized when discussing the Dental Research Section is the effect the training of research personnel has had on teaching of dental materials in the schools and, in fact, on many techniques taught in restorative dentistry. The Federal dental services have sent many of their best officers to the Section for training and many have received advanced degrees using the research training in the Section for credit. The cooperative program with Georgetown University has resulted in 16 master's degrees and two doctor's degrees. Eleven foreign guest workers, for the most part representing dental schools, have been trained and returned to teaching and research.

3. The publication of scientific data and the explanation of the physical-chemical reactions of materials, for example, the setting mechanism of cements, the oral environmental effects on surfaces, and the effects of particle shapes of alloys used for amalgam have led to many material developments and to superior techniques for using materials. The explanation of the cause of delayed expansion of zinc-containing alloys resulted in the elimination of the long used, undesirable, palming technique for mixing.

4. In addition to publication, a much used method of communication was the production of motion pictures on the properties and techniques for using many materials such as amalgam, cements, resins, gold alloys, etc. These pictures are in constant use in schools for explaining the basic

properties of materials and the effect handling has on the clinical results.

5. The research reports and communications have been very productive in introducing new materials and equipment ideas in the fields of both clinical dentistry and dental research. The early work of Souder produced the dental interferometer which has been adopted as standard around the world for measuring the setting changes in amalgam. The NBS standard MOD steel die is probably the widest used device for evaluating precision casting. This was the result of the precision casting work of Coleman. The fused-quartz tube method of measuring the thermal expansion of solids, first developed by Hidnert and Sweeney in 1928, probably has been used more than any other equipment for expansion measurement of solids and especially for dental investments.

The panoramic x-ray equipment now in universal use in many clinics, was perfected by Hudson, Kumpula, and Dickson and is now commercially available with continuing expanding uses in dentistry for recording the condition of teeth and oral structures. This item has resulted in great savings to the Federal dental services, more than enough to repay the total cost of the whole Research Section's expenditure of public funds.

The turbine contra-angle high-speed handpiece developed by Nelsen and Kumpula is probably the most important advancement in dental equipment in this century. It has inspired manufacturers to use the principle to develop very sophisticated clinical turbines and has revolutionized the practice of operative dentistry. It not only makes the work of cavity preparation and tooth reduction faster and easier for the dentist, but more important it is much more comfortable to the patient, so much so that no modern dentist today can operate without high-speed handpieces. The number of these instruments in use, both in this country and foreign countries, is estimated to be in the hundreds of thousands.

The many instruments modified, or new, developed for use in specification tests are too numerous to mention, but the method developed by Paffenbarger for testing standard consistency of cements made it possible to compare on an equal basis the properties of different brands of both zinc phosphate and silicate cements. The use by Sweeney of cross index marks or pin inserts on dentures as reference points for measurement of microscopic dimensional changes, served to evaluate the accuracy and stability of a wide variety of denture base materials from vulcanite to methyl methacrylate resins under clinical conditions. The technique has been used to study the effect of curing and repairing processes on stability or warpage of dentures in service.

The early discovery of cristobalite for use as an investment material by Paffenbarger and Sweeney was rewarding even though the patent was finally

awarded to previous investigators using an entirely different source and method of preparation.

Schoonover developed methods for determining the number average molecular weight of acrylic resin which helped explain many problems in curing and construction of dentures. This was the first report issued from NBS on effect of molecular weight distribution on properties of a polymer.² The relationship between properties and molecular weight has been given extensive attention by research personnel of industry and government since then, as it showed that chain length is as important as elemental analysis in the area of polymeric materials.

The development of spherical-particle alloy for amalgam by D. F. Taylor brought a new and promising type of alloy into general use. The control of properties by suitable size distribution and the low packing pressures required have made this one of the most significant innovations in amalgam research. Indications are that it may be the most popular form of amalgam alloy in the future. The explanation of the setting mechanism of zinc oxide and eugenol cements by Copeland and Brauer and the development of a new cement, o-ethoxybenzoic acid (EBA), by Brauer are additional landmarks of the program. The consistent progress made by Bowen in the field of composite filled resins has resulted in the marketing of several products that are bringing a new era in the quality of esthetic tooth restorations for anterior teeth. The advancement toward adhesive materials is also very promising and points the way to a major breakthrough in tooth restoration.

The development of methods for determining the structure of natural teeth by Brown and Moreno and physical properties of enamel and dentin by Stanford have advanced the understand-

ing of the physical-chemical reactions that can take place in the tooth. This will be of assistance in obtaining a better rationale for the cause of caries.

The following special items and the names of those most responsible for them are given—not in any order of relative importance:

- (a) Physical methods of evaluating dental amalgam—Souder, Sweeney, Caul, Burns, Dickson, and Oglesby
- (b) Precision casting—Coleman
- (c) Chemical analysis of gold alloys—Gilchrist and Swanger
- (d) Analysis of dental cements—Isaacs, Schoonover, Brauer, and Copeland
- (e) Tests and evaluation of cements—Paffenbarger
- (f) Packaging of cements for military uses—Fischer and Burns
- (g) Chemistry of resin polymers—Schoonover, Brauer and Caul
- (h) Physical properties, methods of resin evaluation—Sweeney
- (i) Gallium alloys as dental filling materials—Waterstrat and D. L. Smith
- (j) Turbine contra-angle high-speed hand-piece—Nelsen and Kumpula
- (k) Panoramic x-ray equipment—Hudson, Kumpula and Dickson
- (l) Standards and specifications for dental materials—Souder, Taylor, Sweeney, Paffenbarger, Beall, Caul, Burns, Brauer, Dickson and others
- (m) Promotion of national and international standards for dental materials—Paffenbarger, Sweeney and Dickson
- (n) Development of EBA cements—Brauer
- (o) Composite filling material—Bowen

² J. Amer. Dental Assoc. 25, 1487 (1938).

II. Future Needs for Research in Dental Materials

The Need for Basic Research in Dental Materials

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The field of dental materials has benefited from basic studies of the silver-tin alloy system, of cobalt alloy systems, of polymers, and of many other areas. Future basic studies of the surface phenomena of wetting, spreading of liquid films, adhesion, diffusion into dental tissues, boundary interactions, and principles of viscoelasticity related to dental materials offer productive opportunities. Basic research is essential if advances are to be made in the improvement, modification, refinement, and development of servicable materials for the practice of dentistry. It is anticipated that such studies will increase in importance in the next quarter century and that basic scientists in many fields will be contributing to the improvement of dental service.

Key words: Basic research related to dental materials; dental materials; interdisciplinary research; training of dental researchers.

1. Introduction

Those who have followed the growth and development of dental materials throughout the world during the past century readily recognize the significant changes that have occurred in the research activities in this field. There is no evidence to indicate that further changes will not continue to occur in the years ahead. Certainly the field is not dormant nor static at the present time.

The changes that have resulted since the last part of the 19th century represent the efforts of many persons who have conducted research studies, made laboratory and clinical tests and evaluations, and altered or modified materials, techniques, and devices in order to serve the needs of the dental profession to render more and improved service to the patient. This has required all forms of research studies, as noted by this symposium, including basic studies; practical, applied, or clinical testing; and developmental projects. It has required the effort, knowledge, and experience of investigators throughout the world, located in private or government supported institutes and laboratories, universities, and dental schools, manufacturer's laboratories, as well as dentists in private or group practice. Not only have multiple institutions contributed to the progress that has been made, but also the training and background of the individual investigators has been of a multidiscipline character.

At this time in history, when the multidiscipline approach to research is being recognized and encouraged, those in the dental materials field can take pride in the fact that for half a century interdisciplinary studies have been common practice. This practice has increased in recent years. The basic scientist working with the clinician; the bio-

logically trained scientist working with the physical science investigator; or the engineer, physicist, or chemist working to solve a problem of dental practice, all have made contributions to this field. The future holds even greater promise for interdisciplinary studies. As the subjects of bioengineering, biomaterials, and biomechanics are extended into medical science, it is satisfying to know that a similar relationship has existed and promises to continue in the science of dentistry.

2. Types of Research

Perhaps no one should claim that one type of research is more important or desirable than another. It can be recognized to advantage, however, that different forms of research exist, and through the combined efforts a contribution to society is made. Some forms of research appeal to certain investigators more than others, resulting in a greater degree of concentration on one type of study than on another.

Basic research in the physical sciences represents those studies that explore the fundamental nature of a compound, a reaction, a physical state, or condition, a mathematical relationship to a physical phenomenon, and describe the characteristics observed. Such studies explore the fundamental physical forces and processes of nature. Basic science studies, however, are not limited to physical phenomena. Studies of a basic or fundamental nature are common in the biological, social, behavioral, political, and economic fields of endeavor. Perhaps all basic research studies attempt to explore the fundamental nature of the subject, in contrast to the practical, applied studies which translate into service the fundamental concepts.

Generally it is recognized that basic or fundamental research studies involve investigations of a new, different, and exploratory nature. The scientific judgement of the investigator suggests that more knowledge in a particular area will contribute to the welfare of mankind and aid in the solution of present or future problems. The history of scientific advances is filled with examples of such basic and fundamental studies. One needs only to recall the advances resulting from basic studies in the field of relativity, x-ray and other forms of radiation, atomic structure, and many other basic investigations to recognize that research in the fundamentals of science, is important as a foundation for scientific endeavor. Productive basic research studies provide results that can open whole new approaches and solutions to practical problems. From the results of basic research studies, new concepts are established which advance the technical and scientific skills in many related fields.

Studies in areas of basic research are confronted, however, with numerous problems of varying magnitude. Frequently such studies are time consuming, require the service of specialized and highly skilled personnel, or cannot be assured of success and practical application, in advance of the project completion. The practical applications and potential significance of such basic studies frequently are the subject of debate and speculation among investigators having more practical interests. Under these conditions, basic research studies frequently encounter difficulties in securing a source of support funds, other than benevolent foundations or some government agencies. Even from these sources the basis of justification is critical and requires well documented and carefully planned statements of experimental design and procedure. This is proper, however, and only suggests that basic research studies are involved and complex, requiring the utmost in well coordinated efforts and skillful management for success.

The ultimate gratification comes usually to the investigator who is successful in his endeavors, and ultimately sees his results applied to the solution of practical problems. Perhaps there are relatively few investigators who delight in conducting basic research studies only for the sake of collecting such data. Rather, it is their hope to open a whole new solution to practical problems, when such studies are undertaken by other investigators. It is important to recognize, therefore, that normally following a successful basic research investigation there will emerge numerous practical research studies of varying magnitude and nature. Often the dividing line is a thin one between basic, fundamental research studies and practical research investigations.

3. Basic Research in Dental Materials

The field of dental materials has been fortunate to have benefited from a variety of basic studies

on various materials in the past. The National Bureau of Standards has contributed much to these basic studies. Frequently these have resulted in eventual applications to the solution of practical dental problems. Only a few need be listed to illustrate the benefits from basic research studies in dental materials.

One that is recognized by all who are associated with restorative materials and the practice of dentistry, is the metallurgical study of the silver-tin alloy system and the reaction with mercury to produce dental amalgam. Many investigators have contributed to the understanding of these alloys, and the studies continue. The results have led to a gradual improvement in the quality of dental amalgam during the past 75 years, with better restorations for the patient.

Another example of productive basic metallurgical studies involves cobalt base alloys for use in removable cast partial restorations. From these studies, practical prosthesis are a reality. Closely associated with this development, and of equal importance to the success of the small cast restoration, have been the basic studies of the precision casting process. Dentistry has been accepted as a leader in this specialized interest of precision casting, with numerous basic studies reported, as well as practical applications described.

The development of the plastics industry within the past 50 years has stimulated many basic studies into the nature of plastics and the potential application in restoring lost tooth tissue. Another group of materials that have special dental applications, made possible from basic chemical research studies, are the several types of elastic impression materials presently in use in dental practice. These hydrocolloid and synthetic rubber compounds are examples of basic chemical studies, leading to practical applications which have resulted in altered methods and improved dental practice.

Anyone who is familiar with the investigations that have been conducted at the National Bureau of Standards, recognizes the contributions that have been made to world dentistry through the development of physical test methods for various dental materials, and the establishment of standard test procedures and specification methods. To a considerable degree, basic research studies were involved in the development of this program. Subsequent assistance from the American Dental Association, the Federation Dentaire Internationale, and now the United States of America Standards Institute, has carried forward the initial basic undertaking, and developed practical means of evaluation. Basic studies related to this program undoubtedly will continue.

The list might be extended to include devices like hand pieces and x-ray machines, and the discussion expanded with documentation, but that is unnecessary to indicate that basic research studies in dental materials have been productive in the past, and have led to practical and applied studies

with benefits to dental practice. To extend this discussion would tread on the subjects of other speakers in this program.

4. Current Basic Investigations With Promise

It might be well to list, without elaboration however, some current studies of a fundamental nature which promise significant benefits to dentistry in the years ahead. Some have been conducted here at the National Bureau of Standards and others are being investigated elsewhere. Several will be described in detail later in this program, so it is sufficient to take note here only that unknown benefits to dentistry in the years ahead can be anticipated from these efforts.

One valuable area of study is that of composite materials, particularly in the area of filled plastics. This subject is being explored by many investigators. Another is the study of the basic nature of the zinc oxide-eugenol compounds and the effects of chemical modifiers on the characteristic properties of these materials. Practical results are beginning to emerge from each of these long and difficult basic studies.

Studies on stress analysis in dental restorations and supporting structures, by photoelastic and other methods of analysis have involved numerous basic problems. In like manner the studies that are being conducted on the friction and wear of materials used in the mouth require basic evaluations that are new to dentistry.

In the same way studies on tissue reaction and compatibility with restorative materials include many basic concepts in biological and physical sciences. The studies being conducted on clinical evaluation and correlation with laboratory observations, presently are basic in nature but can produce long range practical benefits for the dental profession.

5. Future Basic Investigations

As one surveys the horizon of the years ahead, one sees the opportunity for basic research investigations that can lead to productive practical problems extending into most areas of dental materials scientific endeavor. It can be anticipated that the fundamentals of the surface phenomena of

wetting, spreading of liquid films, and adhesion to tooth tissue will be further studied basically and become better understood. Further studies with the electron microscope and electron probe should provide a basic understanding of diffusion into dental tissues, and the interaction occurring within the material or at the boundary surface. Future studies will show the true potential benefit of the laser beam and the related process of holography. Further studies in the principles of viscoelasticity related to dental restorations, involving fundamental mathematical evaluations and interpretations to dental problems will continue.

This list might be extended into many other areas of basic studies and investigation. Even though other persons might choose other examples of basic studies from the past or into the future of dental materials research, these suggested studies indicate the importance of basic research to the field of dental materials.

Since basic studies related to many disciplines are involved in so much of the current dental materials research and investigation, the education, training, and interests of the investigator have been enlarged significantly in recent years. The training of the dentist and the dental teacher likewise has been influenced by this trend in materials research. A broad spectrum of physical science training presently is necessary for the application of these principles to dentistry, whereas in the past the biological sciences were predominant in the training of dental investigators and practitioners. It seems probable that this trend in training will continue in the years ahead.

Most research investigators have a definite concept of what constitutes basic research, even though it may differ to some degree from one person to another. It is recognized by all, however, that basic research is essential and fundamental if advances are to be made in the improvement, modification, refinement, and development of serviceable materials for the practice of dentistry. Basic research studies in dental materials have come to be recognized as being essential to the further advances in this area of dental science. It is anticipated that such studies will increase in importance in the next quarter century. So long as the dental profession is concerned with improved dental service for the patient, it seems certain that the basic scientist in all fields will be offering his assistance to make that service a reality.

Research Needed by the Federal Dental Services*

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The dental research laboratories of the Federal Government function within the Departments of Commerce; Health, Education and Welfare; and Defense. These laboratories and the multidisciplinary scientists therein along with those of the Veterans Administration provide a much needed national resource. The Federal Dental Services have problems in common with each other and with the profession at large, in addition to having problems unique to themselves. Each Federal Dental Service needs a scientific staff capability to solve its own immediate problems or to contract for the solutions.

Key words: Capabilities and needs of Federal Dental Services; dental research laboratories, Federal; dental staff; Federal Dental Services.

1. Introduction

Half a century ago it was an innovation at the National Bureau of Standards to apply the scientific approach and the science of metrology to solve a specific dental problem generated by the Federal Services—how to assure the procurement, storage, and delivery of a dependably usable material to a Federal dental clinic.

This 50th Anniversary of the Dental Research Section, National Bureau of Standards, is an excellent time to take a look at dental research progress, dental research resources, and how these resources may be best applied in the future—particularly to problems of the Federal Dental Services.

Since metrology broke the ice with dentistry, scientists of other disciplines have become intrigued with dental problems and have contributed immensely toward the establishment of an organized body of knowledge relating specifically to dentistry. Concurrently, there has been a proliferation of laboratories devoted to dental research and development. As a result, there has been a tremendously significant improvement in the methods, materials, and equipment used in dentistry.

2. Dental Materials Research in the Federal Government

At least three cabinet departments of the Federal government have dental research laboratories—Commerce; Health, Education, and Welfare; and Defense. The Veterans Administration has an extremely active research program with a number of laboratories. These laboratories and the dedicated scientists of many disciplines who staff them are a true national resource that has taken many

years to develop to its present capability. This resource is needed by the nation in its struggle to cope with the ever escalating problem of assuring oral and dental health to a growing population—and to assist the Federal Dental Services in discharging their responsibilities.

To examine dental research requirements of the Federal Dental Services it is necessary to study the functions of the individual service and the environment in which it operates. The Federal Dental Services have problems in common with each other and with the profession at large. In addition, because of special operational conditions, each service and agency has problems and research capabilities which are unique to itself.

The *Department of Health, Education and Welfare* (HEW) is the major federal instrument for dental research support. HEW is concerned with all aspects of the dental and oral health of the entire population. Its *National Institute of Dental Research* (NIDR) conducts broad extramural and intramural research programs primarily of a basic dental research nature that are designed to advance fundamental techniques and to establish a broader base of knowledge for development application. HEW's *Division of Dental Health* has been assigned the task of researching ways and means of increasing the productivity of dental manpower; of upgrading the teaching of dental personnel; of improving the distribution, organization, and financing of dental services; and of developing better preventive, control, and treatment procedures. HEW also maintains a uniformed dental service as a part of the *United States Public Health Service* (USPHS) which participates in clinical investigations related to the overall objectives of the department. The USPHS has a special interest in indigenous ethnic groups along with its concern with the health of the population as a whole.

*The opinions expressed herein are those of the author and do not represent official USAF policy.

The *Veterans Administration* (VA) gives special emphasis to the study of normal aging, chronic and degenerative processes associated with aging, the detection and localization of oral lesions, oral tissue metabolism, and problems dealing with tissue restoration of war incurred wounds or losses caused by surgical treatment for oral cancer. The VA research program is a continuing effort to enhance the ability of this agency to maintain the oral health of debilitated patients. No other agency is so directly concerned with this population group. The VA program has made important contributions to the research community and the profession through its cooperative studies with schools, other government agencies, and related medical areas. In addition, it provides opportunities for performing cooperative studies as the need arises.

The *Department of Commerce* (National Bureau of Standards) (NBS) with its Dental Research Section, which we are saluting at this 50th Anniversary Symposium, occupies a particular niche in the hearts of all those interested in the advancement of the science of dentistry. Begun in 1919 in response to the needs of the uniformed services, its value to the services, and to the profession as a whole, is fully recognized by the leadership of the dental profession. Its research program is currently carried on in cooperation with the Council on Dental Research of the American Dental Association, The National Institute of Dental Research, the Army Institute for Dental Research, the Dental Sciences Division of the Air Force School of Aerospace Medicine, and the Veterans Administration.

The unique capability of NBS for physical research is not duplicated anywhere else in this country. All dental health components having a direct interest in this area contribute to this capability through the activities of the Dental Materials Group, a constituent of the International Association for Dental Research. Representatives of organized dentistry, the Federal Dental Services, and the dental industry unite with an interchange of ideas in this activity because it is one of a kind. Their affiliation with different levels extends also to the Federation Dentaire Internationale and the International Organization for Standardization. All of this adds to the singular effect of NBS on the dental research community.

Another unique feature of the cooperative program is the fact that participating agencies have had the advantage of assigning guest workers to the cooperative program and thus have gained staff members with a knowledge and capability in research disciplines.

In the *Department of Defense* (DOD) context, research is thought of as research and development. The broader connotation encompasses all research, development, test and evaluation (RDT&E) activities sponsored by DOD. DOD research in the dental area is concerned with specific

answers to particular problems of the uniformed services and requires tangible results from funds expended. Therefore, within the DOD, emphasis is on development, test, and evaluation. Common to all the dental services within the DOD—Air Force, Army, Navy—is the problem of how to most efficiently and effectively manage an overwhelming demand to treat oral and dental disease. In this objective, the Federal Dental Services have common cause with all elements of dental research—universities, industry, and other government agencies. However, this demand is made more acute by the requirement that the dental services of DOD must maintain the effectiveness of the man in the field, the integrity of air crews, ship and submarine crews, and the personnel of support elements essential to all three services.

Within DOD, the Air Force, Army, Navy each have problems peculiar to their particular branch. Each service requires a capability for rapid response to requests from the field for effective answers to practical problems that may not have application to the profession as a whole. There is a need for a capability to adapt and design equipment and facilities that meet special requirements of the individual agency; and there is a requirement for a user test capability for the evaluation of equipment, materials, techniques, and management concepts. For example, the Air Force has long been concerned with dental problems associated with altitude, acceleration, and, more recently, man in space. The Navy has had a special interest in problems related to extremely cold weather and extended submarine operations. The Army has concentrated on solutions to the need to treat their large number of patients with traumatic injuries and those needing prostheses as a result.

To meet its requirements, both common and special, each Federal Dental Service needs an informed staff representing a sufficiently broad spectrum of professional, scientific, and technological disciplines. The staff must have a suitable facility in which to work. The staff must maintain an awareness of current knowledge in dental and related sciences. It must assure a close liaison with universities, industrial, and other government laboratories. The research staff of a Federal Dental Service must know who is studying what and which laboratory has the expertise and apparatus to address particular problems. The staff must perform investigative studies pertinent to operational problems peculiar to its own service. To augment and complement this capability each Federal Dental Service needs a provision and funds to negotiate contracts for special studies and for cooperative efforts in areas of mutual interest.

3. Summary

In summary, the Dental Research Section of the NBS triggered the impact of basic sciences on the dental profession. This impact and the results of

it, have had a most beneficial effect on the profession and the services it provides the nation and humanity everywhere. Recognition of these facts has led to a greater interest and support of dental research by the government. There has been a minimum of duplication due to the special objectives, interests, and requirements of the various agencies involved. The Federal Dental Services

have a continuing need for research in areas applying to the population as a whole and to specific problems relating to special operational conditions. Finally, each Federal Dental Service needs a scientific staff capability to solve its own immediate problems or to contract with university, industrial, or other government agency laboratories for their solution.

Research Needed by the Dental Industry

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Dental industry requires new research information which must come from nonindustrial research-oriented institutions. Two major requests of dental industry are for basic research and better clinical correlation with laboratory data. Many compilations of physical test data on a variety of existing materials or ill-defined experimental ones are being reported, but the major need is for evaluation of these same materials in well controlled clinical applications. More rapid access to results of investigations, especially government-supported grant research, is needed.

Key words: Clinical and laboratory data correlation; dental industry research needs; dental materials; dental research, necessity for rapid communication of.

1. Introduction

The research needs of the dental industry could be discussed from several viewpoints; for example, the need for money, for equipment, for personnel, better management and administration, and so on. All of these needs are internal within each organization in the dental industry and are essentially our own problems.

On the other hand, I have chosen here today to discuss the subject of the research needs of the dental industry from the aspect of needs that can be satisfied by external sources. I would like to consider how the laboratories supported by government, the schools, and others, whose only business is research and whose only products are information and research papers, can assist us in furthering the work of the dental industry and thereby help dentistry in the long run.

As stated, this discussion is directed to the needs of the dental industry and needs, by their very nature, are something that we do not have or do not have enough of. The assessment of one's needs must always be based on a critical examination of what is now available. This is exactly what I have done. It is certainly not my intention to fault any group whose services may lie within the area of this discussion. On the other hand, it is intended merely to review the situation with some suggestions that perhaps "something must be added."

2. Dental Industry Background

By way of background I should point out, first, that the dental industry is in business to make and market materials and equipment for use by the dentist, the dental laboratory technician, and ultimately the public. It is supposed to be a profit-making industry.

The profit motive, as a basis of operation, creates very profound differences in research personnel and research efforts in the dental industry compared to that of the so-called supported institutions. The goals of our research efforts must be specific and directed towards getting answers quickly to the multitude of problems at hand, not just any answer, but one which will be bought by the customers. Moreover, this answer must be obtained in the most economical way and its manner of pursuit has to be continually justified so that it will be acceptable and will produce the desired profit. The attendance at meetings, the writing of papers, the delaying completion of the project for several months or even a year to investigate a tangential but fascinating avenue of research, all play a very secondary role to the industrial scientist in his struggle to get materials out the front door. I believe we, as a group, would like to be as serendipic as one can be in the academic world, but these pursuits have to be very materially tempered by the economic press.

The dental industry is quite small as chemical industries go. The sale of its products is limited to the dentist population and the quantities involved for sale to this limited group of customers are tiny. Therefore, the industry is just not financially able to support extensive research programs aimed at developing fundamentally new information about matter, and must of necessity look elsewhere for this kind of data.

3. Research Needs of Dental Industry

In the last few years a great deal of money and effort has gone into dental research. In a published survey for 1966, Perlman said research grants were allotted 10.2 million dollars, scholarships 1.4, and training grants another 5.1 million. There were reported to be 1,288 researchers in schools in that

year. Undoubtedly this expenditure has continued and even increased in the last years since then, and the likelihood is that such support will continue into the future, even though prospects look somewhat gloomy right now. This will not last—we just cannot afford to cut off even the majority of the projects sponsored by NIDR, Public Health, the Army, the Navy, and the Air Force, and the internally supported projects within some of the dental schools.

Perhaps, however, this is a time when the research efforts that have been made in the past and are currently going on, should be examined with regard to goals and their real value to dentistry and to the dental industry, which depend on and must use much of this information to provide better dental care. With all the effort that is being put into this type of work, I feel it is very opportune that the research group in the dental industry is invited to indicate its needs.

To make this discussion more meaningful, I have taken the liberty to carry this invitation to the industry personnel and have conducted a small survey of a number of dental-materials industrial researchers asking them to indicate their needs from research oriented institutions supported outside of the dental industry itself. While I must admit that some of the comments and the frankness of those interrogated were surprising to me, there were certain dominant clearcut ideas almost universally expressed which could be valuable as a guide in planning the nature of future research projects.

3.1. Need for Basic Research

First, there is a crying requirement for more fundamental or more basic research in dentistry and secondly, for more and better clinical correlation of the laboratory test data that is being produced from many sources. In these two areas the dental industry is just not geared to function, especially, in basic work. In contrast, research institutes and organizations are usually equipped with excellent instrumentation or at least instrumental availability, and in my opinion they have personnel who are well oriented to and are quite capable in the basic sciences. They should be supplying fundamental information, for example, on teeth, their composition, the forces involved within the tooth, the nature of changes of oral tissue upon application of various dental procedures, or with time, the physical requirements which must be met for successful restoration of the function of oral tissues, just to mention a few. I am sure you are well aware of the basics in dentistry.

In a number of instances research institutions have taken upon themselves or have been directed by someone to engage in activities which are interpreted as product development to fulfill some specific urgent need or other, which is current at the moment. No matter how one looks at this endeavor,

it seems to be in competition with the dental industry development laboratories which generally are better equipped for product development through their own orientation, close contact with the dental profession, incentive, and even the profit motive. It seems to us from where we sit that there would be a greater contribution to the industry and to dentistry if the research-oriented institutions would establish the principles on which products can be developed. In the past there has been some history of doing this pioneering, for example, Taylor and Demaree in the spherical alloys, Bowen in his composite restorative materials, Brauer in the inauguration of the EBA's, Phillips putting fluoride in filling materials, among several others. However, there seems to be a tendency of late through some pressure or other to develop complete or more or less finished products. Perhaps the industry is somewhat at fault in not taking up the ideas coming forth fast enough and gives the appearance of inadequately fulfilling the best needs of dentistry.

As an illustration of this need for basic work let us consider, for example, the program of the 1969 meeting of the Dental Materials Group—IADR. I have made a tabulation of the papers that were presented and arbitrarily divided them into four subject categories, determined from the title, the abstract, and listening to some of them myself.

Papers which could be considered as descriptions of tests, new or otherwise, constituted 15 percent of the presentations. New and more-or-less finished materials not previously described were the subject of 14 percent. Papers which discussed some aspect of existing materials accounted for 59 percent, of which 38 percent dealt with the subject of amalgam alloys, or amalgams, or handling amalgams. Basic research papers concerning some phenomenon or reporting facts which could be construed as contributing to the general fund of dental information, constituted only 12 percent of the offerings.

These percentages more or less speak for themselves and would substantiate, I think, the need mentioned. There is an overabundance of testing, retesting, and testing again, on current materials, ad nauseum.

Be all this as it may, at least to industry personnel, it appears that much of the data cannot be used and more attention could be given to acquiring basic information.

3.2 Need for Improved Clinical Correlation in Laboratory Testing

The second area expressed as being greatly needed is more effort directed to better correlation of the quantities of physical data being accumulated today, with clinical function. The clinical evaluation of materials and processes, whether it be dental or medical is extremely difficult, probably the most difficult type of research to carry out. It requires very careful and detailed planning, the

institution of extensive controls, the development of careful and uniform observation techniques which at best can be only empirical and subjective, the selection of satisfactory material in sufficient numbers to be really significant, and some sort of useful and understandable tabulation of the results. All this is tedious, time consuming, expensive, and quite frequently disappointing in the clarity of answers that result from the experiment. Also, more times than we would like to admit before the experiment can be completed, the material being evaluated becomes obsolete and then the experiment is reduced to an exercise in futility. There have been a few brave souls who have ventured forth into this area and are producing some very notable contributions such as Ryge, Paffenbarger, Myers, Phillips, and a few others. Unfortunately, the formidableness of this type of research has scared off, or so it seems, many who actually are equipped to contribute greatly. I fail to understand why the materials departments of most dental schools, with their attendant clinical facilities, do not take up this opportunity to contribute to dental materials development in a useful manner.

The dental industry is not actually interested in comparing one brand of material with another brand of the same type of material, although this seems to be a very favorite endeavor. We are interested, however, in learning what the generic types of dental materials do to the oral tissues and, of course, what the oral tissues do to materials and what are the requirements from a clinical viewpoint for satisfactory replacements.

The dental materials industrial researcher is constantly asked to produce and continually improve materials and equipment and to design procedures for replacement of tooth and other tissues, but few guidelines exist as to what strength, hardness, fatigue, or other detailed characteristics are actually required. It is somewhat akin to trying to build a bridge without knowing what is going to go over it or how long it will be. Good clinical study will assist materially in answering the questions with facts that are needed in the design of materials. Here then is our second major need, a difficult one no doubt, therefore a real challenge, so let us pick up the challenge.

3.3 Need for Improved Communication of Current Research Results

The communication of the results of investigations by research institutions to others outside of their own agency, which sponsors the research, has not been the best. In fact, it is quite poor. In many cases, the dental industry and other interested parties have had to wait until the information was published in a journal or in a report issued by the National Technical Information Service a year or so later. When something that is worthy of note is accomplished by a research institution, it should

be made available to dentistry through the industry. That is what the industry is for. There is no need to bury research work in secrecy until the project is completed or dropped, especially when it is supported by public funds. It has been suggested that this whole matter of communication be looked into by the several grant-issuing agencies and that they do some soul searching. If research institutions wish to convey the fact that it is their desire to aid the public and to produce better dental services ultimately through their work, then it would certainly seem that it would pay to team up by better communication with the industrial research groups, who will have to produce the product eventually anyway. As it stands now the usual channels of publication and reporting are woefully inadequate and behind in keeping up with the work that is being done. As suggested, the burden of the dissemination of information lies with the sponsoring agency and much more would be accomplished if these agencies would recognize this responsibility and attempt to issue informative reports on a regular, rapid, and broad basis.

These three points constitute the major areas which were almost universally mentioned as needed by dental industrial research personnel to pursue their efforts in the adaptation of ideas and findings of research laboratories and make them practical in the form of dental products.

3.4 Additional Dental Industry Research Needs

There are several other areas which might be said to be of lesser concern to industrial research personnel, but should nevertheless, I feel, be mentioned.

One point is the request by many for the development of more realistic physical tests. At the present time, the testing procedures for dental materials are more or less haphazard in their validity of basis of selection. The tests that are part of the various specifications are based on a few physical properties of existing products and the limitations are those of the existing products. While we may be getting by with this at the present time, we should be striving for well organized tests that will simulate aspects of clinical service and define the service attributes of a material more specifically. Such tests, coupled with actual clinical observations, will establish what limits are really necessary from a functional standpoint, and the requirements of the specifications will fall in line and be more meaningful in the judgment of materials.

It has been whispered that some of the physical test data are being developed by individuals who have a very limited background in the science of dental materials. They sometimes arrive at implications and conclusions supported only by a bit of statistical juggling. There are many grants at present, so called training grants, issued to individuals who carry out a few physical tests on one product or another. Eventually the results are published.

Unintentionally, some misleading information is put into our journals, especially the popular ones.

The publication of this type of data and the manner in which it is developed and concluded, unfortunately for us, gives the impression right or wrong that there is some incompleteness in dental research. Perhaps this is part of the training grant situation and, if it is, then the procedure should be altered so that the trainee can still get this needed support but merely write a term paper which will be buried in a library some place or in somebody's desk drawer. This could be quite easily accomplished by the sponsoring agency changing its publication requirements, so training becomes indeed a training course and not a paper mill.

Up to now I have probably sounded, although unintentionally, somewhat critical of the present state-of-the-art, so let us turn to a couple of farther out thoughts for the future.

A single central research control agency, possibly in the ADA or NIDR or other governmental institution is suggested to consider the problems of dentistry and parcel out the projects and investigations on the basis of dental need and likelihood of success, rather than fancy proposals. Perhaps this is already established, but it is not evident to us.

There are several agencies at the present time which attempt to pass out research projects, but to industry people there appears to be a competition between these agencies even though there probably is not. At any rate the job has the appearance of not being done and there seems to be considerable duplication and needless effort. A central agency could control this effort more usefully.

For many years there has been much effort to develop specifications for existing materials. Recently, with the formation of the USASI Committee from the older Dental Materials Group

Specification Committee and the addition of others, the tempo of specification writing and test procedures development has increased notably. Any good specification for a material will have behind it a battery of tests which will have been developed through actual laboratory evaluation and the amassing of sufficient data to prove that the tests can be carried out with reasonable uniformity in several laboratories by a number of different operators. Much of this work is going on at the headquarters of the ADA, which is contributing very heavily and effectively to this effort. A number of schools have been cooperating and are spending time and money on test development. Likewise, industrial research laboratories are doing the same and have contributed in a great measure to the mass of data that backs up a number of these tests.

All of this work costs money, considerable money. Why not set up a series of grants to any institution, including industrial laboratories, for test development and data accumulation for specification work. Good physical facilities are available in the industrial laboratory, as is wide testing know-how. Use should be made of it, but at the same time it could be supported and the burden spread.

4. Summary

I have discussed with you briefly here the research needs of the dental industry—the needs that can come from outside the industry itself, from institutions that are in the research business and supported by grant funds from one source or another. More extensive basic dental research, carefully controlled clinical studies to correlate physical laboratory data and establish realistic limits, and better communication, are the fundamental needs of the dental industry.

Research Needed for Dental Education and Practice

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The current research effort in dentistry, and that which will occur during the next decade indicate that dental practice will be characterized by certain trends. These trends will require an acceleration of research on adhesive film forming systems, sealants for pit and fissures and means of improving anticariogenic characteristics of restorative materials. The interdisciplinary aspects of dental materials will be increasingly important. Greater focus will be on the biological properties of materials, materials and devices for oral rehabilitation, materials for implantation and the interaction of tissue and substances used to restore lost tooth structure. Further definition of the oral cavity can be expected to become a responsibility of the materials scientist. Increased emphasis can be expected in dental education on a more intimate basic science-clinical application orientation.

Key words: Dental education; dental materials, research needs; dental practice future; dental research; materials, dental, research.

1. Introduction

We are now living, and shall continue to exist, in a research oriented society. While too little attention appears to be focused on the quality of research, the sheer magnitude of the investigative effort in science is impressive. The health professions, and especially dentistry, are no exceptions. It would be naive and dangerous to believe that this ever broadening base of knowledge will not change decidedly the nature of dental care and the content of the dental school curriculum. It is upon that premise that the following remarks are based.

It is indeed difficult to trace a profile of any profession a decade hence, particularly in one such as dentistry where such a marked transition is occurring, not only in the specific treatment of dental disease but also in socio-economic attitudes that have not as yet acquired a definite character. I am all too aware that even with much more tangible data, predictability may sometimes go awry.

However, it is becoming apparent that certain trends are crystallizing in dentistry and I would characterize them as follows: (1) The present inroads that are now being made in reaching a total comprehension of the etiology of dental caries and designing the related therapy to arrest this disease will soon make certain dental restorative procedures obsolete and the general nature of dental service may be quite different from that of the present. (2) With more emphasis upon the dental specialties, group practice will become more popular. (3) Greater demands will be made upon research and teaching programs that will extend dental treatment to the entire population. In other words—community dentistry. (4) In order to pro-

vide a broader type of dental service, the role of the dental auxiliaries will be expanded, as will their training.

Let me defend these predictions and attempt to relate them to research in dental materials science.

2. Future Trends in Dental Research

In recent years, at least one-third of the dental research effort in the United States has been devoted to ways for preventing dental caries while another one-third has been concerned with eliminating diseases of the soft tissues. The response of the profession to the rapid escalation of research in these fields has been one of increasing alarm that coincident with any substantial reduction in the incidence of dental caries and/or periodontal disease will be a reduced need for the dentist, a fear that he will eventually be phased out of the health professions and will become somewhat of a historical curiosity. The outcry first occurred when fluoridation became a recognized mode for the arrestment of dental caries on a mass scale. To be sure, the goal of any health profession is that research will lessen the demands that are placed upon it.

Preventive measures such as fluoride therapy, which were the fruits of dental research, have already altered the nature of dental practice. However, they have certainly not led to a lessened need for the dentist or his auxiliaries. To the contrary, dental research has permitted the profession to initiate programs of total oral care rather than simply playing catch-up with the overwhelming backlog of dental treatment that has existed and which will be required by an ever expanding population. Furthermore, in being offered superior service, the

public has become more dental conscious and motivated to seek dental care—thus actually increasing the demand for a lower dentist-patient ratio.

Parallel to this apprehension of the young dentist of the impact upon his profession of research in the biological sciences, one often hears depressing predictions coming from the dental materials teachers or researchers. Since the remaining one-third of the bodies and monies now involved in dental research are directly concerned with improving dental materials and instrumentation, it is predicted that this research in the physical sciences will shortly spill forth an avalanche of superior materials and that most of the former problems associated with the clinical failure of materials and appliances will be conquered. In turn utopian technics will attain such a degree of perfection that further research will be unnecessary. It is further rationalized that as dental disease becomes better controlled through preventive measures, it must therefore follow that the need for restorative materials and appliances will become less important, as will the personnel involved in their development.

I do not share this alarm. Conversely, the theme of this paper is centered on an opposing premise—namely, that although the teacher or researcher in dental materials in the year 2,000 will likely be concerned with entirely new problems and will be attacking them in a vastly different way, his relevance to the profession will be even more secure, as will the horizons for a meaningful career in research or education.

As I have suggested, any realistic evaluation of the accomplishments that are now being made in providing a means for irradiating dental caries clearly indicates that the magnitude of this disease will diminish in a somewhat regular order. If a major breakthrough should occur, restorative dentistry will then be concerned principally with replacement of the fractured tooth or the one lost from periodontal disease. In any case, it is reasonably safe to predict that within the foreseeable future the carious lesion will no longer be the focus of attention, or of time, of the profession. The arrestment of dental caries will in turn trigger other widespread changes in the nature of dental practice. For example, the need for endodontic treatment will become less. Since fewer teeth will be lost as a result of caries, a lower number of prosthetic appliances will be required.

Thus it might be envisioned that the typical dental practice of the future will emphasize: (1) preventive dentistry, (2) restorative measures that will be necessitated from the loss of tooth structure due to reasons other than caries, (3) the maintenance of the health of the supporting tissues, and (4) the treatment of dental disorders that have previously been neglected by virtue of the overwhelming preoccupation with the ravages of caries.

If one accepts as a basis for discussion that such trends could be the natural outgrowth of current programs of dental research, where does the dental materials scientist fit into such a scheme? First, as for the dentist, the time allocated to certain materials or technology, will be weighted entirely different from allocations of today. Materials and concepts that at present may receive only a casual glance will come to the fore while some of the classical systems upon which we have lavished our energies will be of secondary interest.

For example, although this is almost sacrilege to say, in time dental amalgam will no longer occupy its lofty seat as the material upon which the attention of dental materials researchers has for so long been concentrated. For all of its merit as a system that has served dentistry so heroically and one that has offered so much scientific intrigue, the need for research on dental amalgam will diminish since it will be replaced by other materials or therapies. The same may be said for a number of other materials, such as silicate cement and the current resins. They will be supplanted in time (and please don't ask me to suggest a target date!) by adhesive restorative materials that will hopefully approach or duplicate the physical and chemical properties of the tooth itself.

It would be naive if I were not to acknowledge that this learned audience is quite sensitive to the importance of research in the area of dental adhesives. However, since the title of my assignment was to be centered upon the future needs of dental materials research as they relate to practice and education, this subject affords an unusually good example of the type of investigative effort with which we should and will be occupied. No other affords greater opportunities for a broad spectrum of dental applications, for the outlet of an imaginative mind, or for the interplay between disciplines that have historically been the trademark of the science of dental materials, and of the 50 year leadership given to us by the dental program at the National Bureau of Standards.

Adhesive systems afford opportunities to render a type of dental care that is not possible with existing materials. Furthermore, they fit nicely into the framework of the future practice of dentistry as I have sketched it. For example, the elimination of the microleakage phenomenon would alter much of the basic biological and physical concepts that now prevail in restorative procedures. The adhesive dental restoration would conceivably be less complicated to place, biologically superior and physically improved. However, the true lure of dental adhesive molecules lies in uses other than for the restoration of a carious tooth or the attachment of orthodontic brackets, important though these may be. Adhesive films applied to tooth structure, if durable, could inhibit the formation of the dental plaque and thereby the caries process or the deposition of calculus. Certainly adhesive phenomena, yet to be adequately explored

by the dental materials scientist, are involved in the retention of dentures, the bonding of ceramics to metallic restorations, the retention of re-implanted teeth and of resin implants to tissue and in the efficacy of maxillo-facial appliances.

Each of these uses is different in the sense of the structures that are involved, the respective interfaces and phases, the conditions to which the bond will be subjected, and the physical and biological properties of the system. The scientist in dental materials is the most likely candidate to lead meaningful programs in the development of such compounds, by virtue of his experience with the physical behavior of materials in the oral cavity, the highly specific test methods and specifications he has developed for assessing materials and his obvious ability to synthesize various disciplines into one that serves the multiple and complicated demands that dental treatment requires.

There is yet another example that might be used to illustrate the need for adhesive systems since it is one which could be part of the routine type of therapy offered in the dental practice of tomorrow. I am, of course, referring to a sealant for pit and fissures in the child patient. This is a dental materials problem, even though it is essentially preventive dentistry. A number of persons in this audience are already deeply involved in this area of research. An adhesive and durable restorative material that would prevent the propagation of caries in these vulnerable areas has great import to the treatment of mass populations. As I stated earlier in this paper, I am convinced that the profession will be forcefully moved, both by direct means and emotionally, to provide dental care to all segments of the population and in all countries. Of immediate application in mass care would be the arrestment of existing caries or its prevention in the young population. Adhesive sealants, particularly if anticariogenic, could become a major treatment objective for such programs. Furthermore, it would not be heresy to suggest that in certain instances this type of care might be administered by properly trained dental auxiliaries.

I am certain that most of you are in complete sympathy with the concept that we must lend our assistance in every way possible to make dentistry available to everyone and especially to those in underdeveloped areas in this and other countries. The mode for accomplishing this is indeed controversial and does not concern this group. What *does* is the development of materials and the training of people to cope with the magnitude of the problem. Those materials and that type of training may be considerably different from what now prevails.

If one acknowledges that the broad area of dental adhesives is a reasonable example of the type of research that fits into the context of "Dental Practice in the Year 2000", then it seems logical that the interests of the dental materials scientist

will slowly and methodically, and I would emphasize the latter, shift from studies such as the niceties of phase reactions in amalgam or the dimensional changes that occur in gypsum products. Merely to further accumulate such information as a sort of capital investment will not be sufficient. Instead the scientist will be exploring the interaction of polymeric systems to both hard and soft tissues, will develop criteria for relating biological characteristics of materials to their structure, will define the exact nature of tooth structure at interfaces, and will better characterize the stress patterns placed upon dental restoratives, appliances or films.

I have used the example of adhesion because it does embody so well the changing complexion of dental materials research and its application as I see it, as well as the responsibilities which may thereby accrue. I have suggested, by using this particular illustration, that the breadth of dental materials research and education will range even further from very complex problems to those that are inordinately simple. For example, to develop a system that will adhere to the formidable tooth structure in its aqueous environment will continue to require the attention of unusual research skills and talents. On the other hand, the application of that adhesive to a pit and fissure will be a very simple treatment as compared to existing operative procedures. Thus one sees the need for sophisticated research done in great depth, to be paralleled by training programs for the dentist and especially for auxiliaries who may be required to utilize the end product of that research.

As I just stated, the role of adhesive molecules in dental application is merely one of many that could be cited to indicate the future nature of dental materials research and its application. These include the evolution of implant materials for prosthetic appliances, of materials that will be more esthetic and superior in properties than the ones now used for maxillo-facial appliances, of methods for providing a more precise restoration of teeth that are lost from accident or diseases of the soft tissue, of ways for producing mineralized tissues or methods for protecting such tissues and specialized materials for all of the various dental specialties. As dental care becomes more specific, greater emphasis will be placed upon diagnostic aids and devices for maintaining a better control of dental treatment. The researcher and manufacturer of dental materials long ago demonstrated his ingenuity in that field and will no doubt be called upon to develop technology for monitoring physical and chemical changes in dental structure, for minimizing the human variables in providing dental care and for ways to reduce the cost of the dental operation.

Whether it be fundamental research in such divergent areas or other programs designed to further the education of the dentist and his aids, the point has been made that the field will remain

a most viable one, hopefully unfettered by previous tradition as to its limits. Personally I have every confidence that the scientists and educators now in this field do have the wisdom to make that adjustment and rise to meet, not obstacles, but an everchanging science landscape. Elaborate apparatus plays an important role in science today but we are too inclined to forget that the most important instrument in research must always be the mind of man. Kettering has said, "A problem is not solved in the laboratory. It is solved in some fellow's head. He only needs the laboratory apparatus to get his head turned around so he can see the right thing". A multitude of opportunities for scientific enrichment in our discipline can be seen without much movement of the head.

3. Future Trends in Dental Education

I would like to spend just a minute to relate the foregoing sketchy remarks to dental education. If dental education in the future assumes the same posture that has prevailed in the past, it by necessity will reflect changes in dental practice. Therefore, as emphasis is placed upon the dental specialties, on community dentistry and upon caring for all types of dental disorders, the dental school curriculum will witness a more intimate relationship between the basic sciences and the clinical subjects. No doubt this will be reflected in a more vertical alignment of courses. This will be true for each individual science, including dental materials. Every effort will be extended by dental school administrators to organize a proper atmosphere to fertilize this type of orientation.

The dental materials course must eventually change to reflect the new duties of the dentist and the changing nature of his practice. Certain materials will become obsolete, others will receive greater stress. In all likelihood the systems and the techniques that will eventually be paramount are as yet still under research. In the undergraduate training of the dental student it seems logical that there will be less emphasis upon those materials and techniques that will have become principally the responsibility of the technician, assistant or hygienist. However, as dental schools assume a greater role in the training of dental auxiliaries, the content of the courses given to those groups will be considerably strengthened in materials and it will no doubt be presented at a higher level.

In addition, there will be greater emphasis upon

the biological characteristics of materials and the interaction of materials with their environment. The dental materials science course could very well encompass the physical structure and physical constants of all oral tissues.

4. Summary

In summary, I am convinced that our future lies in a greater interdisciplinary approach, not only in the specifics of research on materials but in relating that research to the other physical, biological, and clinical sciences. Furthermore, communication on an international basis at a level far greater than that which now exists is essential in order to make best use of the talents now available, to prevent duplication of effort, and to concentrate a multitude of single isolated investigations into unified attacks on problems of mutual interest. I guess what I am saying is that the profession will demand more from this science than any other discipline in turns of adjustments to newer areas of investigation and at a high level of competency. At the same time it will be charged with accepting a greater responsibility in the training of individuals who will deliver dental service. The dentist will request, and rightly so, materials and techniques for handling a different type of dental practice than he is conducting today and he will expect educational programs for auxiliaries that will be heavily weighted in the subject matter pertinent to usage of these materials. Coincident with this, one may anticipate that the dental manufacturer will in turn become more specialized, skillfully developing what at present might be called bizarre products.

I guess my major concern in this transition lies in our capability and desire to attract future researchers and teachers. We are now and will continue to be competing with scientists and educators in fields that now appear to have a greater allure and upon which the future practice of dentistry seems to be more directly based. I contend that the science of dental materials will comprise a pillar for that foundation as strong as that of any other discipline—but only if it accepts a critical, reflective attitude so that it can envision and react to the new challenges which a changing profession will offer. If it does, then the values and rewards are such that this science can compete on a scientific and academic level equal or superior to that with which we are now blessed.

III. Metals Research

Amalgams in Dentistry

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Corrosion is a major factor in the failure of amalgam restorations through the deposition of corrosion products which may cause chronic periodontitis or through corrosion fracture of the margins which may cause secondary caries. Galvanic corrosion attacks only the tin-mercury γ_2 phase. Mercury released by this corrosion causes a mercuroscopic expansion resulting in a deflection of the amalgam from the cavity wall at the margin. Corrosion can be considerably reduced by minimizing the porosity of the amalgam restoration through overfilling the cavity, burnishing the margins, eliminating excess by carving and using zinc-containing amalgams.

Key words: Amalgam, dental; amalgam, dental, effect of technique on corrosion; clinical failure of amalgam; corrosion, dental amalgam; dental materials; marginal fracture, dental amalgam; mercuroscopic expansion, dental amalgam; porosity of dental amalgam.

1. Introduction

The 50th anniversary of the Dental Research Section of the National Bureau of Standards coincides with another noteworthy date: it is exactly 150 years ago this year that dental amalgams first made their appearance in the service of dentistry. Countless teeth have been restored and preserved in the course of the past century and a half, thanks to the development of these materials. There is some uncertainty about who can claim to have invented amalgams for the restoration of human teeth; it seems to have been the British chemist, Charles Bell, in 1819, who produced an amalgam of silver filings and mercury; his product was advertised under the name "Bell's putty". A few years later, in 1826, the French dentist, Onesiphore Taveau, claimed to have invented an amalgam suitable for filling carious teeth; the material was made by mixing mercury with filings cut from silver coins and went under the name *pâte d'argent*, i.e., silver paste.

We know that amalgam as made according to Bell and Taveau had several unfortunate properties: the consistency of the freshly made mixes was harsh or sandy, they hardened slowly and were subject to excessive expansion. It was soon discovered, however, that the latter two drawbacks could be greatly reduced by adding tin filings to the silver filing or by cutting filings from an alloy of silver, copper and tin, i.e., the metals which even today are still the main components in dental amalgam alloys.

The dental amalgams were received with great interest by the profession, which is not perhaps surprising in view of the apparent simplicity of amalgam technique; the filling materials which amalgams could replace were primarily a variety

of metal foils, particularly gold foil. In those days it was a very tedious task preparing a good filling of gold foil; it frequently took more than three hours. By comparison amalgam was advertised as a material of which a filling could be made in just three minutes, painlessly and at no discomfort to the patient. Only some of the details of the amalgam techniques of those days are known but there is no doubt that cavity preparation techniques, matrix techniques, and the actual amalgam technique were extremely primitive. It is scarcely surprising therefore that amalgam fillings frequently caused very serious secondary injuries, and that many dentists reacted strongly against the application of amalgam as a filling material.

The debate on the use of amalgams in operative dentistry was confined almost exclusively to the United States, where the material had been introduced by the Crawcour brothers in 1833 and where the famous amalgam war raged until 1856. It was in this country too that almost all the advances took place that have since led to the amalgam alloys and amalgam techniques of today. The people who headed this progress were men like Josiah Flagg, founder of the constructive critical-analytic method in operative dentistry generally, and amalgam technique in particular; G. V. Black, who on the basis of extensive and detailed experiments defined the optimum composition of the amalgam alloy, and also systematized the technique and morphology of cavity preparation; Wilmer Souder, the first head of the Dental Section of the National Bureau of Standards, recognized as the founder of the science of dental materials and author of the first standard specifications for a dental material, viz., amalgam alloy; and many other authorities most of whom are present with us today

and still active in the field of research into dental materials.

It is important for me to stress that all the research carried out today in the amalgam field is based on the comprehensive and careful studies of these authorities—and would not have been possible without their vital contributions.

All organized research requires a specific objective in order that we may formulate and attack the appropriate problems. The study of dental amalgams is pure applied research, which means that it is justified only inasmuch as it is demonstrated to be of use to operative dentistry.

The debate in earlier decades was on whether amalgams were of any use whatever as a filling material. Modern amalgam research on the other hand is given the task of examining (1) the extent to which amalgam fillings fail, (2) an analysis of the physical and chemical processes leading to failure, and (3) the influence of materials and technique on these processes, particularly with a view to discovering whether it is possible by altering the composition and properties of the materials and by changing the technical working methods to halt or delay the processes.

2. Definition of Amalgam Failure

A failing amalgam filling can be defined as a filling that has been a contributory cause of secondary injury in the organ of the tooth, i.e., the tooth itself and its surrounding connective tissue. In the following discussion it is a condition that the amalgam fillings initially were morphologically correct, which means among other things that the surfaces of the fillings were smooth and that a careful inspection revealed neither marginal excess nor marginal deficiency. It is moreover a condition that the fillings have been made of alloy and mercury, fulfilling the requirements of the relevant ADA specifications.

The only forms of secondary damages of clinical significance are chronic gingivitis and secondary caries.

Chronic gingivitis occurs in this connection when solid products of corrosion, which promote the retention of materia alba and plaque, are deposited on the surface of amalgam fillings on the peripheral surfaces of the tooth in close relation to the gingiva. Figure 1 shows a typically corroded Class II filling in which the gingival and central one-third part are covered by a crust of dark products of corrosion, the occlusal portion remaining clear of corrosion. Figure 2 is an enlarged view of part of the surface of an experimental noncontaminated filling from a laboratory experiment; the filling had originally been smooth and polished but after four months' corrosion in artificial materia alba its surface was roughened by small surface blisters and solid corrosion products. The small hemispherical nodules are drops of mercury covered by a thin crust of deposited products of

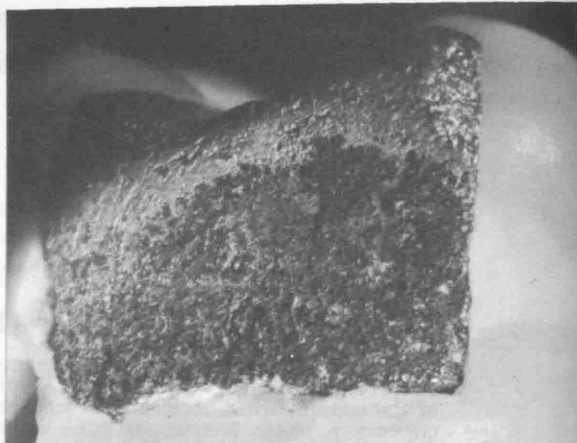


FIGURE 1. Typical corroded Class II filling with the gingival and central area covered by a crust of dark products of corrosion while the occlusal portion remains clear of corrosion.

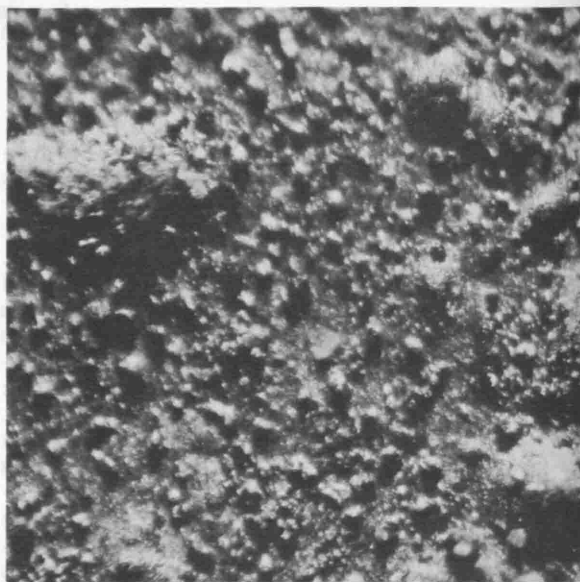


FIGURE 2. Enlarged view of the surface of an experimental non-contaminated amalgam specimen showing small surface blisters and solid corrosion products after four months exposure of the original smooth polished surface to artificial materia alba. Magnification—140X.

corrosion. Although the accepted view of the causal relation between corrosion of fillings and gingivitis is to some extent based upon presumption, it seems to be probable enough to provide sufficient grounds for a study of the circumstances influencing the process of corrosion.

3. Corrosion of Amalgam

Schoonover and Souder were the first to discover that galvanic corrosion attacks only the tin-mercury γ_2 phase, and that only the tin dissolves—the released metallic mercury remaining in the

amalgam; much of the tin is deposited locally, either within the corroded amalgam or on the amalgam surface. Many subsequent studies have served to confirm this view.

It is typical of amalgam corrosion that in oral conditions it can occur only in the presence of a difference of oxygen concentration on the amalgam surface; the area with the lowest concentration of oxygen forms the anode. Areas of this nature regularly occur in the most gingival parts of fillings on peripheral surfaces where the amalgam is covered by gingiva or plaque; the surfaces of the filling facing the cavity, and the walls in the pores of the amalgam also have a relatively low oxygen tension.

Since it is only the γ_2 phase that is subject to galvanic corrosion, it is important that we become familiar with the morphology of this phase. If the individual γ_2 grains do not anastomose, only the surface grains in contact with the electrolyte can be dissolved by corrosion—which would have to cease once this dissolution had terminated. Figure 3 shows a section of an amalgam with a relatively high content of mercury. The amalgam was exposed for four months to corrosion in a 1 percent NaCl solution; the corroded surface of the amalgam—facing downward in the picture—is partly covered by products of corrosion. The γ_2 phase is observed only in the upper part of the section as irregular, dendritic grains; nearer the surface the phase has dissolved, and the amalgam has become severely porous. There is no doubt that in this case the surface γ_2 grains anastomosed with all deeper lying γ_2 grains. Experiments in which the γ_2 phase was dissolved with the aid of a 10 percent sodium citrate solution have revealed that even in well-condensed amalgams all the γ_2 phase always forms a cohesive network of crystals. Corrosion can therefore continue into the depth of the amalgam until the whole of this phase has disappeared. As far as the structure of the γ_2 phase is concerned, there is no essential difference between the various types of amalgams; spherical and nonspherical, with or without zinc, mercurized or non-mercurized; all show the same network structure of the γ_2 phase. As there is only a slight difference in the amount of γ_2 phase between an amalgam with a high content of mercury and one with a low content, the corrosive properties would for all practical purposes be independent of the amalgam's content of mercury.

The intensity of corrosion of dental amalgams on the other hand depends very much on the porosity of the amalgams. Porosity exposes a greater area of the γ_2 phase and thus increases the anode area. Experiments with a 1 percent solution of NaCl as electrolyte have shown that intensity of corrosion triples when porosity of the amalgam increases from approximately 1 to 4 percent. It was also shown that amalgams containing zinc corrode less than amalgams without zinc. The primary reason for this does not appear to be the

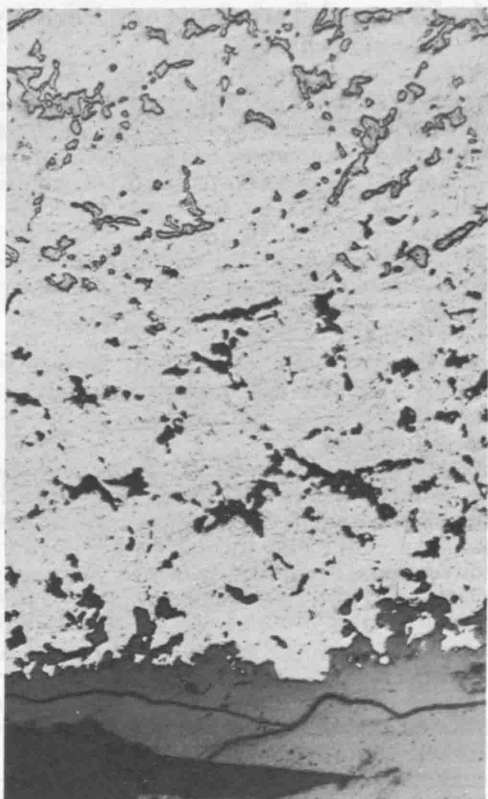


FIGURE 3. High mercury content amalgam after four months exposure to 1 percent NaCl solution.

Corroded surface (facing downward in picture) is partly covered by corrosion products. The γ_2 phase (irregular dendritic grains) is present only in upper part of the section, having been dissolved in the lower portion to form porosity. Magnification—approx. 227 \times .

difference in the chemical composition of the alloys but is probably due to the fact that the zinc-free alloys are not so easily wetted by mercury as those with zinc, which results in a slightly higher porosity in the amalgams. It is a fact that zinc-free amalgams characteristically have a slightly higher porosity than those with zinc, and that this porosity is often localized as small nests in the amalgam.

Since otherwise the three main phases, γ , γ_1 and γ_2 , present in all standard amalgams can from an electrochemical point of view be considered identical, it is unlikely that amalgams produced from different brands should demonstrate different degrees of corrosion.

The means at our disposal to reduce the rate of corrosion in amalgams are therefore as follows: (1) omission of zinc-free alloys, and (2) use of a filling technique that reduces porosity of the amalgam as much as possible. Since porosity can vary considerably according to the filling technique, this latter factor is the most important.

4. Effect of Technique on Porosity of Amalgam

Detailed analysis of filling techniques have shown that the consistency of the amalgam when it is placed in the cavity is the factor of prime importance as regards porosity of the condensed amalgam. A relatively dry and more or less crumbling amalgam will always result in greater porosity than a soft, plastic amalgam from which a considerable quantity of excess mercury can be expressed.

Curve P in the diagram (fig. 4) shows the average porosity in cylindrical, mechanically condensed amalgam specimens, dependent on the content of mercury in the amalgam when condensation commenced.

The vibration technique, requiring as it does a dry amalgam, will thus always produce a high degree of porosity in the amalgam. The same applies in the case of hand-condensed fillings made by conventional technique in which the amalgam is triturated with excess mercury, most of the excess being expressed before the amalgam is placed in the cavity. Fillings according to the so-called dry or Eames technique are also fairly porous. The lowest porosity is achieved when a significant quantity of mercury is expressed in the cavity and when each new increment is condensed in the free mercury thus expressed—the mercury being removed only when it forms a layer of more than approximately $\frac{1}{4}$ mm on top of the condensed amalgam. The latter method has been given the name "wet" technique, wet being a reference to the mercury content.

Porosity in fillings made by vibration or by hand condensation with dry or with conventional techniques is concentrated at the bottom and particu-

larly in the bottom corners of the individual condensed increments. Figure 5 illustrates porosity in the bottom corner of a well condensed, typical Class II filling made by conventional technique; the gingival part of the section is about $\frac{3}{4}$ mm long. Figure 6 shows the same part of a filling made by wet technique; the much lower porosity is remarkable. The diagram (fig. 7) shows porosity and γ -phase content in gingival corners in Class II fillings condensed by means of dry technique with two different condensers (Ap and Af), by conventional technique (B) or by wet technique (C). The diagram shows that the wet technique is an effective means of reducing the porosity of the amalgam, and that it does not lead to a higher mercury content in the condensed amalgam than do the other forms of amalgam technique. It may be noted that G. V. Black many years ago stressed the importance of using relatively plastic amalgam during condensation.

With regard to the relation between plasticity and porosity it is worth mentioning the rather marked tendency of manufacturers in recent years to market rapid-setting alloys with greatest possible one-hour strength. The clinical value of such alloys is open to doubt. During condensation amal-

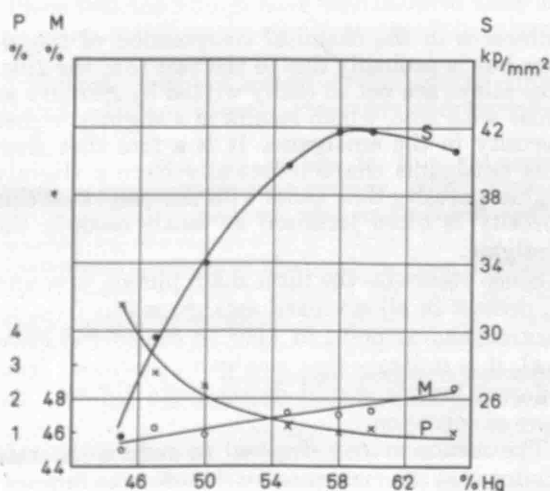


FIGURE 4. Relationship between mercury content of mix and porosity (P), mercury content (M) and strength (S) in cylindrical, mechanically condensed amalgam specimens.

To convert kp/mm² to MN/m² multiply by 9.807.

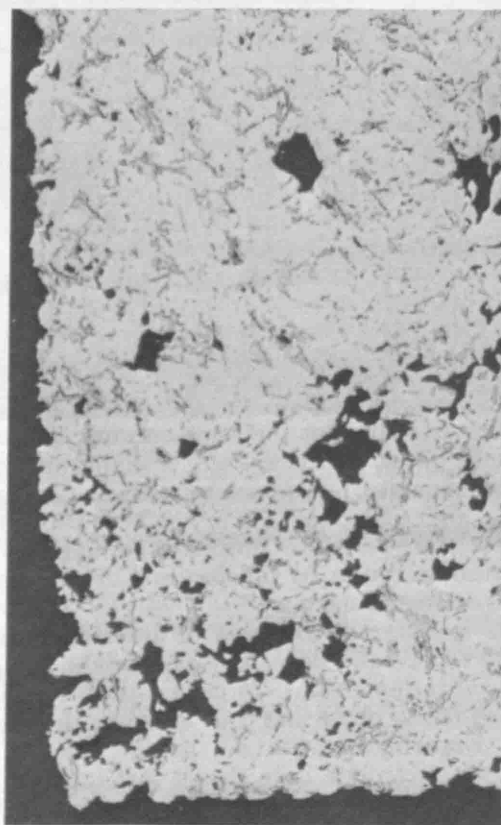


FIGURE 5. Porosity in the bottom corner of a well condensed, typical Class II filling made by a conventional technique. Magnification—approx. 115X.

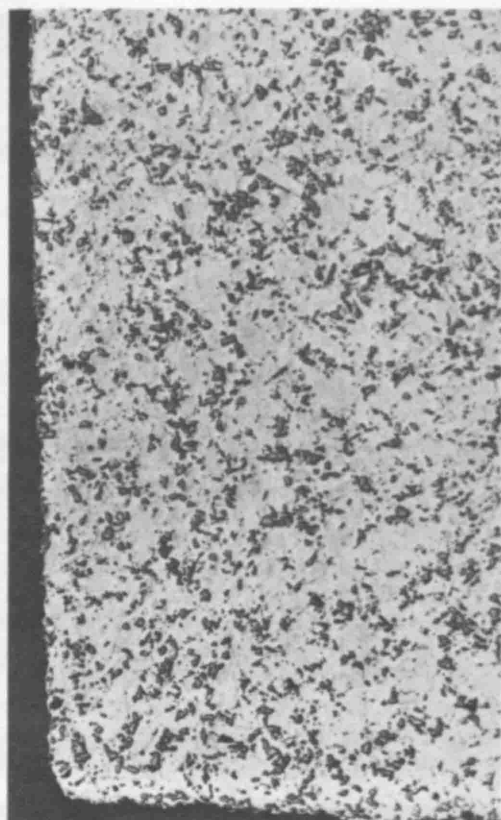


FIGURE 6. Reduced porosity (compare with fig. 5) in the bottom corner of a well condensed typical Class II filling made by a wet technique. Magnification—approx. 115 \times .

gams of this type quickly become dry and crumbly, and can therefore result in a significant increase in the porosity of fillings and a similar increase in the likelihood of corrosion. Increased porosity means at the same time a decrease in strength of the amalgam: a 1 percent increase in porosity has about the same effect on the strength as a rise of 10 percent in the mercury content of the hardened amalgam. The rate at which a freshly triturated amalgam loses its plasticity can be registered in a simple manner, for example, by measuring at various times after amalgamation how much mercury can be expressed from the amalgam. The difference in the percentage mercury content between an amalgam which has been condensed as early as possible and an amalgam which is condensed later can be called the mercury absorption of the amalgam. According to a standard method used for routine tests in Copenhagen, an amalgam which has a mercury absorption of 2 percent five minutes after finishing the trituration, i.e., 4½ minutes after the earliest possible condensation, is considered optimum for medium-size fillings. The great majority of amalgams however have a much higher mercury absorption during this period.

To summarize the factors that—in amalgam

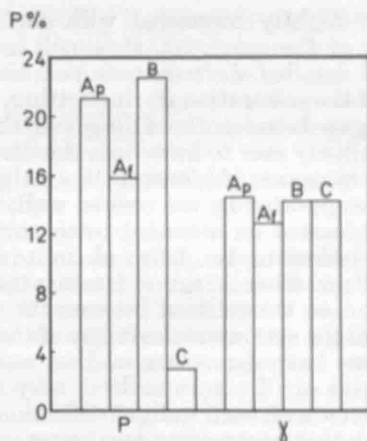


FIGURE 7. Porosity and γ -phase content in gingival corners in Class II fillings condensed by a dry technique with two different condensers (Ap and Af), by a conventional technique (B) and by wet technique (C).

fillings on peripheral dental surfaces—can lead to minimizing secondary damage to the gingiva we can draw up the following list:

1. Avoid as far as possible use of zinc-free alloy.
2. Do not condense the amalgam for a longer period than that corresponding to a mercury absorption of 2 percent.
3. The amalgam should be condensed not with a vibrator but with a hand condenser.
4. The condensation technique should follow the main principles of the so-called "wet" technique.
5. The surfaces of the filling should be made as smooth as possible in order to reduce the chances of retention of plaque and the resulting increase in corrosion intensity.
6. Patients should be instructed to maintain the highest level of oral hygiene because this brings about a reduction both of the anode area and of the time a given part of the filling surface is covered with plaque and can thus operate as an anode.

There is no doubt that certain details of cavity preparation, matrix technique, and condensation technique also affect, though indirectly, the tendency of amalgam to corrode. I do not however intend to discuss these in detail here.

5. Marginal Inaccuracies of Amalgam Restorations

As mentioned in the introduction, secondary caries is the other form of damage that can result from the failure of amalgam fillings. Secondary caries can be defined as a type of caries with a causal relation to marginal inaccuracies of restorations.

There are many causes of marginal inaccuracies in amalgam fillings. A very frequent cause is marginal excess or deficiency; but as these defects are

only very slightly connected with the material properties of the amalgam, they will not be the subject of detailed discussion at this time. Contraction of the restoration during setting, with the resulting gap between the filling and the cavity wall, is unlikely ever to have been the direct cause of secondary caries; if however the amalgam margin is not supported by the enamel wall, then this margin if located on a loaded tooth surface will during mastication be deflected in toward the cavity wall; whether marginal fracture then occurs will depend on the relation between the width of the gap and the maximum flexibility of the margin. Calculations have demonstrated that weak amalgam margins can fracture under a very moderate load and even with such a slight deflection as 2 μ m. This shows that contracting amalgams involve an increased risk of marginal fracture and that they should not therefore be accepted.

It is a recognized fact that delayed expansion can in certain circumstances produce a marginal step of a size very likely to lead to secondary caries. Delayed expansion can also cause crevices in cases where the side walls of the cavity diverge toward the surface of the tooth. The cause of this is that the delayed expansion frequently occurs at considerably varying rates in different directions in the amalgam, and is greatest in the direction parallel to condensation. Delayed expansion can thus be a contributory cause of marginal fractures in which the fracture surface stretches considerably under the margin of the cavity.

It is not too complicated a process to avoid the causes of marginal inaccuracy already mentioned, and it is therefore unnecessary to go into further detail.

However, there is one further cause of marginal defects, namely marginal corrosion, which very frequently and seriously predisposes the margin of the filling to fracture. Figure 8 shows an occlusal

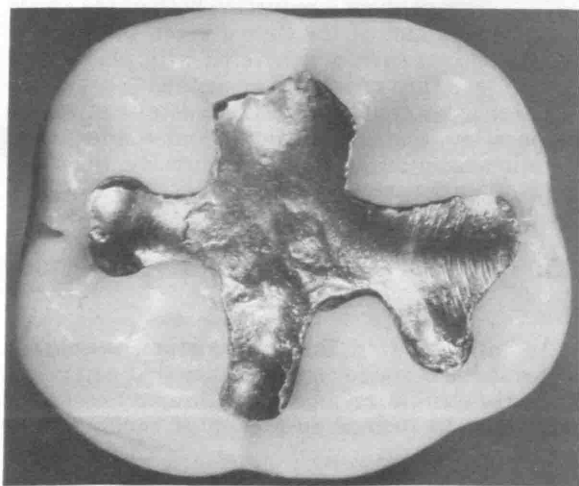


FIGURE 8. Occlusal filling with typical, marginal corrosion fractures.

filling with typical, marginal corrosion fractures. An analysis of the processes leading to corrosion fracture is rather complicated, involving both the materials science and technology, of amalgam.

The processes are as follows: shortly after a filling has been made, saliva penetrates between the filling and the wall of the cavity; because of the relatively low concentration of oxygen on the surface of the filling facing the cavity wall this surface will form the anode in a galvanic corrosion element. The mercury released by corrosion diffuses into the amalgam and causes mercurioscopic expansion. As this expansion involves only the surfaces facing the cavity wall, the margins of the filling are deflected away from the walls. Figure 9 shows the state of the filling margins after mercurioscopic deflection. Mercurioscopic expansion is fairly considerable, even when only relatively small quantities of mercury are absorbed; the amalgam expands about 5 percent linearly when it absorbs 1 percent by weight of mercury; the expansion increases significantly with increasing porosity of the amalgam. During mastication the unsupported amalgam margin will be deflected in toward the wall of the cavity, and it will fracture if the width of the corrosion gap exceeds the maximum flexibility of the margin. Figure 10 shows a typical corrosion fracture with the resulting V-shaped marginal defect; it has been shown that

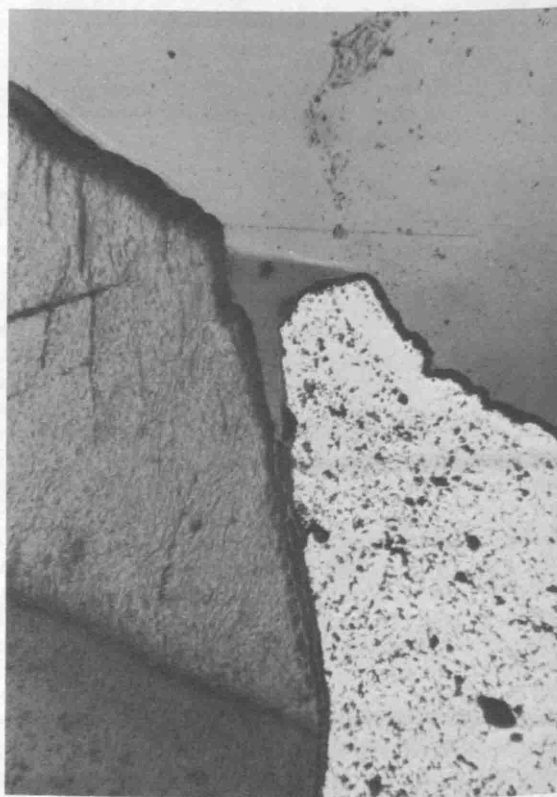


FIGURE 9. Filling margin after mercurioscopic deflection.

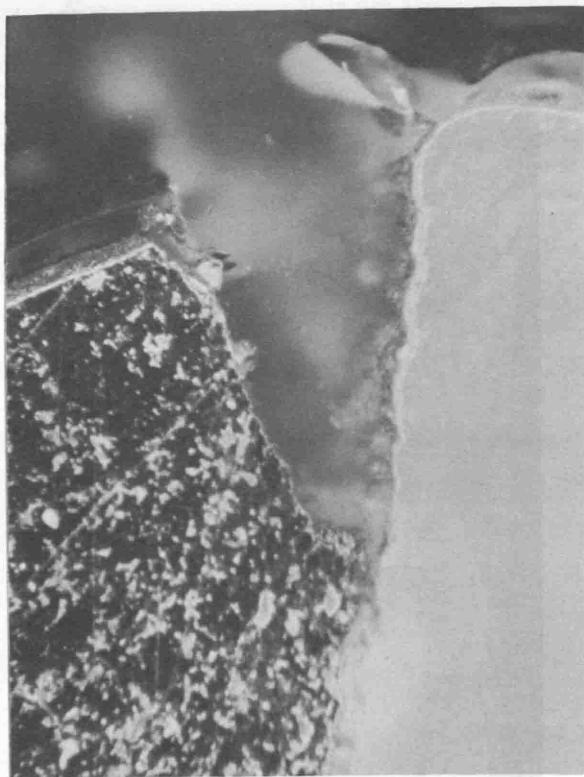


FIGURE 10. Typical corrosion fracture with resulting V-shaped marginal defect.

the risk of caries is very small when the width of the defect is less than $50\text{ }\mu\text{m}$; if this dimension however exceeds $50\text{ }\mu\text{m}$, the risk of secondary caries grows almost in proportion to its size.

An understanding of the processes which result in marginal corrosion fracture permits an analysis of the factors that influence these processes from the point of view that if it is possible to prevent or delay them, it will also be possible to prevent or delay corrosion fractures.

For marginal corrosion to occur requires—as already mentioned—that saliva penetrates the gap between filling and cavity wall. Two methods have been used to prevent this penetration, namely an improvement of the adaption of the amalgam to the cavity wall, and a varnishing of the cavity wall, primarily with copalite varnish; both of these methods reduce saliva penetration considerably—but not enough to prevent corrosion or merely influence the rate of corrosion.

The special structure of the γ_2 phase, even in well-condensed standard amalgams containing a minimum of mercury, shows that alterations in the quantity of this phase by modifying the condensation technique is also unable to reduce or prevent corrosion.

In contrast, porosity of the amalgam margin plays a decisive role in the rate of fracture. A high

degree of porosity increases to a great extent both the rate of corrosion and, independent of this, the mercuroscopic deflection of the margin. Increasing porosity reduces at the same time the margin's maximum flexibility to a marked degree. In order to reach a state in which it can fracture during mastication a porous amalgam margin requires less mercuroscopic deflection and it deflects more quickly than a margin with no or less porosity.

All such factors which influence the porosity of the amalgam margin are thus of significance to corrosion fractures. The diagram (fig. 11) shows the result of experiments on the significance of some technical factors for marginal porosity; A represents the dry technique, B the conventional technique, and C the wet technique. 1 means just filling the cavity with neither excess nor deficiency and without any further technical procedures, 2 means overfilling the cavity and eliminating the excess by carving, while 3 means overfilling, burnishing the margins, and then removing the excess by carving. It is seen that technique no. 3 ensured by far the lowest level of porosity; when this technique was followed, it was unimportant whether technique A, B, or C was employed. It may be added that the content of mercury in the amalgam margins examined was independent of the technique used; only in technique 1 it was somewhat higher.

It is probable but not directly proved that the marginal porosity will be increased by the use of nonzinc amalgams and rapid-setting amalgams.

Figures 12 and 13 illustrate the porosity in amalgam margins made by different techniques. Figure 12 shows a margin with a porosity of approximately 10 percent as a result of technique B-1, in other words, a conventional technique without overfilling or burnishing. Figure 13 is a margin

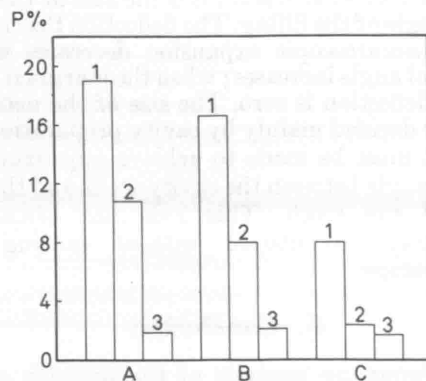


FIGURE 11. Effects of some technical factors on marginal porosity.

A—dry technique
B—conventional technique
C—wet technique

1—cavity not overfilled, margins not burnished
2—cavity overfilled and excess removed by carving
3—cavity overfilled, margins burnished and excess removed by carving.

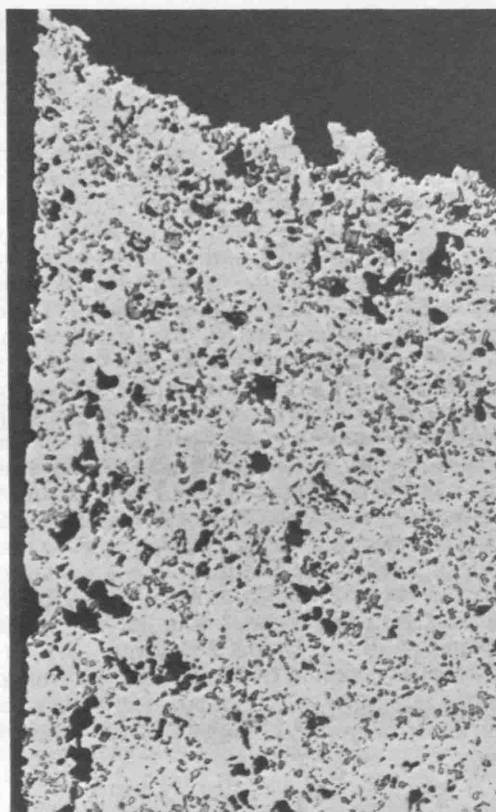


FIGURE 12. Amalgam margin with about 10 percent porosity produced by a conventional technique without overfilling or burnishing. Magnification—approx. 115X.

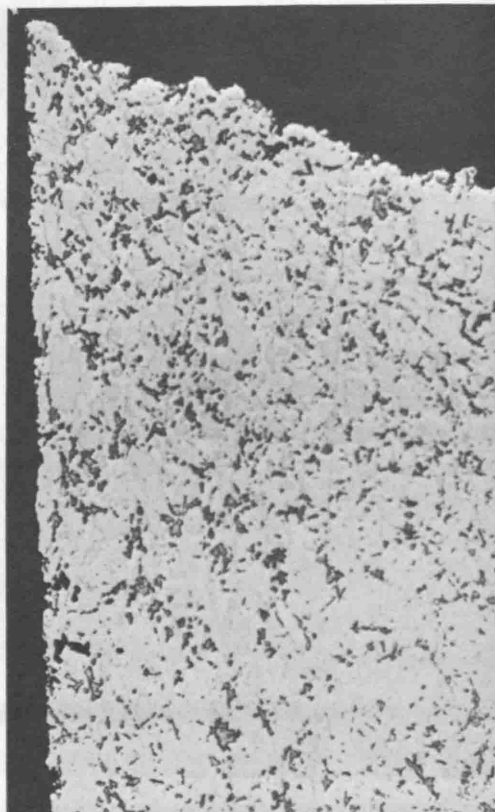


FIGURE 13. Amalgam margin with about 1 percent porosity after overfilling, burnishing and removal of excess. Magnification—approx. 115X.

with about 1 percent porosity after overfilling, burnishing, and removal of the excess.

Another factor of great importance to the occurrence of corrosion fractures is the size of the marginal angle of the filling. The deflection that results from mercurioscopic expansion decreases as the marginal angle increases; when the marginal angle is 90°, deflection is zero. The size of the marginal angle is decided mainly by cavity preparation. An attempt must be made to achieve approximately a right angle between the cavity walls and the surface of the tooth. This rule can often—but not always—be obeyed without causing any disadvantage.

6. Conclusion

The foregoing analysis of the primary causes of the failure of amalgam fillings provides the conclusion that moderate changes in the properties of the alloy, the amalgam technique, and cavity preparation can produce vast differences in quality of fillings. It is accepted that many amalgam fillings demonstrate excellent restorative properties; insofar as the analysis of the causes of many

amalgam-filling failures is correct, it is also a fact that the percentage of good quality fillings can be increased considerably by observing the conclusions of the analysis of defects.

The main recurring theme in this analysis of defects has been the corrosion of amalgam and the necessity of observing various details in the technical procedure; there is no doubt that future research into the properties of amalgams must be centered upon these two factors.

The deep corrosion in current standard amalgams depends primarily on the network structure of the γ_2 phase; if this structure can be broken, the deep corrosion will simultaneously cease. This appears to be possible only by a radical modification in the composition of the alloy, in which all the tin or most of it is replaced by another metal. Copper is not applicable in this connection because, among other things, it may form a rather rapidly corroding cohesive copper amalgam phase in the other amalgam; silver seems to be unsuitable too. On the other hand, palladium has certain properties that are promising.

If the amalgam technique is to produce fillings of high quality it is essential that several details of the technique are executed with pedantic accu-

racy. For various reasons it is not always possible to meet this condition in clinical practice—which must be regarded as a fault in the technique. Future research into amalgams must certainly be concentrated on this point also. The spherical amalgams may have a promising future in this respect; if their chemical composition were such that, during setting, a coherent, corrosive phase did *not* form, they might form the basis for a new and simplified filling technique very close to the ideal.

I want to close this paper with the following

general conclusion: Vast improvements have been made in the quality of dental amalgams over the past 50 years, particularly due to the research and standardization work carried out by the Dental Research Section of the National Bureau of Standards, to the benefit of the dental profession, particularly, and humanity in general. I feel convinced that you will continue in the future to make significant contributions to the development of this important material. It is a great pleasure to be your guest here, and I thank you most warmly for your gracious invitation.

Basic Metallurgy of Dental Amalgam

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An "equilibrium" mixture of components of dental amalgam would contain the phases β_1 , γ_1 and γ_2 shown by Gaylor. Because dental amalgam is formed clinically at relatively low temperature only γ_1 and γ_2 are generally found. The tensile strengths of the Ag-Hg and the Sn-Hg matrix phases of dental amalgam are considerably below the tensile strength of the amalgam while the tensile strength of Ag_3Sn is considerably above that of the amalgam. Cleaning the alloy powder with 5 percent HCl promotes better bonding between matrix and Ag_3Sn and significantly increases the tensile strength. The γ_2 phase of amalgam is the only phase subject to destructive corrosion. The γ_2 phase has been successfully eliminated from amalgam by two methods: (1) by inclusion of powder consisting of the Ag-Cu eutectic in the alloy and (2) by substitution of 10 percent Au for Ag in the alloy.

Key words: Amalgam, dental; amalgam, metallurgy; amalgam, strength; corrosion of dental amalgam; dental materials; metallurgy of dental amalgam.

1. Introduction

Probably the most successful prosthetic material ever devised by man is dental amalgam. This accounts, no doubt, for the millions of man hours of labor which have been devoted to research on this material and the volumes of literature devoted to reporting this research.

No group has contributed as much toward the excellence of this material as the research group at the National Bureau of Standards. It is they who have set the high standards for the development of a fine product.

In any review of the literature covering dental amalgam, one can only hope to scratch the surface if he is to keep inside a reasonable time limit. Much good work must be summarized in a sentence or perhaps not mentioned at all. This paper will attempt to review what the authors consider to be the most significant advances in the knowledge of the basic science involved in the composition, strength and chemical properties of dental amalgam.

2. Constitution

Although the first person to use an amalgam as a dental restorative is not known, the first scientific investigation of dental amalgam must surely be credited to G. V. Black, beginning about 1895. It was he who showed that the most useable dental alloy was one containing near 75 atomic percent Ag and 25 percent Sn, with perhaps a slight substitution of Cu for Ag (about 5%) desirable.

Since the time of Black's work only minor changes have been made in the basic composition of dental alloy. Research efforts have been concen-

trated on the determination of the setting reaction or reactions and the constitution of the set amalgam. Although advances in knowledge have been almost continuous, probably no single bit of information could be considered to be a breakthrough for dentistry such as Black's original contribution. Nevertheless, a number of significant advances have been made.

Probably of foremost importance were the accurate determinations made of the binary constitution diagrams for Ag-Sn, Ag-Hg, and Sn-Hg and determinations of crystal structures for most of the important phases in these systems. Outstanding among these investigations were those by Murphy and his co-workers [1]¹. Almost no major changes have been made in the constitution diagrams published by this group. Generally accepted phase diagrams for these binary systems are shown in figures 1, 2, and 3.

For the Ag-Hg system, Murphy established two peritectic reactions resulting in two phases of restricted composition. The β phase was determined to be hcp with $a = 2.98\text{\AA}$ and $c/a = 1.62$ and the γ phase complex bcc with $a = 10.0\text{\AA}$. Berman and Harcourt [2] described two naturally occurring phases of the Ag-Hg system (α and γ) and suggested the name moschellands-bergite for the γ phase. Its composition is best represented as Ag_2Hg_3 and the unit cell contains 50 atoms.

Nial, Almin, and Westgren [3] determined the structure of Ag_3Sn to be slightly rhombically deformed hcp with four atoms per unit cell and $a = 2.995\text{\AA}$ and $c/a = 1.596$ at 25 atomic percent Sn.

¹ Figures in brackets refer to the literature references at the end of this paper.

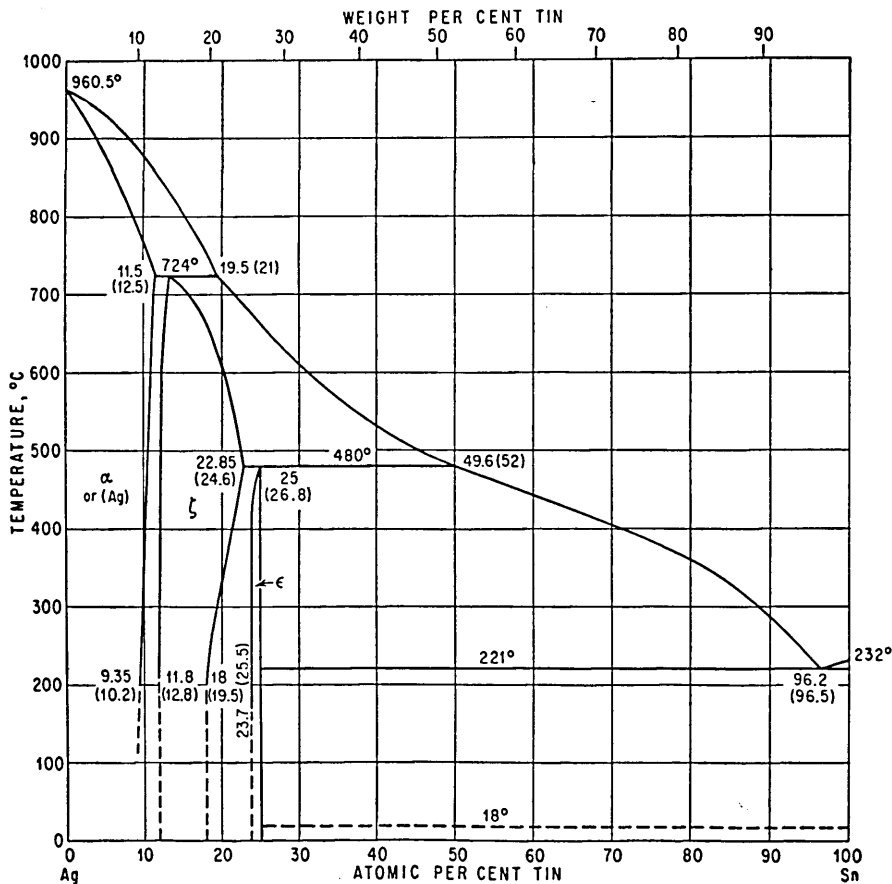
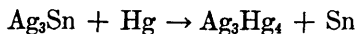


FIGURE 1. Constitution diagram for the Ag-Sn system.

V. Simpson [4] reported the γ phase of Sn-Hg to have a simple hexagonal structure with $a = 3.213\text{\AA}$ and $c/a = 0.931$ at 7.19 atomic percent Hg.

Although a number of researchers had studied the ternary system of Ag-Sn-Hg between about 1910 and 1930, undoubtedly the most extensive investigation was that by Gayler [5] from about 1933 to 1937. Her 70° C and 100° C isotherms for the system are shown as figures 4 and 5.

Prior to Gayler's studies, McBain and Joyner [6] had proposed the first "setting reaction" for dental amalgam:



Gayler showed that Sn did not form as a product of the reaction and explained the setting by complex reactions which probably do not go to completion. She proposed the following equations:

1. $\text{Ag}_3\text{Sn} + \text{Hg} \rightarrow \beta_1 + \gamma_2$
2. $\beta_1 + \gamma_2 \rightarrow \beta_1 + \gamma_1 + \gamma_2$

Her nomenclature follows from figure 4.

Troiano [7] agreed with Gayler concerning the equilibrium phases expected to be present,

(β_1 , γ_1 and γ_2), but disagreed with the steps involved, in order to attempt to account for the nonequilibrium manner in which dental amalgam was prepared. He proposed the following equations:

1. $\text{Ag}_3\text{Sn} + \text{Hg} \rightarrow \gamma_1 + \delta_2 + \text{Ag}_3\text{Sn}$ (unreacted)
2. $\gamma_1 + \delta_2 + \text{Ag}_3\text{Sn} \rightarrow \gamma_1 + \gamma_2 \rightarrow \gamma_1 + \gamma_2 + \beta_1$

Troiano defined δ_2 as Sn_7Hg which was later shown by Fairhurst and Ryge [8] to be γ phase of the Sn-Hg system. He also defined γ_1 to be Ag_3Hg_4 . Extensive investigations of the setting reactions for dental amalgam were made from 1952-60 by Moffett, Ryge and Barkow [9]. This group used a recording x-ray spectrometer to determine the phases formed and their chronological appearance. They concluded that Hg reacts with Ag_3Sn to form a matrix of Ag_2Hg_3 (γ_1) and the hexagonal γ phase of the Sn-Hg system (γ_2). These phases could be detected within 10 minutes of the beginning of trituration and no other new phases were identified at any time.

Schmitt [10] used selective etching techniques to distinguish only three phases in set amalgam, the original Ag_3Sn (γ), γ_1 and γ_2 .

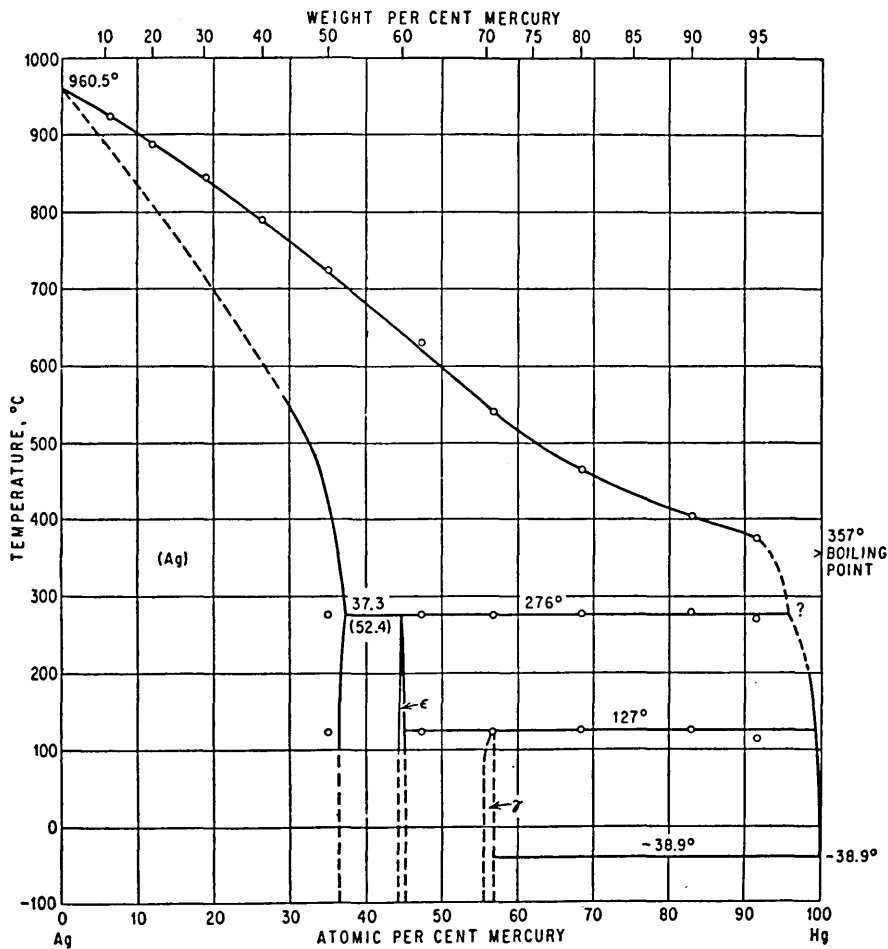


FIGURE 2. Constitution diagram for the Ag-Hg system.

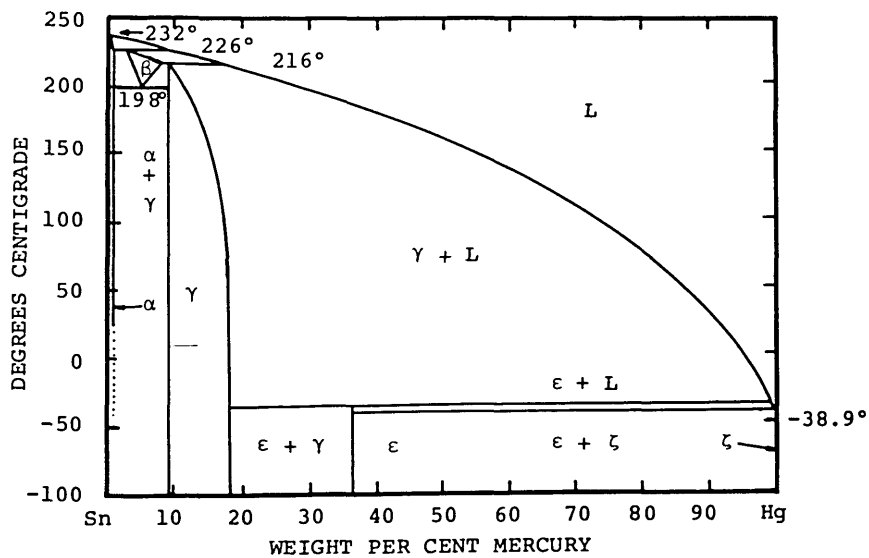


FIGURE 3. Constitution diagram for the Sn-Hg system.

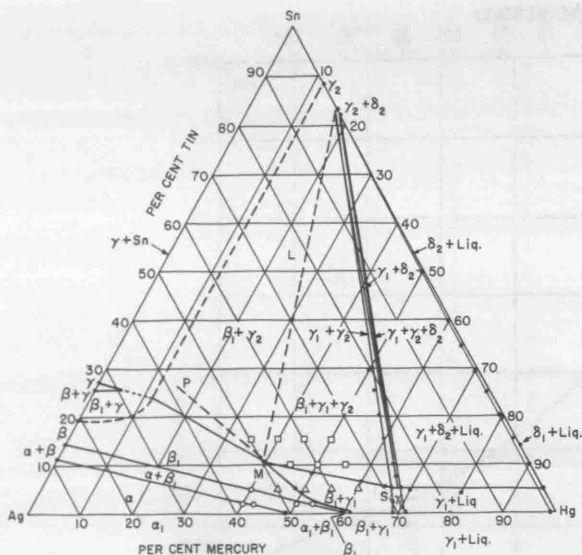


FIGURE 4. 70 °C. Isotherm for the Ag-Sn-Hg system [5].

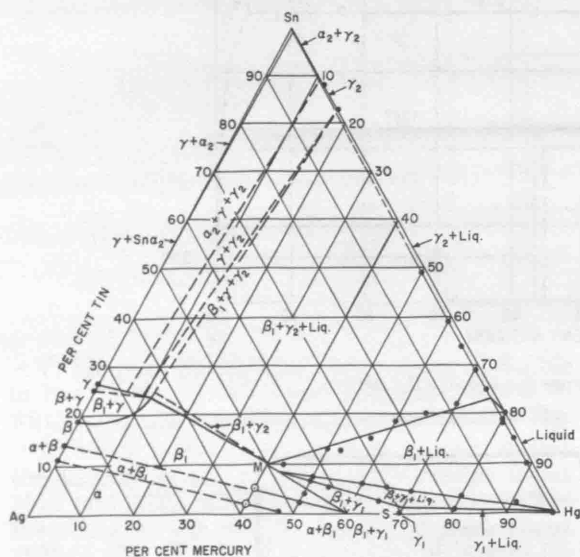


FIGURE 5. 100 °C isotherm for the Ag-Sn-Hg system [5].

A great deal of impetus toward further research into the structure of set amalgam was provided by the development of spherical-particle alloys by Demaree and Taylor [11]. Using this type alloy, Wing and Ryge [12] identified the same three phases in set amalgam, (fig. 6) (γ , γ_1 and γ_2) and made the interesting observation that most of the original alloy particles remained unreacted, even in large excess of Hg (70 percent). It appeared that the reactions were "self limiting."

None of these latter studies of the setting of dental amalgam were able to identify at any time during setting the presence of the β_1 phase called for by Gayler and Troiano. Johnson [13] showed the presence of the β_1 phase in dental amalgam, but

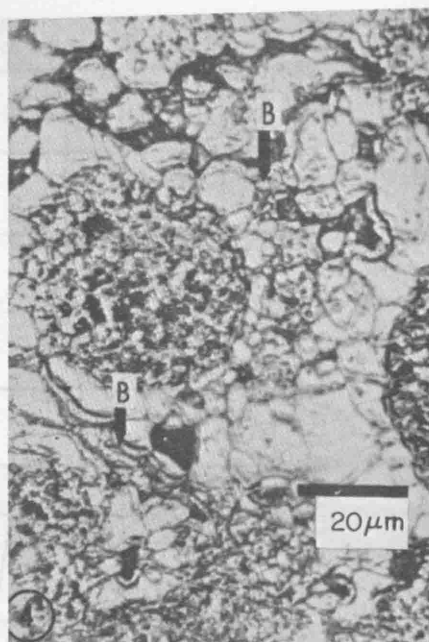


FIGURE 6. Microstructure of dental amalgam.
B indicates the Sn-Hg phase [12].

only after the set amalgam had been stored at elevated temperatures (38° and 60° C) for considerable periods of time. He considered that the β_1 phase formed by a diffusion controlled transformation of the γ_1 phase, the transformation rate being very temperature sensitive.

More recently, Otani [14] has identified the β_1 phase in dental amalgam stored at room temperature for two years. Furthermore, Otani, Tsutsumi and Yamaga [15] have demonstrated the strong dependence of the phase relations on temperature. In dental amalgam allowed to set at temperatures above 80° C, in fact, no γ_1 phase was found at any stage, only β_1 and γ_2 . The same amalgam, however, when moved to room temperature for 48 hrs, showed the formation of γ_1 phase at the expense of part of the β_1 . Thus, the final amalgam prepared in this manner satisfied Gayler's diagram.

It is interesting to note that the photomicrographs of both Johnson and Otani (fig. 7 a & b) showed the β_1 phase as being continuous with the original γ particles. An amalgam made entirely of this "monophase" would be expected to have excellent mechanical and electrochemical properties.

It appears at this point that there is no basic disagreement among the investigations reviewed above. It is apparent that Gayler is correct in her assessment of the phases present in an "equilibrium" dental amalgam at, say, body temperature, i.e., $\beta_1 + \gamma_1 + \gamma_2$. It is equally apparent that a transition temperature exists near 80 °C, since Gayler's 100 °C isotherm shows $\beta_1 + \gamma_2 +$ liquid and Otani's dental amalgams allowed to set at any temperature above 80 °C showed β_1 and γ_2 as the only solid

phases. Therefore, dental amalgam prepared above 80 °C, then cooled to body temperature, will contain a near-equilibrium mixture of $\beta_1 + \gamma_1 + \gamma_2$.

Dental amalgam prepared under clinical conditions, however, is not at equilibrium and the work reviewed here has shown clearly that the β_1 phase is not present at any stage in the setting of the amalgam—at least in a distinguishable quantity. In time, however, β_1 phase forms at the expense of part of the γ_1 phase—the higher the temperature the more rapid the transformation. Therefore, dental amalgam prepared at room or body temperature will eventually contain a near-equilibrium mixture of $\beta_1 + \gamma_1 + \gamma_2$ as required by Gayler's diagram. The higher the temperature the sooner will equilibrium be established.

The exact mechanism by which the setting of dental amalgam takes place is still not thoroughly understood. It is greatly complicated by the fact that one begins with a problem of sintering in a liquid medium and ends up with a problem in solid state diffusion. The one point that has become clear, however, is that every change undergone by the system is a striving for the attainment of the state of equilibrium required by Gayler's isotherm.

3. Strength

Three intermetallic phases are the main constituents of dental amalgam, designated γ , γ_1 , and γ_2 as described previously. Since the alloy is produced by sintering in the presence of a liquid phase, many metallurgical factors influence the properties of the final material. Table 1 gives an indication of the complexity of the manufacture of this alloy and the effect on some properties.

Before a discussion of the strength of dental amalgam is presented, the mechanical properties of the three phases, γ_1 , γ_2 , and γ , will be discussed separately.

3.1. Silver Amalgams

The largest volume of dental amalgam is occupied by the Ag-Hg phase, present as an intermetallic compound closely represented by the formula Ag_2Hg_3 . At present, there is no general theory explaining the mechanical properties of intermetallic compounds.

The fracture strength of Ag-Hg alloys was determined by Young and Wilsdorf [16, 17]. Because of the large difference between the melting temperatures of the two components, preparation of the cast alloys proved difficult. Suitable tensile specimens, however, were prepared simply by mixing Ag powder (99.99 percent purity) with Hg and compacting the mixture into a die at room temperature. The Hg content was controlled by varying the reaction time and the amount of Hg available. Alloys were prepared in this manner containing 15–70 weight percent Hg.

The tensile strength of these specimens is shown in figure 8, ranging from more than 9,000 psi (62 MN/m²) at low Hg contents to about 2,000 psi (14 MN/m²) for alloys containing 50 to 70 weight

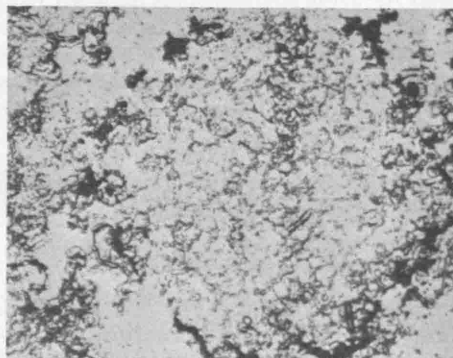


FIGURE 7a. Alloy particle surrounded by β_1 phase [13].

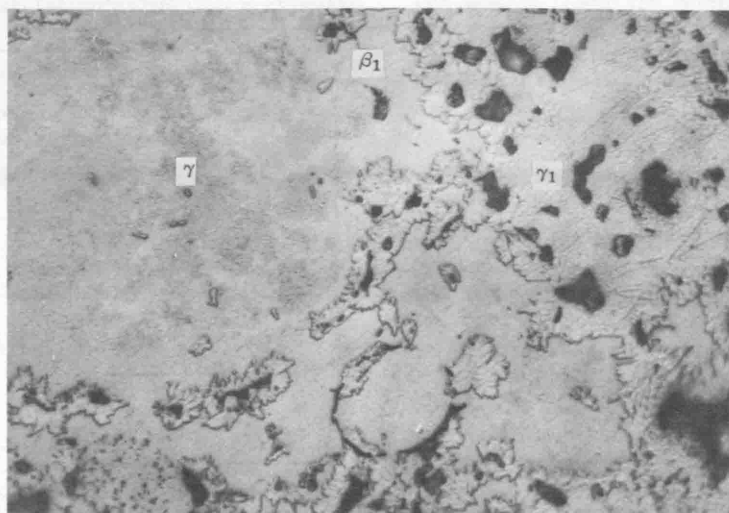


FIGURE 7b. β_1 phase in dental amalgam [14].

TABLE 1. Metallurgical factors which influence dimensional stability, flow, and strength of dental amalgam

Metallurgical factors	Mechanical properties affected
Silver-tin alloy: Composition Particle size Particle shape	Increased tin content→abnormal contraction Increased silver content→abnormal expansion Smaller particle size→strength attained in shorter time →decrease in expansion Spherical powders are not so sensitive to packing pressures as cut alloys and therefore often yield more desirable over-all properties.
Alloy: mercury ratio	Increasing the amount of mercury→reduction in compressive strength →undesirable increase in flow Too little mercury→expansion of amalgam decreases unduly
Trituration	Increasing the time of mixing→increased strength →undue reduction of expansion
Condensation	Increased pressure→decrease in expansion →decrease in flow
Contamination	Through moisture (for alloys containing zinc)→delayed and rather excessive expansion

percent Hg. In order to assure complete bonding, specimens were pressed at 100° C for 3 days and tensile tested. Although the strength was greatly improved for alloy compositions between 15 and 60 weight percent Hg (fig. 9), the strength for the Ag-70 weight percent Hg specimen was comparable to the value shown in figure 8. Since the latter composition is near that of the Ag-Hg matrix phase of dental amalgam, it must be concluded that its strength is considerably lower than the tensile strength of dental amalgam, the latter value being 7,000-9,000 psi (48-62 MN/m²).

3.2. Tin Amalgams

The second constituent in the "matrix" of dental amalgam is a Sn amalgam containing approximately 18 weight percent Hg. It has been identified as Sn₈Hg and is generally referred to as the γ_2 phase. Since the exact composition is not known

with certainty and since some γ_2 grains could have a lower Hg content, tensile specimens for Sn amalgams containing from 2 to 20 weight percent Hg have been tested.

Alloys were prepared by casting and also by a powder metallurgical technique [16].

The cast alloys were obtained by sealing instrument grade Hg with chemically pure Sn into an evacuated quartz tube and holding it for 30 minutes at 250° C. Frequent agitation assured homogeneity. The liquid alloy was quenched in liquid nitrogen for solidification. After annealing for 7 days at room temperature, tensile specimens were machined having a 1-in (25 mm) gage length and 0.250-in (6.35 mm) diam. Cylindrical compression specimens were 0.375 in (9.52 mm) in height and diameter.

Powder-compacted specimens were prepared by mixing 325 mesh Sn powder with Hg in a plastic

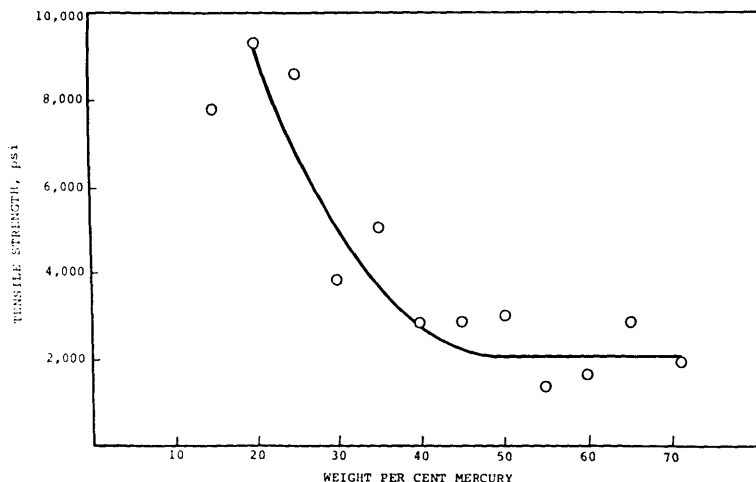


FIGURE 8. Tensile strength of cold-pressed Ag amalgams.

(To convert psi to MN/m² multiply by 6.895×10⁻³).

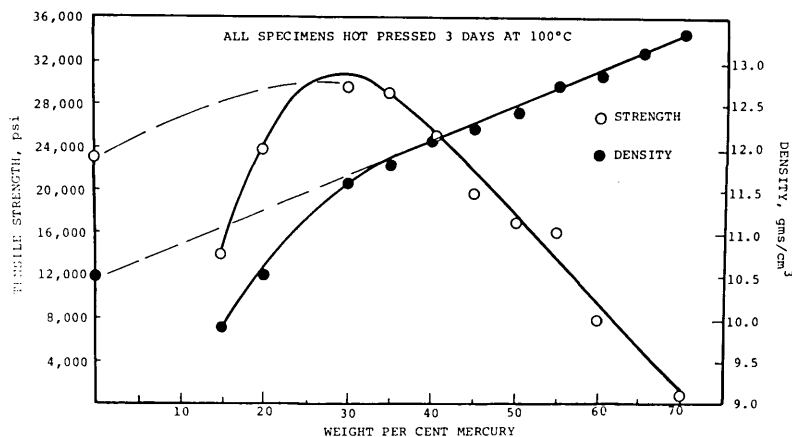


FIGURE 9. Tensile strength of hot-pressed Ag amalgams.

(To convert psi to MN/m² multiply by 6.895×10^{-3}).

capsule in a Spex mixer mill. The plastic mass was immediately compacted in a die having the dimensions of a flat standard tensile specimen.

The data obtained are shown on figure 10. Rising from the fracture stress of pure Sn at 3,600 psi (25 MN/m²) to almost 10,000 psi (70 MN/m²) at 8 or 9 weight percent Hg, the tensile strength decreased sharply as the Hg content was increased from 12 to 20 weight percent. It should be noted that the stress maximum coincided with the phase change from the $\alpha + \gamma$ phase field to the γ phase of the system, which at room temperature may contain approximately 9–18 weight percent Hg. Beyond 18 weight percent Hg, free Hg coexists with the solid γ phase.

The information from the phase diagram offers a possible explanation for the variation of strength and ductility with Hg content. Between 2 and 9 weight percent Hg, γ is present in the α solid solution as a second phase and thereby an effect comparable to precipitation hardening is expected

to occur. The low strength above 18 weight percent Hg is due to the presence of liquid Hg which acts as crack nuclei in the alloy.

With the exception of the 20 weight percent Hg alloy, powder compacted specimens showed much lower strength. Since the reaction between Sn powder and Hg is very fast, the compacting was virtually done with γ particles. Consequently, the bonding between the particles was poor. Porosity was not more than 4 percent.

Compression tests on cast specimens showed measurable ductility, particularly for those with low Hg content. A value of 10,000 psi (69 MN/m²) was obtained for the 20 weight percent Hg specimen.

As indicated above, the γ phase of the Sn-Hg system is of importance in dental amalgam, the most likely Sn-amalgam present containing about 18 weight percent Hg. The tensile strength of this alloy was found to be rather low, about 3,000 psi (21 MN/m²), and the compressive strength about 10,000 psi (69 MN/m²). Both values are considerably below the corresponding strengths of dental amalgam.

3.3. Dental Amalgam Alloy

“Dental amalgam alloy” is the name commonly used for the powder which, when mixed with liquid Hg, yields dental amalgam. Its chemical composition is Ag₃Sn. It is present in appreciable quantities as “unconsumed” alloy in the amalgam and consequently, must play a role in its mechanical properties.

For the preparation of the alloy a vacuum technique was used [16] since alloys melted and cast in conventional ways were found to be extremely brittle. This latter was probably due to the introduction of oxygen since molten Ag is known to attract a substantial amount of oxygen which, upon solidification, precipitates at grain boundaries.

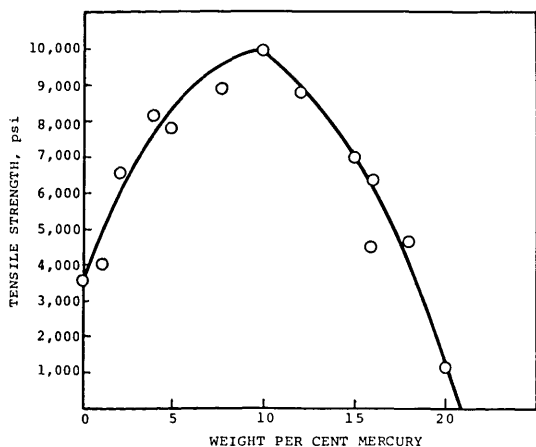


FIGURE 10. Tensile strength of cast Sn amalgams.

(To convert psi to MN/m² multiply by 6.895×10^{-3}).

3.4. Dental Amalgam

Dental amalgam alloy is the product of a peritectic reaction and contains 26.85 weight percent Sn. The times required to reach phase equilibrium are extensive and appear to be prohibitive when manufacturing the alloy. In order to determine the sensitivity of the strength of dental amalgam alloy to compositional changes, two additional alloys containing 23.85 weight percent Sn and 29.85 weight percent Sn were prepared. The former, therefore, contained more of the β (Ag-Sn) phase while the latter contained more of the Sn-rich eutectic.

None of the specimens showed any ductility beyond 1 percent strain, so that only the fracture strength for tensile loading and compression could be determined.

The compressive and tensile strengths of chill cast Ag_3Sn were determined to be 75,000 psi (520 MN/m^2) and 25,000 psi (170 MN/m^2) respectively. Corresponding values for annealed dental amalgam alloy were considerably lower. Young [16] found evidence for precipitated films in annealed specimens, which could be responsible for the reduced strength. It appears reasonable to assume that chill-cast or slowly cooled alloy is representative of dental amalgam alloy used in clinical application.

The tensile strengths of chill-cast Ag-Sn alloys with Sn contents 3 weight percent higher or lower than the γ composition were found to be slightly increased (see table 2) though not to a marked degree. The microstructure, of course, was different, containing β crystals in one alloy and δ crystals in the other. As far as dental amalgam is concerned, this strength difference is hardly of concern. It should be noted, however, that the difference in microstructure is most likely to influence the amalgamation reaction.

Briefly, it has been shown that Ag_3Sn is considerably stronger than dental amalgam and, consequently, must have a decisive influence on the strength of the latter.

TABLE 2. Fracture strength of silver-tin alloys

Alloy containing weight-percent Sn	Heat treatment	Tensile	Compressive
		psi	psi
23. 85	Chill cast.....	30, 600	77, 700
23. 85	Annealed.....	*25, 000	65, 200
26. 85	Slowly cooled.....	23, 000	-----
26. 85	Chill cast.....	25, 000	75, 000
26. 85	Annealed.....	*17, 500	44, 800
29. 85	Chill cast.....	26, 500	73, 200
29. 85	Annealed.....	*14, 000	49, 300

Tensile specimens had a 1 in (25 mm) gage length and either a gage diameter of 0.140 in (3.56 mm) or 0.25 in (6.35 mm), the latter being indicated by *. Compression specimens were 0.375 in (9.52 mm) long and 0.375 in (9.52 mm) in diameter. (To convert psi to MN/m^2 multiply by 6.895×10^{-1} .)

The clinical importance of Ag-Sn amalgams in dentistry has determined the nature of the research that led to the excellent restorative we have today. The restrictions in producing the amalgam under clinical conditions are a challenge to the metallurgist. First, the amalgam must be made easily and quickly in the dental office at room temperature. Second, it must be capable of being molded to fit the cavity in a tooth so that mechanical forces will keep it in place. Third, setting must occur at 37 °C, with the amalgam reaching a high strength in a reasonably short period of time.

Two of the most important clinical requirements should be mentioned at this point: (1) a linear expansion of the restorative of not more than 20 $\mu\text{m/cm}$ and (2) a high resistance to creep (in dental literature, usually referred to as "flow").

Since dental amalgam is brittle, the compressive strength has been used as a convenient and important criterion for assessing the effect of certain metallurgical variables. The nature of these variables will be indicated by a selection of publications.

In 1949 Phillips [18] investigated the time dependence of the setting of amalgams. He found that the 10-hr strength was about 80 percent of the final, and that full strength was often attained after setting times of 24 hr. Some alloys, however, required about 7 days to attain full strength, so from this time on compressive strengths were usually given in terms of "7-day strength."

A detailed study showing the effect of varying condensation methods and time, specimen size, and deformation rate was reported by Taylor, Sweeney, Mahler and Dinger [19]. They also reported elastic moduli ranging from 1.2 to 2.1×10^6 psi (8.3 to 14.5×10^3 MN/m^2) for five dental amalgams. Studies of this nature, going into considerable detail with respect to clinical factors, were carried out through the 1950's and virtually concluded at the beginning of the last decade. At that time some concern was noted about the strength of dental amalgam in tensile loading.

Souder and Paffenbarger [20] reviewed the early work on that subject through 1942 and emphasized that the tensile: compressive strength ratio was extremely unfavorable, namely 1:8 or even poorer for some preparations.

The renewed interest in tensile strength in the 60's coincided with (1) the availability of spherical dental alloy powders, used initially at the National Bureau of Standards by Demaree and Taylor [11], (2) the marked improvements in metallographical techniques in handling dental amalgam by Wing [21], and (3) the successful application of the diametral test to this material by Burns and Sweeney [22].

Prior to the last mentioned investigation the measurements were made on tensile specimens the shape of which had been conditioned by the brittleness and the manufacture of the material. In gen-

eral, the gage length was less than 0.5 in (13mm) (Ward [23], Taylor [24], Rodriguez and Dickson [25], and Mahler and Mitchem [26]). Additional studies were carried out in 1964 by Hollenback and Villanyi [27] and in 1968 by Nagai and Ohashi [28]. In general, these investigators found a 7-day tensile strength between 6,000 and 8,400 psi (41 and 58 MN/m²). The data on each material in each series of measurements were reproduced only over a wide range of values since the fracture of the dumb-bell shaped specimens was sensitive to surface flaws.

Following the work of Burns and Sweeney [22], the diametral tensile test has been used to provide reliable data for dental amalgam. The advantage of this method lies in its insensitivity to surface conditions of the specimen. The cylindrical specimen is placed between the plates of a testing machine and compressed transversely. A convenient specimen diameter is 4mm, the length of the cylinder is usually between 5 and 10 mm. According to a treatment by Timoshenko [29], the tensile stress, σ , is related to the compressive load, P , the diameter, d , and length, l , of a right cylinder by the equation

$$\sigma = \frac{2P}{\pi dl}$$

where σ is the tensile stress in a plane normal to the plane of the load.

Using the above method, Eden and Waterstrat [30] measured a tensile strength of spherical-particle dental amalgam of almost 8,000 psi (55 MN/m²); Young and Wilsdorf [17] reported

9,000 psi (62 MN/m²) (fig. 11), Modjeski and Nuckels 10,600 psi (73 MN/m²) [31] and Nagai et al. [32] 10,000 psi (69 MN/m²).

A comparison of tensile strengths obtained from dumbbell shaped specimens and from diametral tests indicates frequently a higher value for this property from the latter test, so that the ratio of tensile and compressive strengths is approximately 1:6. However Burns and Sweeney [22] obtained comparable values for the diametral and the axial loading methods.

Recently, Lautenschlager, and Harcourt [33] pointed out that the diametral test is only applicable to homogeneous materials and that in specimens with pores and second phase particles the actual values may be altered. Seen in this light, it is interesting to note that Nagai et al. [32] found substantial strength differences for conventional and spherical alloys when specimens compacted at different pressures were subjected to the diametral tensile test. While conventional alloys showed a strength reduction of about 50 percent for a lowering of the condensation pressure from 850 to 71 psi (5.9 to 0.49 MN/m²), the strength difference for spherical-particle alloys was in general not more than 25 percent and often less.

At this time it is not possible to arrive at an understanding of the mechanical properties of dental amalgam. After having obtained a clearer picture of the microstructure during the past decade, it is obvious that this 3-phase alloy does not fit into any of the alloy categories from which the metallurgist can draw on a theory of strengthening. Most of the information on the strength of

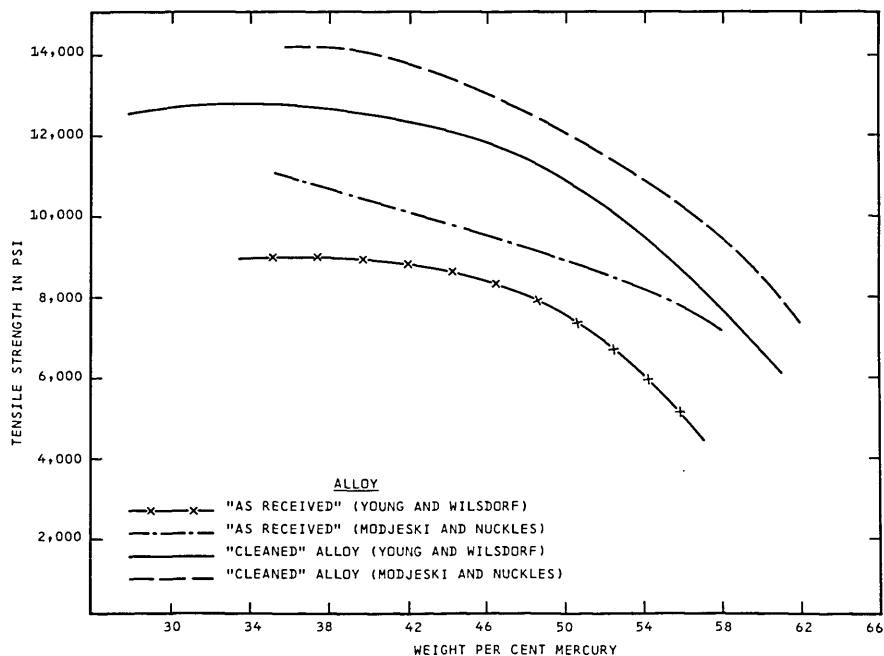


FIGURE 11. Tensile strength of dental amalgam [17].
(To convert psi to MN/m² multiply by 6.895×10⁻³).

dental amalgam is based on macroscopic tests. In order to separate different parameters, such as alloy particle size and shape, Hg content, trituration time, condensation pressure and time, specific surface area, and others, detailed studies of the microstructure are needed. This includes an understanding of the influence of pores on the shape of the phases, the effect of surface contaminants, and the atomic structure of phase and grain boundaries, to name a few topics only. Nevertheless, advances in the understanding of the strength have been made in recent years and these will be reviewed together with new measurements on relevant properties.

Strength measurements on dental amalgam normally show wide scatter, exceeding by far the experimental error. Anticipating that surface contaminations of the Ag_3Sn particles could cause flaws in the amalgam and possibly would act as crack nuclei or, in any event, be detrimental to the bonding between phases, Young and Wilsdorf [17] prepared surface clean dental alloy. They washed spherical alloy powder in 5 percent HCl and dried the particles with ethanol. It was observed that the reaction time for amalgamation was reduced by this process and that the strength of the resulting amalgam had increased from 9,000 to 12,500 psi (62 to 86 MN/m^2). Modjeski and Nuckels [31], using the same method, obtained tensile strengths of 14,000 psi (96 MN/m^2). An explanation of the strength increase will be offered in a subsequent paragraph.

The macroscopic failure of dental amalgam is classified as brittle fracture, i.e., the separation occurs in a catastrophic fashion. Information on the fracture mechanism is incomplete. Asgar and Sutfin [34] employed a microbend tester and used light microscopy in order to study the subject on a microstructural basis. They observed that cracks went through voids and propagated through the matrix phases (γ_1 and γ_2 are traditionally called the "matrix") in an intercrystalline manner. These results were confirmed by Caron's [35] investigation of fracture due to compressive loading. The latter author also reported the fracturing of alloy particles in specimens produced at high packing pressures.

The application of electron fractography allowed additional observations at the submicroscopic level. A schematic representation of the microstructure of dental amalgam prepared from spherical alloy particles is shown in figure 12. Using replica techniques, Young and Wilsdorf [17] concluded from fracture surfaces that cracks propagated in an intercrystalline manner for amalgams prepared from untreated alloy powder. They noted, however, that the Sn-Hg phase showed a certain degree of ductility during failure, as evidenced by small dimples on the surface. The fracture surface of Ag-Sn crystals showed primarily facets, indicating intergranular and/or interphase fracture, the latter of which was typical for cracks

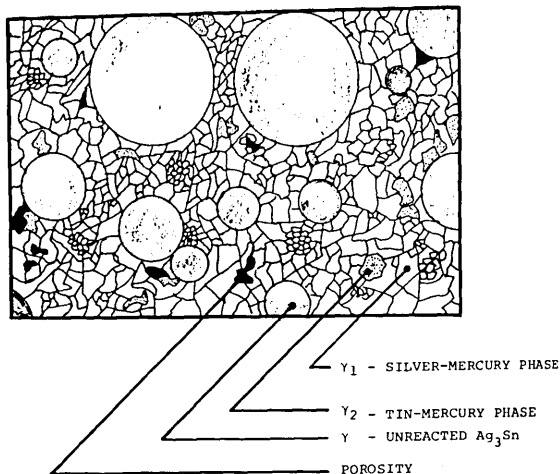


FIGURE 12. Schematic representation of micro-structure of dental amalgam.

going around the unconsumed Ag_3Sn particles. Dental amalgam made from "cleaned" alloy particles also fractured in an intergranular fashion with one remarkable difference—cracks were found not to avoid Ag_3Sn particles but proceeded through the particles by cleavage. This observation gives a lead to an explanation of the increased strength of amalgams made from "cleaned" alloy. One could reason that the fracture of Ag_3Sn particles is either due to a notch effect, which would have weakened the relatively high strength Ag_3Sn , or the bonding between the matrix and the particles was improved by the cleaning techniques. Since the amalgam showed a definite increase in strength, it must be concluded that the bonding between matrix and Ag_3Sn was improved.

At this stage of the development of the metallurgy of dental amalgam it is not possible to assess the influence of porosity on the mechanical properties in a quantitative manner. In the past, the fundamental studies have tried to minimize porosity by using high condensation pressures (see for example, Young and Wilsdorf [17] whose samples had a porosity of less than three percent). However, it can be expected that porosity in clinically prepared amalgam is higher and present techniques of investigation have to be improved in order to make better quantitative measurements. It is felt that the use of the scanning electron microscope could be very helpful in this respect.

Another mechanical property of considerable importance for the clinical behavior of amalgam is creep. Extensive studies have been carried out, but the actual mechanism in terms of advanced solid state theory is still elusive. The intriguing problems associated with the behavior of dental amalgams have attracted a larger group of solid state researchers, and a number of fundamental data which are needed for even a first understanding of the often unexpected properties of the alloy are beginning to appear in the literature. The work

on elastic constants of the γ , γ_1 , γ_2 -phases and dental amalgam by Grenobie and Katz [36] may be quoted as an example. On the basis of their measurements they attempted to develop a model of the elastic behavior of dental amalgam which with further refinement could provide information on the viscoelastic behavior and on the effect of porosity and mercury content on strength.

4. Chemistry

The constitution and mechanical properties of amalgams are primarily bulk properties of the material and can, in general, be considered to be unaffected by the environment, within practical limits, at least for a period of a number of years. Yet all metal or alloy surfaces react with their environment to produce changes in the surfaces. These changes depend on many variables, among which are the particular constituents present in the environment, the composition of the metal itself, the physical character of the surface or interface with the environment, the flow of material past the surface, and the temperature.

The many variables involved make the study of the chemistry of the system of dental amalgam plus oral environment a difficult one. In vivo studies are beset with the difficulties that no two human mouths offer the same environmental constituents, no two amalgam surfaces placed in teeth are ever identical, and flow situations are never the same for any two fillings. In vitro studies, on the other hand, while allowing much closer control of variables, have the decided disadvantage of being very unlike clinical conditions. This not only makes factual correlations difficult to make but also makes it difficult to convince clinicians that correlations exist even when they are apparent to the laboratory scientist.

Nevertheless, advances in the understanding of the corrosion of dental amalgam have been made, especially in the last decade or so.

Prior to about 1940, although numerous studies related to the corrosion of dental amalgam were made, the major emphasis was generally placed on the pathological effect on body tissues of galvanic currents produced by dissimilar metals in the mouth. Little effort was made to note the effect on the metals themselves.

In 1941 Schoonover and Souder [37] published the first really extensive study of the corrosion of dental amalgam. They reported rapid corrosion of dental amalgam in contact with Au in both 1-percent NaCl solution and in an artificial saliva, but only gradual corrosion with loss of luster when it was not in contact with Au. Potential difference between the two metals varied between 445 and 548 mV.

Examination of 40 to 50 freshly extracted teeth containing amalgam fillings showed that, where adaptation of the filling to the cavity wall was poor, corrosion was often so severe that the amal-

gam had lost most of its strength. This was attributed to the presence of concentration cells.

Fusayama, Katayori, and Nomoto [38] disagreed with the results of Schoonover and Souder. For essentially the same conditions the Japanese researchers reported no significant corrosion of the amalgam surfaces except for a slight roughening around the region of contact with the Au. The amount of corrosion was not considered to be clinically significant.

Swartz, Phillips, and El Tanir [39] observed the tarnishing of amalgams in solutions made up of various concentrations of Na_2S , NaCl and H_2O_2 , as well as in air, distilled water, and an artificial saliva. The degree of tarnish was determined simply by visual observation. They concluded that the highest degrees of tarnish occurred in Na_2S solutions, the rate and severity of attack increasing with sulfide concentration. Medium tarnish occurred in the artificial saliva. Experiments with zinc and nonzinc amalgams indicated no measurable difference in the susceptibility of the two types to tarnishing.

Wagner [40] was the first investigator to indicate that one specific phase of dental amalgam was more susceptible to corrosion than the others. He pointed out that the γ_2 phase was most subject to chemical attack and, further, that in amalgams with a high Sn content, the γ_2 phase could be continuous and corrosive attack could penetrate deeply into the amalgam. He also, however, pointed out the importance of corrosion products as marginal "sealants."

Jørgensen [41, 42] reported agreement with Wagner both on the continuity of the γ_2 phase in dental amalgam and the primary importance of the corrosion of this phase. He found continuous γ_2 networks even when condensation reduced the Hg content as low as 40 weight percent.

Wagner's and Jørgensen's conclusions led Guthrow, Johnson, and Lawless [43] to an extensive study of the corrosion of the individual, isolated phases of dental amalgam in Ringer's solution and in artificial saliva. Potentiostatic measurements (figs. 13, 14, and 15) were complemented with electron micrographs of the surfaces (figs. 16, 17, and 18). This study supplied conclusive confirmation for the preferential and destructive corrosion of the γ_2 phase. Only deposition (or tarnishing) occurred on the γ_1 phase, while the γ phase was essentially neutral.

Otani [44] has summarized much of the research in Japan on the corrosion of dental amalgam. In general, polarographic techniques have been used rather extensively to attempt to determine the effect of manipulative variables on corrosion in various media. From their work, it appears that the more Hg an amalgam contains, the greater the corrosion; the higher the condensation pressure, the less the corrosion; spherical-particle alloys provide amalgams with higher corrosion

resistance; but, in general, dental amalgam is a highly corrosion-resistant material.

Mueller, Greener, and Crimmins [45], Mueller Sarkar, and Greener [46] and Mueller and Greener [47] have made extensive electrochemical studies of amalgam corrosion both with open circuit and anodic polarization techniques. These measurements were complemented with optical,

electron microscope, and electron microprobe examinations of the specimen surfaces. They investigated a number of alloys and the effects of clinical variables such as trituration time and Hg to alloy ratio and the effect of residual strain energy on the corrosion rates. In general, practices which resulted in the formation of more γ_2 phase led to more corrosion. They also noted that the

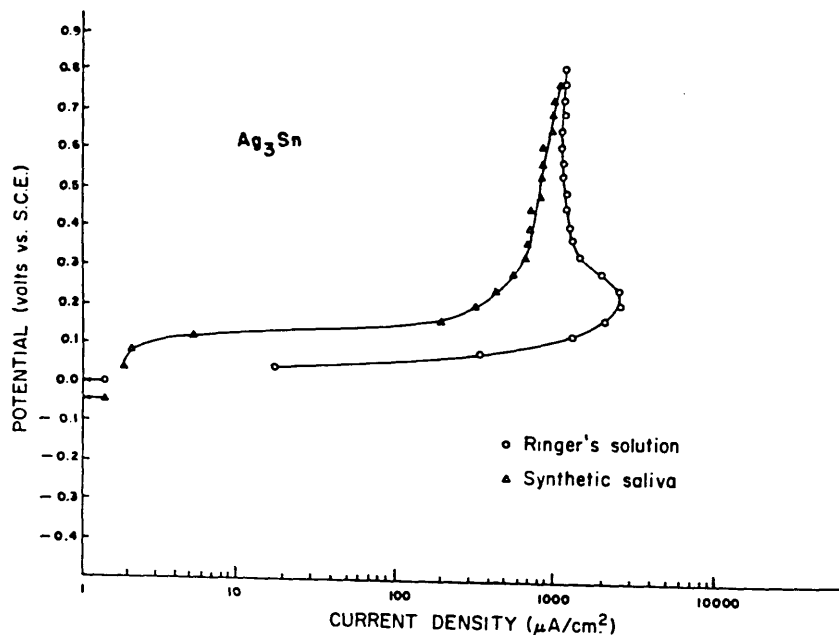


FIGURE 13. Potential-current relations for Ag_3Sn in corrosive media [43].

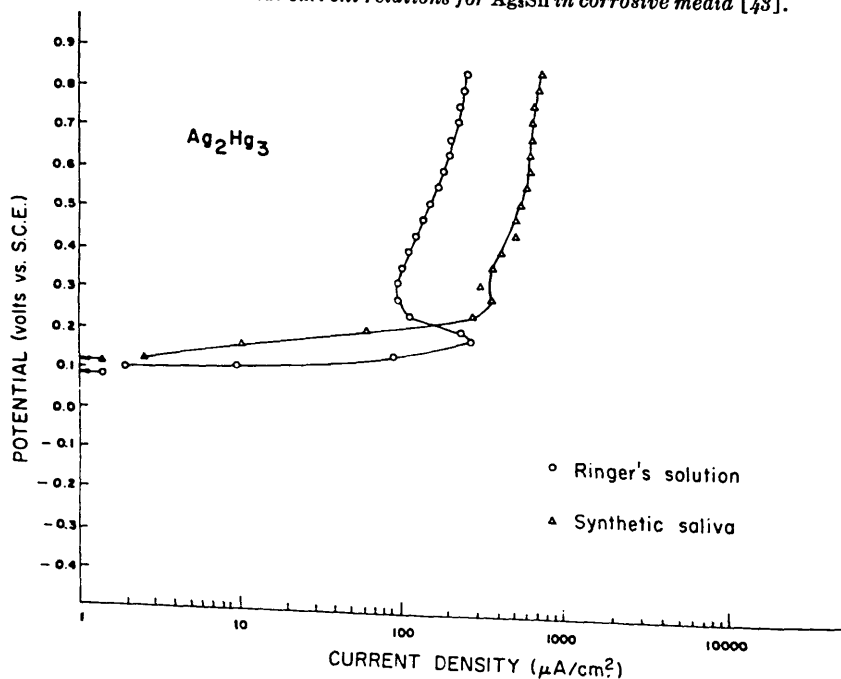


FIGURE 14. Potential-current relations for Ag_2Hg_3 in corrosive media [43].

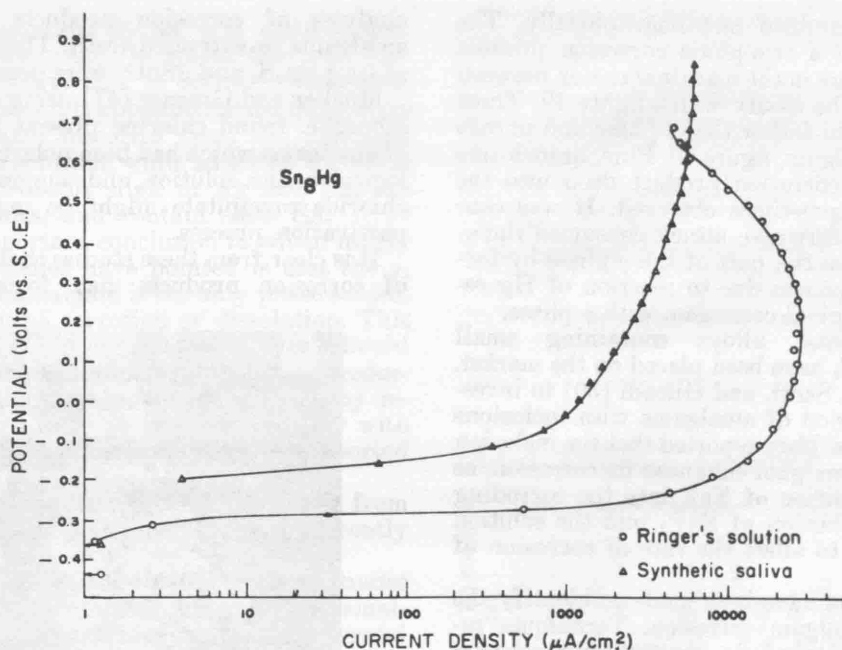


FIGURE 15. Potential-current relations for Sn_8Hg in corrosive media [43].

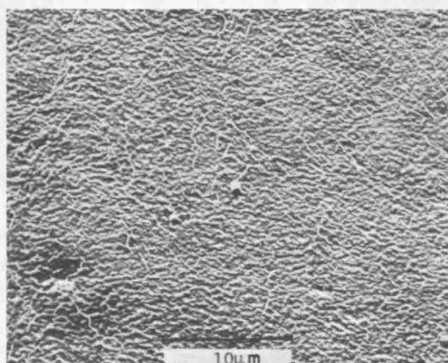


FIGURE 16. Electron photomicrograph of γ phase after polarization in Ringer's solution for one hr at 0.08 V. (Orig. mag. $\times 3000$) [43].

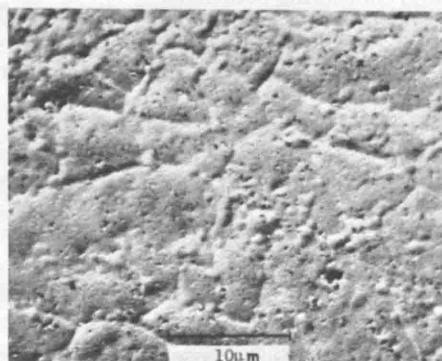


FIGURE 18. Electron photomicrograph of γ_2 phase after polarization in Ringer's solution for one hour at -0.34 V. (Orig. mag. $\times 3000$) [43].

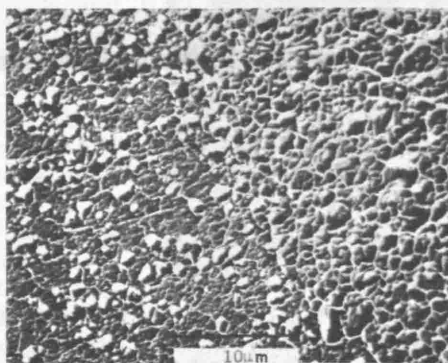


FIGURE 17. Electron photomicrograph of γ_1 phase after polarization for 30 min in Ringer's solution at 0.08 V. (Orig. mag. $\times 3000$) [43].

presence of Zn in the amalgam led to markedly different initial potentials but about the same as for nonzinc specimens after about 24 hr.

Johnson and Lawless [48] reported that stress caused a marked increase in the anodic direction for the corrosion potential of the γ_2 phase, but only a slight change for dental amalgam or the γ or γ_1 phases. This effect was believed to be due to surface film rupture during plastic deformation of the specimens. They concluded that stress is probably not an important factor in the corrosion of dental amalgam under oral conditions.

Mateer and Reitz [49] made a significant contribution toward the understanding of amalgam corrosion in vivo. Ground and polished cross-sections through 50 extracted teeth containing amalgam

fillings were examined metallographically. The authors reported a two-phase corrosion product deposited as layers in the marginal region between the filling and the cavity walls, figure 19. These deposits tended to follow the γ_2 phase and porous areas in the amalgam, figure 20. Fine, branch-like penetrations of corrosion product deep into the amalgam were sometimes observed. It was concluded that the corrosive attack consumed the γ_2 phase, and, indirectly, part of the γ phase by formation of new phases due to reaction of Hg released in the original corrosion, with γ phase.

Recently, dental alloys containing small amounts of SnF_2 have been placed on the market. This led Stoner, Senti, and Gileadi [50] to investigate the corrosion of amalgams with inclusions of such materials. They reported that the inclusion of SnF_2 in an amalgam enhanced its corrosion, as did also the addition of NaF into the corroding solution. The addition of SnF_2 into the solution did not appear to affect the rate of corrosion of the amalgam.

Many attempts have been made to identify the products of amalgam corrosion. Techniques involving chemical analysis, spectroscopy, electron microprobe, and electron and x-ray diffraction have been used on corroded surfaces, neighboring areas, and contacting solutions.

Schoonover and Souder [37] and Hyselova, Zajicek, and Vahl [51] used chemical analyses and agreed that mainly Sn ions were in the corrosion products.

Swartz, Phillips, and El Tanir [39] using x-ray diffraction and Guthrow, Johnson, and Lawless [43] with x-ray and electron diffraction, identified Ag_2S , HgS , and AgCl respectively. The first group also concluded that a complex $(\text{Hg}, \text{Ag}) \text{S}_x$ was present while the latter found complex salts which could not be identified by reference to ASTM files.

Mateer and Reitz [49] made x-ray diffraction

analyses of corrosion products scraped from amalgams in extracted teeth. They reported that at least Sn_2S_3 and βSnO_2 were present.

Mueller and Greener [47] using an electron microprobe, found chlorine present in the γ_2 areas of amalgams which had been polarized in a physiological saline solution and suggested that a tin chloride precipitate might be important in the passivation process.

It is clear from these studies that a wide variety of corrosion products may form when dental

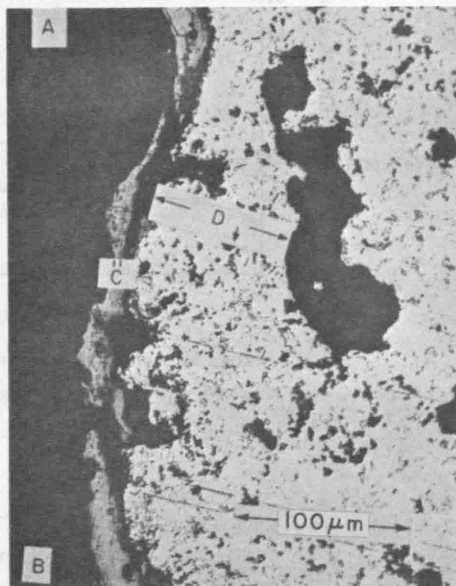


FIGURE 19. Metallographic section through amalgam restoration in extracted tooth.

Cavity wall in enamel (A) and dentin (B) is at left. Light-gray corrosion product (C) has deposited against cavity wall. Darker gray corrosion product (D) has deposited against amalgam and has penetrated into regions which were originally interconnected (γ_2 Sn-Hg and porosity) [49].

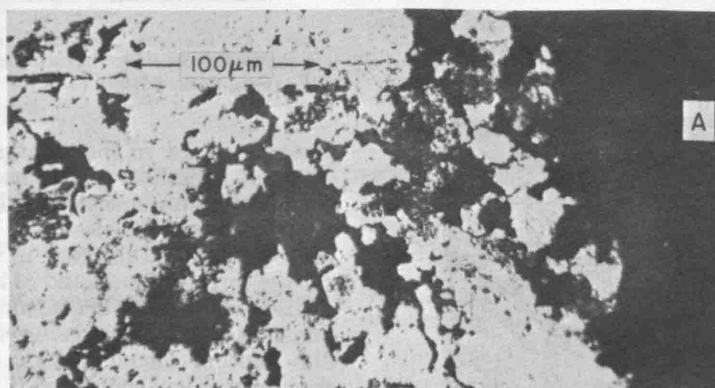


FIGURE 20. Metallographic section showing fatigue crack and bulk corrosion of amalgam in margin region of extracted tooth.

Amalgam fragments have chipped away from cavity wall (A), causing a gutter. Bulk deposition of the dark gray corrosion product has taken place in γ_2 and porous regions within the amalgam, whereas cracking is visible at the exposed surface. The two types of attack appear to contribute mutually in destroying integrity of the restoration [49].

amalgam is subjected to an oral environment. Since the environments to which they are subjected vary widely, this is entirely reasonable. In general, however, it appears that Sn is the main constituent which dissolves from the amalgam and is found in solution, while adhering corrosion products are probably high in Ag and Hg, are primarily sulfides, and contain some Sn.

The most important conclusion to which nearly all corrosion studies have pointed is that the γ_2 phase of dental amalgam is the only phase subject to destructive type corrosion or dissolution. This led Jørgensen [42] to suggest that research should be directed toward elimination, or at least reduction in amount, of the γ_2 phase, perhaps by replacing part of the Sn in the original alloy with Pd. Results of such efforts have not been reported as yet.

Successful elimination of the γ_2 phase from dental amalgam has been reported for two recently developed alloys.

In 1963 Innes and Youdelis [52] reported studies on the dispersion strengthening of dental amalgams. They mixed various amounts of metal powder consisting of the Ag-Cu eutectic (71.9 percent Cu) with powdered Ag_3Sn (78.2 percent Ag, 26.8 percent Sn). The combination was later marketed under the trade name Dispersalloy.

Mahler [53] studied amalgams made from the above alloy. He used an electron microprobe and reported (1) "the presence of a reaction phase surrounding the dispersant particles which was determined to have a composition intermediate between the intermetallic compounds of Cu_3Sn and Cu_6Sn_5 ," and (2) "the absence of the Sn-Hg phase (γ_2) in this amalgam."

Johnson [54, 55], considering Ag-Sn-Hg alloys as electron compounds, showed that it should be possible to dissolve more Sn in the γ_1 phase than had previously been thought possible. Under non-equilibrium conditions, it appears that all of the matrix Sn in dental amalgam could be incorporated in a single phase with the same structure as the γ_1 phase.

Grenoble and Katz [56] showed that the γ_2 phase disappeared from dental amalgams which had been subjected to extremely high pressures at room temperature (about 50 kilobars or 750,000 psi (5,200 MN/m²)).

In order to bring about the elimination of the γ_2 phase at body temperature, Johnson [57] then substituted 10 weight percent Au for 10 percent of the Ag in the original alloy. He reported (fig. 21) that the γ_1 and γ_2 phases formed as usual upon trituration with Hg, but that after 14 days at body temperature, x-ray diffraction patterns showed only the presence of the γ_1 phase. This material had a very high corrosion resistance.

More recent studies by Mahler [58], however, indicate that part of the Sn may be tied up by Au

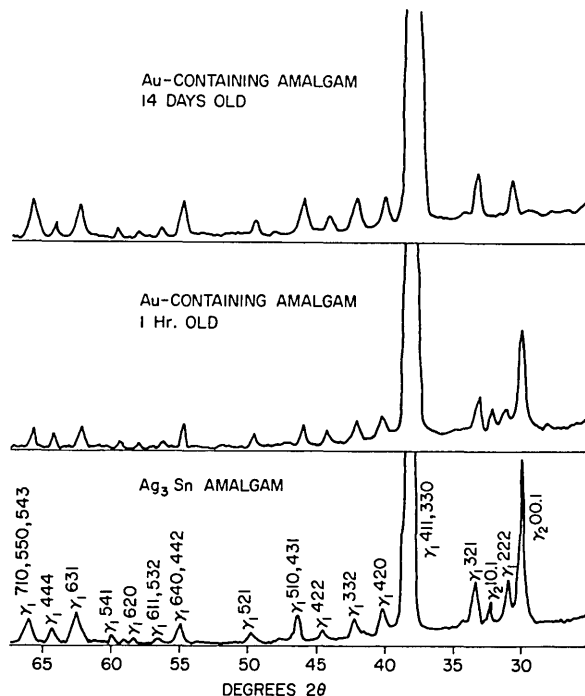


FIGURE 21. X-ray diffraction scans of conventional and Au-containing amalgams showing absence of γ_2 phase in Au-containing amalgam at 14 days [57].

in a "reaction ring" around the alloy particles, apparently similar to that for Dispersalloy.

The question remains open as to how much corrosion of amalgam is desirable. The sealing of margins and crevices by corrosion products has been demonstrated and surely may be desirable. On the other hand, weakening of the amalgam structure by the destructive corrosion of the γ_2 phase has been demonstrated and is also surely undesirable. It may be possible to eliminate destructive corrosion effectively by forming an amalgam without the γ_2 phase, while at the same time allowing the formation of adherent films of oxides and sulfides to accomplish the marginal sealing. Only long-term clinical testing of γ_2 -free amalgams can give the final answer.

5. Summary

A brief review has been made of the significant advances made over the past half century or so towards an understanding of the constitution, strength, and chemistry of dental amalgam.

The conclusion has been reached that an "equilibrium" mixture of components would contain the phases $\beta_1 + \gamma_1 + \gamma_2$ as shown by Gayler's 60 °C isotherm. Because dental amalgam is formed clinically at a relatively low temperature, only the γ_1 and γ_2 phases are generally found. Recent work has shown that β_1 does form, however slowly, thus

showing that the system is striving toward the equilibrium state—the higher the temperature the sooner equilibrium is established.

Although numerous measurements have been made of mechanical properties of amalgams and a much clearer picture of the microstructure has evolved, it is still not possible to attain a complete understanding of the behavior of this material. The major defect appears to be its multiphase nature, which results in poor tensile properties. It does not appear to fit into any of the alloy categories from which the metallurgist can draw on a theory of strengthening. Nevertheless, recent improvements in the study of microstructure, modern advances in the application of electron fractography, recent measurements of elastic constants of the individual phases, and the possibility of the elimination of one phase of the amalgam, all offer considerable hope for a better understanding and improvement of the mechanical properties.

A knowledge of the chemistry of dental amalgam is complicated not only by the multiphase nature of the material but even more so by the extreme complexity of the environments in which tooth fillings are located. Corrosion products and mechanisms have been difficult to identify. Nevertheless, one outstanding bit of information has evolved that the γ_2 phase of amalgam is preferentially attacked in a detrimental manner. The possibility of eliminating this phase, therefore, holds considerable promise toward improving the lasting qualities of the material in an oral environment.

We owe it to those colleagues, both past and present, of the Dental Research Section of the National Bureau of Standards, in whose honor this paper has been presented, that the search for a full understanding of this most useful and intriguing alloy be continued.

6. References

- [1] Murphy, A. J., *J. Inst. Met.* **35**, 107 (1926). Murphy and Preston, G. D. *J. Inst. Met.* **46**, 507 (1931).
- [2] Berman, H., and Harcourt, G. A., *Amer. Min.*, **23**, 761 (1938).
- [3] Nial, O., Almin, A. and Westgren, A., *Z. Phys. Chem.*, **14**, 81 (1931).
- [4] v. Simpson, C., *Z. Physik. Chem.*, **109**, 187 (1924).
- [5] Gayler, M. L. V., *Brit. Dent. J.*, **54**, 269 (1933); **56**, 605 (1934); **58**, 145 (1935); **59**, 245 (1935); **60**, 605 (1936); **61**, 11 (1936).
- [6] McBain, J. W., and Joyner, R. A., *Dent. Cosmos*, **54**, 641 (1912).
- [7] Troiano, A. R., *J. Inst. Met.*, **63**, 247 (1938).
- [8] Fairhurst, C. W., and Ryge, G., *Adv. X-ray Anal.*, **5**, 64 (1961).
- [9] Moffett, J. C., Ryge, G., and Barkow, A. G., *J. Appl. Phys.*, **23**, 1188 (1952).
- [10] Schmitt, G., *Deutsch. Zahnaerztl. Z.*, **15**, 736 (1960).
- [11] Demaree, N. C., and Taylor, D. F., *J. Dent. Res.*, **41**, 890 (1962).
- [12] Wing, G., and Ryge, G., *J. Dent. Res.*, **44**, 1325 (1965).
- [13] Johnson, L. B., *J. Biomed. Mater. Res.*, **1**, 285 (1967), and **1**, 415 (1967).
- [14] Otani, H., *J. Osaka Univ. Dent. School*, **10**, 57 (1970).
- [15] Otani, H., Tsutsumi, S., and Yamaga, R., *J. Osaka Univ. Dent. School*, **10**, 69 (1970).
- [16] Young, F. A., Jr., *D. Sc. Thesis*, Univ. of Va., 1968.
- [17] Young, F. A., Jr., and Wilsdorf, H. G. F., *Research in Dental and Medical Materials*, p. 69 (Plenum Press, 1969), *J. Biomed. Mater. Res.* **2**, 401 (1968).
- [18] Phillips, R. W., *J. Dent. Res.* **28**, 348 (1949).
- [19] Taylor, N. O., Sweeney, W. T., Mahler, D. B., and Dinger, E. J., *J. Dent. Res.*, **28**, 228 (1949).
- [20] Souder, W., and Paffenbarger, G. C., *Physical Properties of Dental Materials*, NBS Circ. 433, 222 pages (1942).
- [21] Wing, G., *Doct. Dissertation*, Univ. of Sydney, Australia, 1961; *Aust. Dent. J.* **11**, 105 (1966).
- [22] Burns, C., and Sweeney, W. T., *I. A. D. R.*, 43d Gen. Meeting Abstr., p. 122 (1965).
- [23] Ward, M. L., *J. Am. Dental Assoc.* **11**, 487 (1924).
- [24] Taylor, N. O., *J. Am. Dental Assoc.* **17**, 112 (1930).
- [25] Rodriguez, M. A., and Dickson, G., *J. Dent. Res.* **41**, 480 (1961).
- [26] Mahler, D. B., and Mitchem, J. C., *J. Dent. Res.* **43**, 121 (1964).
- [27] Hollenback, G. M., and Villanyi, A. A., *J. South. Cal. State D. A.* **32**, 355, 379, 455, (1964); **33**, 423 (1965).
- [28] Nagai, K., and Ohashi, M., *J. Nihon Univ. School of Dent.* **10**, 39 (1968).
- [29] Timoshenko, S., *Theory of Elasticity*, p. 104 (McGraw-Hill Book Co., Inc. New York, 1934).
- [30] Eden, G. T., and Waterstrat, R. M., *J. Am. Dental Assoc.* **74**, 1024 (1967).
- [31] Modjeski, P., and Nuckels, D. B., private communication (1969).
- [32] Nagai, K., Ohashi, M., Habu, H., Nemura, M., Korenaga, F., Goto, N., Nagata, Y., and Fujimoto, Y., *J. Nihon Univ. School of Dent.* **12**, 9 (1970).
- [33] Lautenschlager, E. P., and Harcourt, J. K., *J. Dent. Res.* **49**, 175 (1970).
- [34] Asgar, K., and Sutfin, L., *J. Dent. Res.* **44**, 977 (1965).
- [35] Caron, J. C., *Master's Thesis*, Georgia Inst. Tech. (1967).
- [36] Grenoble, D. E., and Katz, J. L., *J. Biomed. Mater. Res.* **5**, 503 (1971); **5**, 515 (1971).
- [37] Schoonover, I. C., and Souder, W., *J. Amer. Dental Assoc.* **28**, 1278 (1941).
- [38] Fusayama, T., Katayori, T., and Nomoto, S., *J. Dent. Res.* **42**, 1183 (1963).
- [39] Swartz, M. L., Phillips, R. W., and El Tannir, M. D., *J. Dent. Res.* **37**, 837 (1958).
- [40] Wagner, E., *Deutsch Zahnaerztl. Z.* **17**, 99 (1962).
- [41] Jørgensen, K. D., *Acta Odont. Scand.* **23**, 347 (1965).
- [42] Jørgensen, K. D., and Saito, T., *Tandlaegebladet*, **73**, 55 (1969).
- [43] Guthrow, C. E., Johnson, L. B. and Lawless, K. R., *J. Dent. Res.* **46**, 1372 (1967).
- [44] Otani, H., *Ann. Dent.* **27**, 32 (1968).
- [45] Mueller, H. G., Greener, E. H., and Crimmins D. S., *J. Biomed. Mater. Res.*, **2**, 195 (1968).
- [46] Mueller, H. G., Sarkar, N., and Greener, E. H., *Electrochemical properties of commercial dental amalgams*, Annual IADR Meeting New York, N.Y. (1970).
- [47] Mueller, H. G., and Greener, E. H., *Electron microprobe analysis of dental amalgam surfaces*, Annual IADR Meeting, Houston, Texas (1969).
- [48] Johnson, L. B., and Lawless, K. R., *J. Biomed. Mater. Res.* **3**, 569 (1969).
- [49] Mateer, R. S., and Reitz, C. C., *J. Dent. Res.*, **49**, 399 (1970).

- [50] Stoner, G. E., Senti, S. E., and Gileadi, E., The effect of NaF and SnF₂ on the rate of corrosion of dental amalgams. *J. Dent. Res.*, **50**, 1647 (1971).
- [51] Kyselova, J., Zajicek, and Vahl, J., *Deutsch Zahnartztl A.*, **23**, 631 (1968).
- [52] Inees, D. B. K., and Youdelis, W. V., *J. Canadian Dent. Assoc.* **29**, 587 (1963).
- [53] Mahler, D. B., Microprobe analysis of a dispersant amalgam, *IADR Program of Abstracts and Papers*, No. 14 (1971).
- [54] Johnson, L. B., *J. Biomed. Mater. Res.*, **4**, 269 (1970).
- [55] Johnson, L. B., Amount of Sn in the γ_1 phase of dental amalgam, *J. Biomed. Mater. Res.*, **5**, 239 (1971).
- [56] Grenoble, D. E., and Katz, J. L., *J. Dent. Res.* **50**, 109 (1971).
- [57] Johnson, L. B., A new dental alloy, *IADR Program of Abstracts and Papers*, No. 23 (1971).
- [58] Mahler, D. B., personal communication.

Casting Alloys in Dentistry

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A major difference between the two techniques, hygroscopic and high heat or thermal expansion, used for casting gold alloys is that the wax pattern can offer some resistance to hygroscopic expansion of the mold while it does not resist thermal expansion. Researchers have condemned the hygroscopic technique because of nonuniform expansion of the wax pattern but have not given sufficient attention to other nonuniform dimensional changes which are present in both techniques and which may combine to affect favorably or unfavorably the accuracy and retention of the casting. Studies in this field should not be limited to simple measurements of thermal, setting and hygroscopic expansions of the investment but should be expanded to include strength of the investment along with its roughness, strength and behavior of waxes, and shrinkage patterns of molten metals. A need for new types of investments is presented by the recent development of many new nonprecious alloys for dental castings.

Key words: Castings, dental, accuracy; castings, lost wax technique; dental materials; gold alloys, dental; high heat casting technique; hygroscopic expansion; investment, dental; thermal expansion casting technique; wax, inlay casting.

1. Introduction

Casting metals by the lost wax process has been known in art and industry for many years. Since the turn of the century, the idea of using the lost wax procedure in preparing metallic substances to replace the missing portion of tooth tissue has been routine practice in dentistry. Yet, the required accuracy of the fit of the cast structure by the profession has not been completely resolved. The early castings were grossly short of what is considered today, an acceptable fit. This was mainly due to the inferior materials available at the time. The development of the cristobalite investment by two independent research groups, Sweeney and his co-workers at the National Bureau of Standards, and Coleman and Weinstein [1]¹ at the Weinstein Research Laboratories of New York, probably was the most important single achievement in the field of dental castings. Dental gold castings made by using the cristobalite investment were first introduced to the dental profession at the annual meeting of the American Dental Association in Buffalo, New York, September, 1932, by Jesrich. At about the same time, Scheu [2] also presented his hygroscopic casting technique.

2. High Heat and Hygroscopic Techniques

Since 1932, over a dozen dental gold casting procedures and techniques have been introduced

to the profession by various researchers. As examples, Phillips [3], Hollenback [4], Sweeney [5], Coleman [6], Crawford [7], Shell [8], Ireland [9], Smyd [10], Gustafsson and Hedegard [11], Jørgensen [12], Coy [13], Asgar and Mahler [14], Fusayama [15], and Peyton [16], could be mentioned. These are modifications and offshoots of two main techniques, the high heat or thermal expansion technique and the hygroscopic technique. Theoretically, there is very little difference between these two main techniques. All of the investments used today in dentistry have some setting expansion, some hygroscopic expansion, and some thermal expansion. The investments are formulated so that if they are properly handled, the sum of their setting, hygroscopic, and thermal expansion will be equal to the contraction of dental gold alloys and wax. The difference between these two techniques boils down to the fact that in the high heat technique, a major part of metal shrinkage is compensated by thermal expansion of the mold. This is obtained by heating the ring up to about 1200-1300 °F (650-700 °C). The setting and hygroscopic expansions of such an investment are rather low. In hygroscopic techniques the major part of the total expansion is obtained hygroscopically, and the thermal expansion of this type of investment is low.

Although they are alike theoretically, practically there is a great difference between these two techniques. Two of the most important differences are:

1. In the hygroscopic technique the wax pattern is present as one piece and solid while hygroscopic expansion is taking place. Thus,

¹ Figures in brackets indicate the literature references at the end of this paper.

the wax pattern could offer some resistance, whereas in the high heat technique the major part of expansion is taking place while the ring is placed inside an oven and the wax pattern no longer exists as solid or one piece. Thus, it could not offer any resistance to the expansion forces.

2. In the hygroscopic technique the mold temperature is 700–900 °F (370–480 °C). The mold temperature in the high heat technique is about 1200–1300 °F (650–700 °C) or about 400–500 °F (220–280 °C) higher than that of the hygroscopic technique.

These two points could be considered as the real differences between these two techniques. If they were recognized completely and handled properly, many practical problems would be avoided. The classical work of Docking and his associates [17], reported in 1948 and 1949, was the first major research work to clarify the behavior of the hygroscopic investment. Later, Landgreen and Peyton [18], Delgado and Peyton [19], Asgarzadeh and Mahler [20], Lyon and Dickson [21], Ryge and Fairhurst [22], Donnison and Docking [23], Skinner and Degni [24], Mumford [25], Fusayama [26], Mahler and Addy [27], Earnshaw [28], and many others reported their findings on hygroscopic expansion of investments. As a result of these findings, the hygroscopic expansion of an investment is no longer a mystery.

3. Effects of High Heat and Hygroscopic Techniques on the Dimensions of the Casting

The effect of hygroscopic expansion on wax patterns is somewhat different from that of thermal expansion. The shape and size of the wax pattern makes some difference on hygroscopic expansion and the resultant cast piece. As an example, let us consider the behavior of two different patterns such as, one surface inlay (Class I) and three surface inlays (MOD). In the case of one surface inlay, the investment expands away from the wax pattern and it really does not matter to a great extent what type of wax is used. In the case of an MOD pattern however, investment located between the two axial walls during setting and hygroscopic expansion of the investment will be exerting some forces trying to enlarge the size of the wax pattern in the mesial-distal direction. The wax pattern, in the meantime, will be offering some resistance to these expansion forces. Depending on the type of wax used, hard or soft, more or less resistance forces can be offered by the pattern. Furthermore, on the pulpal floor area of the axial walls, the resistance is greater than on the cervical areas.

Some investigators have placed reference marks on the cervical and pulpal floor areas of an MOD type of pattern measuring exactly the distances A and B (fig. 1). Results of these measurements

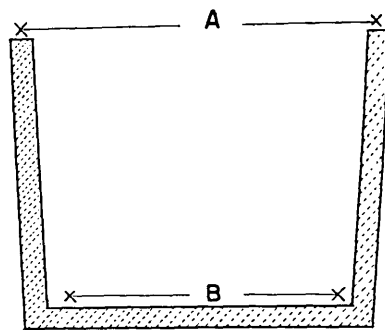


FIGURE 1. Distances A and B were measured precisely before investing the wax pattern and after expanding the investment hygroscopically.

have shown that due to the setting and hygroscopic expansion of an investment, the percent of expansion in cervical areas is more than that in the pulpal floor area. Therefore, the hygroscopic technique has been condemned. Yet the investigators have failed to go ahead and complete the casting procedure. The fact is that the dimensions of dental casting are also changed nonuniformly during solidification and shrinkage of cast molten metal. These studies have clearly indicated that the wax pattern expands nonuniformly under setting and hygroscopic expansion forces of the investment.

4. Effects of Nonuniform Shrinkage of the Alloy and Surface Roughness on the Dimensions of the Casting

Although the nonuniform expansion of the wax pattern has made researchers condemn the hygroscopic technique the nonuniform shrinkage during solidification and cooling of cast alloys has been completely ignored. To explain this point more clearly, let us consider two types of patterns, a full crown type and a Class I type. If a full crown type of casting were made having the exact dimensions of its die, obviously such a casting would not fit. In order to have a full crown type of casting fit onto a die, the casting should be slightly oversized (fig. 2). On the other hand, if a Class I, or one surface inlay, had exactly the dimensions of its die, such a casting also would not fit. The casting in this case should be slightly smaller in order to fit into the die. The question may arise concerning the fit of an MOD pattern. Mesial-distally, it is similar to a full crown, which means the casting should be slightly larger than the dimensions of the die, whereas in buccal-lingual direction, it behaves like a Class I or one surface inlay which means it should be slightly smaller than the dimensions of the die. It should be recognized that the effective shrinkage of metal is also not uniform. In a Class I, or one surface inlay, the alloy shrinks to its maximum amount. It could be visualized that the cast structure, after solidification, may shrink according to its coefficient of thermal contraction. That is to say, for every degree that it cools, it

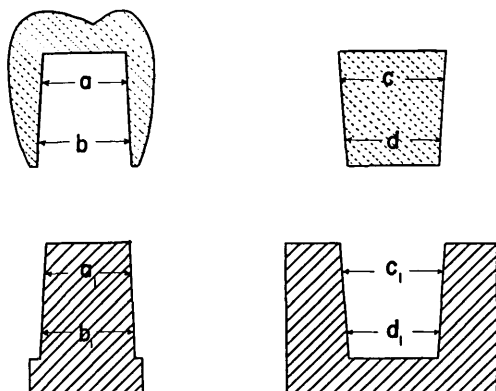


FIGURE 2. Dimensions of a and b on full crown type castings should be larger than a_1 and b_1 . Dimensions of c and d in inlay type castings should be smaller than c_1 and d_1 .

becomes somewhat smaller until it reaches room temperature. On the other hand, in the case of a full crown type pattern, the alloy shrinks its least amount. In this case also, after solidification, metal should shrink according to its coefficient of thermal expansion, but due to the shape of the pattern, it should compress the investment inside of the crown. Due to the fact that metals usually do not possess high strengths at temperatures close to their fusion range, they cannot compress the investment inside of the crown to any extent, and their effective shrinkage at high temperatures is rather low. As the alloy cools, its strength increases and eventually reaches a point where its strength is higher than that of the investment and can compress the investment inside of the crown. From such a temperature, down to room temperature, it may shrink according to its coefficient of thermal contraction. Thus, if all other conditions remained the same, stronger investments would produce full crown type castings which seem to have expanded more. The strength of the investment has little effect on shrinkage of a one surface inlay.

Not only could the magnitude of shrinkage of the cast metal vary in these two types of patterns, the effect of roughness of the cast structure is also quite different. When a wax pattern is properly invested, the investment completely covers all surfaces of the wax pattern. It should be remembered that the wax pattern is invested in a slurry which is made by mixing some water with solid particles of various sizes (fig. 3). To eliminate the wax pattern, a mold is placed in an oven and heated to casting temperature. During this process, the excess water in the investment, as well as the water of crystallization of various solids, will be eliminated. Thus, the smooth surface of the investment next to the wax pattern becomes somewhat rough. Roughness in the case of a Class I, or one surface inlay, acts as an aid to expansion and its effect would be as if the investment expanded more. In the case of full crown roughness,

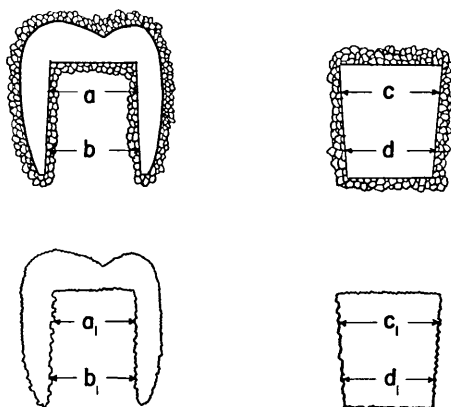


FIGURE 3. Roughness of casting causes a_1 and b_1 to get smaller than a and b . Roughness of casting causes c_1 and d_1 to become larger than c and d .

it will prevent the casting from complete seating, as if the investment did not have sufficient expansion.

To summarize, one may say that in a one surface inlay, the shrinkage of metal is at its maximum, but roughness of the cast structure aids the expansion. Whereas, in full crown type patterns, shrinkage of metal is at its minimum but roughness of the investment prevents the seating of cast crown or acts against the expansion of the investment. If an investment produces roughness to such a degree that the shrinkage of cast metal at its maximum (Class I or one surface inlay), minus the roughness value of the cast piece, is equal to the shrinkage of cast metal at its minimum (full crown type), plus the roughness of the cast piece, then such an investment is capable of producing good MOD castings.

Shrinkage of Metal—Roughness

(Class I)

$$= \text{Shrinkage of Metal} + \text{Roughness} \\ (\text{Full Crown})$$

Usually investments producing smooth casting surfaces could produce good full crown castings, but it would be difficult to produce good one surface inlays. Similarly, investments producing somewhat rougher cast surfaces, may produce good one surface inlays, but it will be difficult to make a well fitted full crown casting.

5. Retention of the Casting

For dentists, retention of casting is another important point. It is preferred if the casting offers some retention in the last millimeter before its complete seating. Questions may arise as to what is responsible for such a retention. If all dimensions of the die were exactly reproduced on the cast, theoretically there should not be any retention up to the last micrometer away from complete seating.

All of a sudden, all surfaces of the cast should contact all surfaces of the die. To analyze the retention, one should recognize what is responsible for it in different shape patterns. Such a study can be done by making castings, seating them on the die, embedding them in some type of bioplastic and cross-sectioning the die and the cast. The space between the cast and the die can be examined under a microscope. Such a study shows that dental castings are far from a perfect fit.

In the case of full crown and MOD type of patterns only on marginal areas are the castings contacting the dies (fig. 4). In the case of Class I and Class V, due to the fact that shrinkage of metal is at its maximum, the line A in the cast is slightly smaller than in the die. Therefore, in Class I some surfaces of the cast can contact those in the die, whereas in the case of Class V, such a contact is not possible (fig. 5). By placing some pins in Class V preparation, one could get sufficient retention (fig. 6). It should be recognized that the pins during setting and hygroscopic expansion will be actually bending slightly and causing the retention. The marginal adaptation of Class V inlay with pin, in a cast condition, probably is not any better than the one without a pin. The fact that castings having some retention can easily be finished and better marginal adaptation can be obtained at the chair during the delivery, is subject of another discussion. It is more interesting to observe the retention of Class III inlays (fig. 7). Under a normal expansion of the investment, the inlay usually has

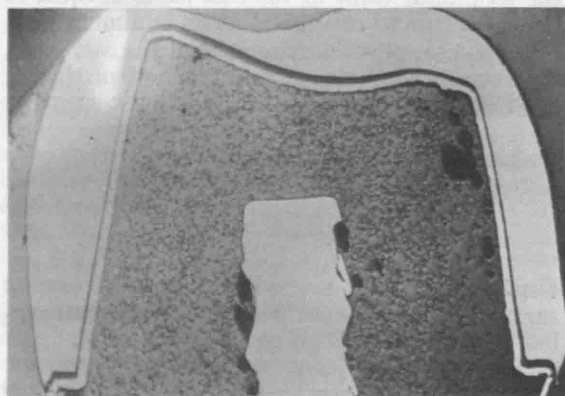


FIGURE 4. The casting contacts the die only on the marginal ridge areas.

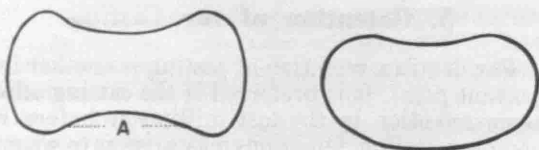


FIGURE 5. In the Class I type of pattern, casting contacts die in some areas.

The distance A is responsible for some retention. In Class V type of pattern, casting does not make any contact usually with the die.

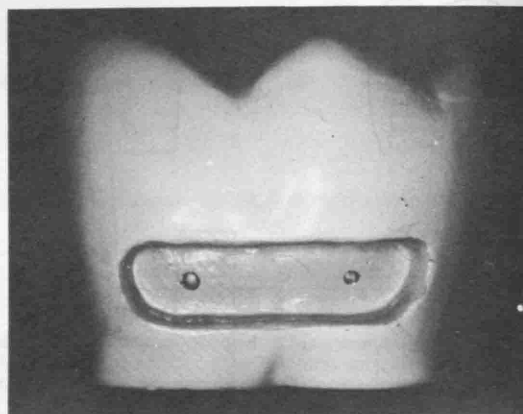


FIGURE 6. Class V pattern with pins. Castings usually have some retention.

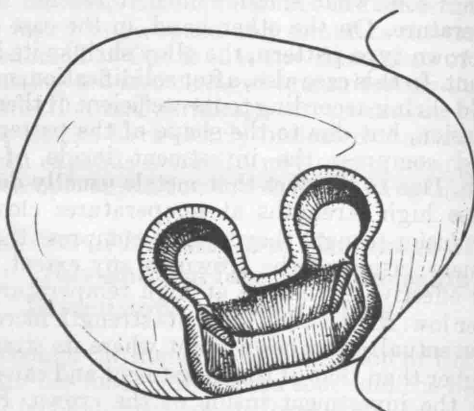


FIGURE 7. Class III type of inlay. The retention can be obtained by contacting the two inner surfaces or by the two outer surfaces.

some retention. By increasing the expansion of the investment, the inlay would lose its retention; by further increasing the expansion of the investment, the inlay regains its retention. The retention first was obtained probably because the inlays were very slightly small, and like Class I restorations, they touched the two inner surfaces of the die. When the dimensions of the cast inlay were enlarged by increasing the expansion of the investment, the cast no longer could contact the surfaces of the die, thus it would lose its retention. By further expansion of the investment, the outer surfaces of the inlay could come in contact.

The retention of many patterns is due to the setting and hygroscopic expansion of the investment which produce non-uniform expansion of the wax pattern of very minute amounts. Both Moore of the Ransom and Randolph Company, and Nieman of the Whip-Mix Corporation have produced investments having no setting and hygroscopic expansion. Thermal expansion of this investment

was sufficiently high to compensate for the shrinkage of gold alloys.

Nieman has even obtained a U.S. Patent for his investment. Although such an investment sounded good at first, the castings had no retention and did not satisfy the needs of the dental profession. The investment was discontinued.

6. Measurement of the Accuracy of Castings

It is relatively simple to measure thermal, setting, and hygroscopic expansion of an investment. It is however, more complicated to measure dimensions of cast pieces and compare those with that of the original die. In this case not only are the various expansions of the investment important, but also the dimensional changes of the wax pattern and the shrinkage of the molten metal. If however, the quality of the fit of casting to a die is to be considered—the main objective of researchers in this field, as well as those in practice—then the roughness of the casting and strength of the investment also should be recognized.

In the past, relatively little research work has been reported in which the fit of dental gold castings were measured and compared. The early work of Vollard and Paffenbarger [29], Hollenback and his group [30], Mahler and his associates [31], are among few published articles in this country concerned with the fit of castings and relating it to some expansion values. Pomes and Slack [32], Suffert and Mahler [33], and Barone and Dickson [34] have measured the roughness of dental gold castings. According to their values, roughness of dental castings could be as high as 0.4 percent. When this value is compared with the total shrinkage of the gold alloys, the role of roughness in the fit of dental castings becomes clear. In figures 8 and 9, the thermal expansion of two investments are shown. Both investments have identical setting and hygroscopic expansion. Two castings of the Bureau of Standards full crown die were made employing identical techniques. One of the castings fit the die (fig. 8) and the other did not (fig. 9). Roughnesses produced by these two investments were different. In figure 8, the roughness measured by the profilometer was 10 microinches whereas the casting in figure 9 has roughness value of 25 microinches.

7. Conclusion

The time has come when studies in this field should not be limited only to measurement of thermal, setting, and hygroscopic expansions of the investment, but should be expanded to include strength of the investment along with its roughness, strength and behavior of waxes, and shrinkage pattern of molten metal.

It should also be mentioned that due to the efforts, and hard research work of Nieman[35],

Moore[36], Watts[37], Collins[38], and a few others, there are good investments available for dental gold castings. During the last fifteen years, many new nonprecious alloys have been developed in industry. The physical properties of some of these alloys promise their potential use in the field of crown and bridge. Yet the available investments are not suitable for their casting. It seems that there is a great need for some basic research in this field with the hope of developing a series of new investments for casting of these new alloys. It may be time to look for the possibility of finding a different binding material than the three already being used. Perhaps a refractory material different from those used today in dentistry should be employed for casting of the newly developed alloys.

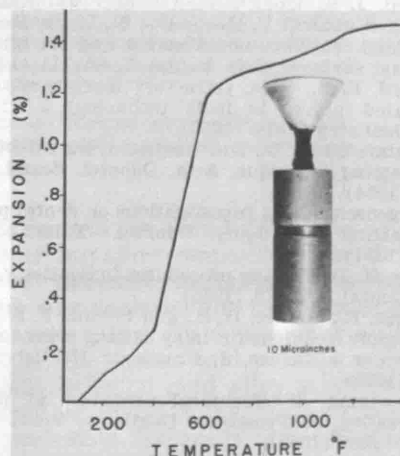


FIGURE 8. The casting fits the Bureau of Standards die.

The investment had 1.35 percent thermal expansion at a casting temperature of 1,000°F. with a roughness of 10 microinches. The setting and hygroscopic expansion of the investment was identical to the one used in figure 9.

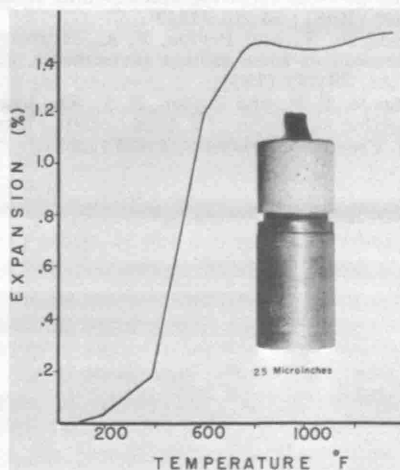


FIGURE 9. The casting does not fit the die.

The investment had 1.45 percent thermal expansion at a casting temperature of 1,000°F. Roughness of the investment was 25 microinches. The setting and hygroscopic expansion of the investment was identical to the one used in figure 8.

8. References

- [1] Coleman, R. L., and Weinstein, L. J., Investment, U.S. Patent 1,932,202.
- [2] Scheu, C. H., A new precision casting technique, *J. Am. Dental Assoc.*, **19**:630 (1932).
- [3] Phillips, D. W., Present-day precision inlay investing and casting technique, *J. Am. Dental Assoc. and Dental Cosmos*, **24**:1470 (1937).
- [4] Hollenback, G. M., Simple technique for accurate castings: New and original method of vacuum investing, *J. Am. Dental Assoc.*, **36**:391, 1948.
- [5] Sweeney, W. T., Cristobalite for dental investment, *J. Am. Dental Assoc.*, **20**:108 (1933).
- [6] Coleman, R. L., Physical properties of dental materials, *BS J. Research* **1**, 867 (1928) RP 32.
- [7] Crawford, W. H., Selection and use of investments, sprues, casting equipment and gold alloys in making small castings, *J. Am. Dental Assoc.*, **27**:1459 (1940).
- [8] Shell, J. S., *Hodgen-Shell Dental Materials*, chapter 8 (The C. V. Mosby Co., St. Louis, Mo., 1938).
- [9] Ireland, J., Vacuum investing and its relation to cast surfaces, *Brit. Dental J.*, **86**:111 (1949).
- [10] Smyd, E. S., Wax, refractory investments and related subjects in dental technology, *J. Prosthetic Dentistry* **5**:514 (1955).
- [11] Gustafsson, C. G., and Hedegard, B., Investing and casting technique, *Acta. Odontol. Scand.* **12**:233 (1954).
- [12] Jørgensen, K. D., Investigations on dental precision casting technique, *Odontol. Tidskr.*, **62**:443 (1954).
- [13] Coy, H. D., Casting procedures in dentistry, *Intern. Dental J.* **5**:173 (1955).
- [14] Asgar, K., Mahler, D. B., and Peyton, F. A., Hygroscopic technique for inlay casting using controlled water additions, *J. Prosthetic Dentistry*, **5**:711 (1955).
- [15] Fusayama, T., Technical procedure of precision casting, *J. Prosthetic Dentistry*, **9**:468 (1959); **9**:1037 (1959).
- [16] Peyton, F. A., Mahler, D. B., and Asgar, K., Controlled water-addition technique for hygroscopic expansion of dental casting investment, *J. Am. Dental Assoc.*, **52**:155 (1956).
- [17] Docking, A. R., Chong, M. P., and Donnison, J. A., The hygroscopic setting expansion of dental casting investments, *Australian Dental J.* **52**:6, 160, 320 (1948); **53**:261 (1949).
- [18] Landgren, N., and Peyton, F. A., Hygroscopic expansion of some casting investments, *J. Dental Res.*, **29**:469 (1950).
- [19] Delgado, V. P., and Peyton, F. A., The hygroscopic setting expansion of a dental casting investment, *J. Prosthetic Dentistry*, **3**:423 (1953).
- [20] Asgarzadeh, K., Mahler, D. B., and Peyton, F. A., The behavior and measurement of hygroscopic expansion of dental casting investment, *J. Dental Res.*, **33**:519 (1954).
- [21] Lyon, H. W., Dickson, G., and Schoonover, I. C., The mechanism of hygroscopic expansion in dental casting investments, *J. Dental Res.*, **34**:44 (1955).
- [22] Ryge, G., and Fairhurst, C. W., Hygroscopic expansion, *J. Dental Res.*, **35**:499 (1956).
- [23] Donnison, J. A., Chong, M. P., and Docking, A. R., The effect of surface area on the hygroscopic setting expansion and strength of casting investment, *J. Dental Res.*, **36**:967 (1957).
- [24] Skinner, E. W., and Degni, F., Hygroscopic expansion of dental investments, *J. Am. Dental Assoc.*, **54**:603 (1957).
- [25] Mumford, G., and Phillips, R. W., Dimensional change in wax pattern during setting of gypsum investments, *J. Dental Res.*, **37**:351 (1958).
- [26] Fusayama, T., Hosoda, H., and Kher, V. M., Influences of clinical variables on a cristobalite investment, *J. Prosthetic Dentistry*, **11**:152 (1961).
- [27] Mahler, D. B., and Addy, A. B., An explanation for the hygroscopic setting expansion of dental gypsum products, *J. Dental Res.*, **39**:578 (1960).
- [28] Earnshaw, R., The effect of restricted stress on the setting expansion of gypsum bonded investments, *Australian Dental J.*, **9**:169 (1964).
- [29] Volland, R. H., and Paffenbarger, G. C., Cast inlay technique, *J. Am. Dental Assoc.*, **19**:185 (1932).
- [30] Hollenback, G. M., and Rhoads, J. E., Comparison of the expansion of the mold cavity with the linear casting shrinkage of gold. *S. Calif. State Dental J.*, **28**:73 (1960).
- [31] Mahler, D. B., and Addy, A. B., The effect of water bath in hygroscopic casting technique, *J. Prosthetic Dentistry*, **15**:1115 (1965).
- [32] Pomes, C. E., Slack, G. L., and Wise, M. W., Surface roughness of dental castings, *J. Am. Dental Assoc.*, **44**:545 (1950).
- [33] Süffert, L. W., and Mahler, D. B., Reproducibility of gold casting made by present-day dental casting technics, *J. Am. Dental Assoc.*, **50**:1 (1955).
- [34] Barone, J. F., Huff, R. L., and Dickson, G., Surface roughness of gold castings, *Dental Prog.*, **1**:78 (1961).
- [35] Neiman, R., Investment composition, U.S. Patent 2,247,395; 2,247,585; 2,247,586; 2,247,587; 2,247,588.
- [36] Moore, T. E., Dental investment material, U.S. Patent, 1,924,874.
- [37] Watts, C. H., Jr., Investment material, U.S. Patent, 2,675,322.
- [38] Collins, P. F., Dental investment composition and process, U.S. Patent, 2,006,733; 1,953,075.

Basic Metallurgy of Dental Casting Alloys

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The complex dental casting alloys have arrived at their present useful state mostly by trial and error. The three areas of technical significance for these alloys are: inertness in the oral environment, fabricability (including soldering), and alloy strengthening. Basic metallurgical studies are being made in this area, and as the gap between the art and basic metallurgy is closed, improvement in properties and the cutting down of precious metal content can be expected. There are prospects of new alloy systems and improvement in casting technique, particularly in automatic casting. Ceramic metal systems need further study. For the long range, investigations of the prosthetic material-human tissue reactions are necessary. To assist studies in this field a dental materials handbook on properties of dental alloys and related materials should be compiled and published.

Key words: Alloys, dental casting; ceramic-metal systems; chrome-cobalt alloys; dental materials; gold alloys; metallurgy, dental alloy; porcelain-gold materials; solder, gold alloy.

1. Introduction

Basic metallurgy of dental casting alloys refers to the established knowledge of interatomic forces, crystal structures, phase equilibria, solid state diffusion and reaction kinetics, plastic deformation, crystal strengthening mechanisms, and the like of such alloys. The assignment to discuss this topic was given with the suggestion that the future developments be kept in mind more so than a review of past accomplishments. In pondering over this suggestion it became apparent that it was an appropriate one in that there is not all that much established basic metallurgy of these alloys to discuss. Dental cast alloys are still in the technological stage in which the art is ahead of their reliance on basic metallurgy. For example, the dental gold alloys are generally complexes of four or five alloy additions involving copper, silver, platinum, palladium, nickel, zinc, tin, indium, and perhaps one or two others, yet the function of these elements is not well documented in the technical literature. Apparently the commercial complex alloys have been arrived at over the years by trial and error. Two particular cases in point are the palladium and zinc alloying additions. We recently found the palladium addition as singularly effective in reducing the tarnish propensity of silver-containing gold alloys. On checking the silver-containing dental gold alloys on the market, it was surprising how many contained the required amount of this alloy addition for tarnish resistance. Zinc appears to be a specific element that minimizes the tendency for gold alloy casting porosity. Here again most dental golds already carry the required zinc addition. Evidently some unsung heroes in the past responded to the feedback from the dental

laboratories and the dental profession by continually modifying alloy compositions, involving hundreds of different melts, until a reasonable optimum was achieved for the various performance characteristics. No doubt many a night was spent with the melter and perhaps a somewhat technically oriented gold alloy salesman seeking the alloys that would be favorably accepted by the dental profession. Naturally little of such findings appeared in the literature not so much by default as by an attempt to preserve secrecy for each little real or imagined discovery.

The chrome-cobalt dental alloys however were developed with the advantage of established metallurgical technology for chemical resistant alloys, namely, the Stellites. However, here the diversity of alloy types applicable to dentistry, at least for the present, is not so wide as in the gold alloys. Nevertheless, some metallurgical art running ahead of basic metallurgy does exist in the case of the base metal alloys for baked porcelain applications.

Another interesting aspect of metallurgical art in dental alloys is the technique of metal joining by so-called soldering. Actually some significant achievements exist in this field, almost completely developed by technicians. Indeed soldering as the metallurgical term is known does not apply, but rather "hard soldering", "brazing", and perhaps sometimes unfortunately "fusion welding". The gold alloy solders must be noble and of the same color as the joined material. Hence the simplest procedure for making a solder is to take the alloy to be joined and lower its melting range about 150° C. with zinc and tin additions. In the hands of a skilled technician, joining gold alloys with such a solder works quite well. For the dental

golds fortunately the metals to be joined are noble, i.e., inherently "clean", and hence fluxing what oxides occur is easily done. The joining of the non-gold cast alloys is however a considerably more serious problem challenging both the metallurgist and the technician.

Perhaps the most interesting area of metallurgical art versus basic metallurgy is the strengthening of the cast alloys. The research as reported in the metallurgical (as distinct from dental research) literature indicates the logical approach for studying the strengthening of alloys (chiefly by age hardening); by starting with binary systems, then going on to the ternaries, etc. Researchers reporting in the dental literature begin, for practical reasons, with the complex alloys already being used by dentists. The complexity of the alloys however limits the attainment of data that reveal the mechanism of alloy strengthening. Thus, although the two approaches are heading toward each other, there is a technological gap.

A brief review of some basic physical metallurgy of cast dental alloys as found mostly in the metallurgical literature will define this gap more clearly.

2. The Basic Metallurgy Limits of Cast Dental Alloys

2.1. Alloy Inertness

The primary nature of the gold alloys is the retention of some of the nobility inherent in pure gold. There are two basic criteria for evaluating the nobility of a metallic element. In one the molar free energy of the formation of a compound from the element is measured for standard conditions. If this free energy value is negative, the compound will tend to form spontaneously under the specified conditions. If the free energy is positive, the compound will tend to decompose back to its component elements. The degree of this decomposing tendency is measured by the positive free energy value. This degree of instability of the compound is a measure of the nobility of the metallic component. If the positiveness of the free energy is maintained at elevated temperatures, where reaction rates may be very high, then this tendency for the compound to decompose at high temperature is the fire-refining phenomenon characteristic of the highly noble metals such as gold and platinum.

A second criterion for determining nobility is the measurement of emf values against a standard electrode in a standard cell under certain specified conditions. Here again positive values of the emf indicate nobility relative to the standard electrode, with the degree of nobility being indicated by the positive emf value.

Neither of these criteria serve too well for alloys. Sometimes a galvanic series is set up for a particular electrolyte, and the metals, which may include alloys, are listed as to their relative anodic

behavior; those on the upper end of the list will behave anodic to those below. No one seems to have made such a list of the different gold alloys for sulfide-producing environments. The rating of gold alloys in tarnish tests is the nearest to such a series. However, such tarnish tests have not been standardized.

In the case of the chrome-cobalt alloys, their inertness in certain environments is attributed not to nobility but to the ability to passivate, i.e., to produce a protective coating automatically on the surface. Here again no criterion seems to exist that would assist the dental profession in classifying such alloys as to their inertness in the oral environment.

Thus we have two important classes of cast dental alloys; the noble and the passive, with no established evaluating procedure for true inertness in the oral environment.

2.2. Fabricability

A significant characteristic of the dental casting alloys is that they cast readily and give faithful replication of the detailed contours of the impression pattern. This requires convenient melting and casting temperature ranges. Also the high density of the gold alloys yields a low kinematic viscosity, so that the molten metal readily flows and fills the mold in all parts. The chrome-cobalt alloys, although of lesser density, also rely on the generally low kinematic viscosity of the metals. Measurements of the speed of mold filling indicate filling rates for small castings in fractions of a second. The solidification takes an additional few seconds. A part of the castability feature of dental alloys is that they react very little with the mold material, so that little dressing of the casting is necessary, at least little enough not to disturb the fit of the casting as a dental restoration, which is a rather precise requirement.

The gold-base alloys are easily joined by soldering with carefully matched soldering alloys. The matching is for color and for tarnish resistance. However the technology seems to be completely in the hands of the technicians and the dental alloy manufacturers. There appear to be no criteria as to surface tension, viscosity, spreading power, or physical properties of the solder metal. The solder joint metallographically appears good, although there is little quantitative data as to the physical properties. Currently the chrome-cobalt alloys are not soldered in dental applications. The metallurgical art on this problem has as yet not been successful. Here may be an opportunity for basic metallurgy to assist in solving the problem of joining the base dental alloys.

2.3. Alloy Strengthening

The essential theory for the strengthening of gold alloys, as reviewed by the metallurgists writing for the dental journals is that an order-dis-

order transformation takes place. This comes from the discovery of Kurnakov and his associates back in 1916 that the stoichiometric compositions, AuCu and AuCu₃, change from random substitutional solid solution to a superlattice type, all in an FCC structure, on cooling below about 400 °C. The superlattice is of course the harder form. The complex dental gold alloys appear to be one-phase alloys after aging and so the order-disorder theory seems to still apply.

In the high fusing dental gold alloys for baked porcelain applications, no copper is added (it stains the porcelain green), but still age hardening occurs; accompanied, incidentally, by much loss of ductility. There appears to be a massive phase transformation—what it is, is not clear. When Fe or Sn are added in small amounts, on the order of one atomic percent, in the presence of Pt in the alloy, age hardening is substantially increased. Apparently Pt_xFe_y and Pt_uSn_v compounds of some kind play a role.

It is interesting to point out that for dental applications the age-hardening of gold alloys is designed to occur automatically by simply avoiding quenching of the casting, by slow cooling in the mold after solidification. Dental laboratories, or dentists doing their own metal casting, are not prone to set up heat treating furnaces scheduled for appropriate age-hardening heat treatment. Here is a good example of a kind of metallurgical art developed between the alloy supplier and the laboratory technician to achieve acceptable results.

On the other hand, in the metallurgical literature there is little evidence that the convenience of the dental laboratory technician is considered. Hence automatic age-hardening by mold cooling is practically never mentioned. Strengthening of gold alloys in general however has been in part systematically pursued. The order-disorder transformation is well recognized for gold alloys containing substantial amounts of copper. The age-hardening due to other causes is however also recognized. In the AuCuAg ternaries there is x-ray evidence of phase decomposition hardening—with the Cu-rich phase perhaps exhibiting a superlattice structure, and the Ag-rich phase adding substantially to the hardening in certain compositions. The AuPtPd ternaries show solid state decomposition into two phases on aging, as do the AuPt alloys, whereas the AuPd alloys do not.

By the time Pt, Pd, Cu, and Ag are added to gold, the hardening is quite significant. All sorts of solid state transformations occur, most of which completely escape the examination with the optical microscope. Apparently the gold alloy technology gap exists mostly between the evolution by trial and error of the complex gold alloys used in dentistry and the physical metallurgy understanding of alloy strengthening in these alloys.

As far as the chrome-cobalt alloys are concerned, these are two-phase alloys at room temperature, one phase being cobalt-rich and one, chromium-

rich. Such alloys are generally not ductile, nor are they amenable to age-hardening. However, the high rigidity of these alloys, twice that of the gold alloys, plus the inherent hardness of two-phase mixtures, makes these alloys directly suitable for stress-bearing applications in dentistry—for example, for partial restorations. However, as Asgar has so ably shown, it is not completely necessary to accept all the loss of ductility usually found in these alloys. By lowering the interstitial carbon and molybdenum, and making one or two other minor modifications, the customary chromium-cobalt alloys can be toughened considerably, without any loss of rigidity, or significant loss of yield strength. Perhaps there is a sacrifice of stable carbides, but this is important only for high temperature applications, and certainly of no value in dentistry. In these chrome-cobalt alloys basic metallurgy is being intelligently exploited for dental applications.

3. Future Expectations for Dental Alloy Technology

Recognizing that a gap exists between metallurgical art and basic metallurgy in cast dental alloys, one might well ask what are the future expectations for dental alloy technology. It should be noted that this gap at present is already being closed in part. The dental manufacturers are staffing their research departments with metallurgists, and currently there is evidence of good metallurgical research being published by them. Furthermore, there is some sponsorship by the National Institutes of Health at several universities on dental materials research, including cast dental alloys. It will take a little time for these institutions to become productive, or at least stimulative, of useful research results, but within 10 years physical metallurgists and dental alloy experts should be speaking the same language.

With this in mind, and knowing the motivations in dentistry, in dental materials manufacturing, and in government support for dental research, some technological expectations can be put forth. This is best done by examining the broad range of past developments up to the present and attempting to sense the momentums into the future.

The nature of evolving systems is that they increase in their complexity by a process of successive mutations that continually increases the adaptability of the system to its surroundings. Each successful mutation is a quantum jump in complexity, or a new branch in the existing branch structure representing the system. Thus we can trace the tree-like growth of an organization, or of a science, or of a specific technology. Having done this we are in the position to make some estimates as to the likely course of future developments in that system.

In the case of dental alloy technology one can rather easily construct the evolutionary process of

say the last 50 years. Shortly after 1919, due mostly to the work by the dental research group of the National Bureau of Standards, it was established that four types of cast gold alloys could serve the needs for the overall range of cast dental alloys. The ancient lost wax process had been applied to dentistry many years earlier, and by gradual improvement in casting equipment and in investment materials the technique used with gold-base alloys became commonplace, available to all dentists.

In the thirties the development of the chrome-cobalt alloys that were chemically passive lead naturally to the mutation of using such alloys in dentistry in place of the costly noble metals where ductility or burnishability was not important.

In the forties the physical properties of gold-base alloys were sufficiently standardized so that most gold alloy manufacturers published physical property charts of their alloys, and the larger companies adopted quality control measures to assure that every melt met the physical properties listed in their charts.

In the late fifties the porcelain jacket technique was perfected using a gold-base alloy. The demands on this alloy are exacting. Its thermal expansion coefficient must match that of the porcelain, it must have high sag resistance at porcelain baking temperatures as high as 1050° C., it must be free of porcelain-staining elements, and it must contain elements that contribute to the shear strength of the porcelain-metal bond, which apparently is chemical in nature.

In the sixties the technique of producing fine-grain castings was brought under control, raising the toughness of the alloys and reducing coring, thereby minimizing heterogeneity of alloy properties. This period saw also the emergence of white alloys for porcelain baking.

What may one reasonably expect of the future? The list below has been developed primarily on the basis of three motivating factors: (1) There is always the pressure to reduce the jewelry aspect of precious metal alloys, i.e., to cut down metal costs by reducing gold, platinum, and palladium content wherever possible. (2) It is always desirable to improve the physical properties such as strength, toughness, and tarnish resistance for the same metal cost. (3) It is always desirable to cut down on the need for technicians' skills in the fabrication of restorations, and obtain results as much as possible automatically and mechanically.

It would seem therefore that in the next few years the following will emerge:

1. Improvement in dental performance of present-day alloys with minor modifications.
 - a. improved tarnish resistance of gold alloys.
 - b. improved mechanical properties in both the gold and the chrome-cobalt alloys.

2. Development of new alloys.
 - a. lower precious metal-content alloys but with no sacrifice in dental performance.
 - b. new precious metal alloy systems.
 - c. new non-precious metal alloy systems.
3. Development of new casting equipment such that good porosity-free restorations are obtained on every casting, requiring little or no dressing.
4. Development of new soldering alloys and techniques, particularly for the high heat alloys.

There are other possibilities that can be projected. Acrylic jacket techniques already in existence might call for new types of alloys. Perhaps completely new metal fabricating techniques, such as electroforming or powder metallurgy, might come into existence in place of casting.

4. Recommended Basic Metallurgy Programs

Up to this point we have reviewed the dental casting alloys both as to their metallurgical art and their metallurgical technology aspects. Based on judgments concerning past alloy developments, a projection of the new alloy developments are given. Now, the motivation for the new developments exist. The question is whether the motivation relying on the slow growth of the metallurgical art, i.e., by trial and error, is sufficient to bring about these improvements in a suitably short time. The answer is probably no in most cases. The purpose of applying basic technology rather than simply the trial and error technique is to shorten the time lag between needs and fulfillment of these needs. In order to bring this about, it would not be wise to assign dental alloy development projects categorically to the metallurgists and anticipate good results in short order. A young metallurgical turk would quickly come up with new alloys, but the chances are that they would not be as good as the ones currently used. Some important but subtle factors would not be taken into account. For example, the proposed alloys might be substantially stronger and have the gold content in what is believed to be the safe range, but after several hundred restorations had been inserted in patients' mouths, it would be discovered that they discolor badly. Another likely occurrence in situations when a young technically trained man is assigned to make improvements in an old established technology, is that old improvements are rediscovered.

The first order of business is then to close the gap explicitly between metallurgical art and basic technology in dental alloys. The young metallurgist with modern sophisticated tools, such as the electron probe, the scanning electron microscope, and the computer, should first learn why the present alloys work as well as they do. For example, one of the first projects to assign to the metallur-

gist entering the dental alloy field is the determination of the mechanism of strengthening of the dental gold alloys by the somewhat automatic age-hardening of dental castings by mold cooling. A second project might be to determine the subtle resistance to discoloration of the dental golds in the oral cavity. It is in the course of such a program, where the metallurgist is forced to learn some of the complicated requirements of dental castings, that he would develop an appreciation of the true objectives of his development research work. It is very probable that in the course of such a program new questions would be raised whereby new and more sophisticated improvements could be conceived in dental technology. For example, how can the bulk of a crown be cast in some inexpensive high strength metal, then be covered with a soft burnishable material that is completely noble?

Another good question for the biomedical metallurgist, for this is what he would become, would be the surface reactions on metal-tissue contact. Many new and interesting avenues would be opened up for exploration. An enormous amount of work will eventually be done on this whole question of prosthetic materials-living tissue reactions.

It is while the biomedical metallurgist is ranging over these wide problems that he would also learn to keep his feet on the ground with such boundary conditions as precision castability, joinability, etc. There is little point in making a superior alloy as to strength and tissue inertness, if it cannot be fabricated or soldered, or if it is nonburnishable.

One interesting area that a metallurgist could get into almost immediately is the development of a technique for producing sound castings. Dental castings as a rule are reasonably sound. The alloys are sufficiently deoxidized to make them gas free. Porosity and surface defects, however, remain the most serious problems in dental castings. Here the metallurgist can quickly bridge the art versus technology gap, because casting soundness is not one of the successes of dental metallurgical art. The reason for this is that except for excessive porosity, or surface defects, the laboratory technician is in the dark as to the quality of the interior of a casting.

Perhaps the largest gap between art and technology in dental alloys is the soldering or joining technique. This technique has been developed almost completely without metallurgy, between the trial and error of the gold solder producer and of the skilled laboratory technician. The metallurgist has a great deal to learn here. However, once the metallurgist has caught up with the technician there is the strong possibility for the development of techniques where manual skill is not required, manual skills being a commodity that is getting scarcer and scarcer. A good joining technique of the furnace brazing type would be

most welcome. Incidentally, the high heat type of dental castings, particularly the base metal alloys are generally not soldered well by the technician. Here the metallurgist has a clear problem to work on immediately.

There is need for the eventual development of a simple automatic casting machine, especially for the high heat alloys. There is no reason why a dental casting cannot be made completely sound, faithful to the mold details, with little or no finishing required, coming directly from some kind of automatic casting machine. This development is of course a little outside the domain of the metallurgist. New heat sources for the melting and the possibilities of vacuum casting have to be explored, and perhaps the development of new investment materials must come about to aid the metallurgist.

One particularly good area for the metallurgist, together with the ceramist for closing the gap we are discussing, is the study of the very interesting and quite successful technique of porcelain bonding to metal restorations. Here, once the metallurgist and ceramist working as a team have caught up with the technique as it is now practiced, new improvements would surely be forthcoming.

Finally some long range projects might be described. With the laboratory tools of today it would not be difficult to document all the phase compositions that occur in the complex gold-base alloys. Quaternary and higher component phase diagrams are too difficult to construct. However a coordination of metallography and rasters available with the electron microprobe (these show area distribution of selected elements in a microstructure) would furnish the next most useful information, short of knowing the phase diagrams. Indeed, such data may actually be more useful than that obtained from phase diagrams. Microprobe analysis can monitor nonequilibrium compositions that occur in castings and on heat treatment.

Another worthwhile long range project would be the determination of distortion, dimensional stability, and residual stresses in dental castings, for both the gold and the base metal alloys. Along these lines a study of the stress distribution in porcelain-on-metal restorations could be important. A tempered porcelain, analogous to tempered glass, where the tensile stresses are all confined to the interior might add to the already considerable usefulness of porcelain facings in dentistry.

Perhaps the most important long range program would be the study of material-tissue reactions. This would naturally overlap medical materials.

5. A Dental Materials Handbook and Dental Materials Publications

The most useful reference sources we have today on dental materials are the textbooks by Phillips and Skinner, and by Peyton. However, being

textbooks, they cannot give space to numerous phase diagrams, microstructures, and mechanical properties for a large variety of alloys. The original sources as references are scattered too widely to be available to all dental materials research workers. Therefore it seems justifiable to have compiled a dental materials reference handbook. The coverage might be in the order of the following:

1. Physical Properties of the (appropriate) Elements (Obtainable from the ASM Metals Handbook)
2. Phase Diagrams

This part should include about 50 commonly used binary phase diagrams involving at least one of the following components: Au, Ag, Pd, Pt, Cr, Co, Ni, Fe, Sn, Hg, Cu, SiO_2 , Al_2O_3 , CaO, MgO , Na_2O , and K_2O . Discussions of each phase diagram should include crystal structure of phases, and lattice parameters, where possible. Likewise there should be about 30 ternary systems described in isothermal diagram form, involving at least two of the components of the above. The phase diagrams can be mostly obtained from Hansen's and from Guertler's compilations. The nonmetallic systems are obtainable from "Phase Diagrams for Ceramists," published by the American Ceramic Society. Quaternary alloy diagrams are not too common or useful. However, in due course there should be electron rasters of complex alloys in the equilibrium state. When these apply to dental material systems, they should be included.

3. Mechanical Properties

The literature should be searched for assembling as completely as possible the mechanical properties of pertinent alloys, ceramics, and polymers. These should include data for cast, wrought, annealed and heat-treated conditions.

4. Corrosion Data

The literature should be searched for electrochemical tarnish, and corrosion data. The literature on electrical contact technology should not be overlooked in this connection.

5. Miscellaneous Properties

Heat conductivity and color data would be useful for certain alloy and ceramic systems.

6. Miscellaneous Materials

Standard information on waxes, resins, investment materials, and cements generally used in dental techniques should be included.

One major advantage of such a handbook would be the sparing of the dental materials textbook authors the chore of including tables of routine data in their books. A textbook should not have to serve as a data reference book, but as an expounder of concepts so that the information in handbooks can be intelligently used. However, the principal advantage would be to facilitate basic metallurgy

research on dental alloys. Indeed handbooks and the like are an indispensable tool and no research laboratory functions well unless the researcher is surrounded by the bric-a-brac of compilations, handbooks, wall charts, and data tables.

The appropriate group to issue such a handbook and renewing it on a five-year basis or so, is the ADA division at the National Bureau of Standards. The first issue need be only a soft cover photo-offset product. The natural demand that would develop will dictate its future development.

To the dental materials researcher it is important that he publish his work and that he follow the work of other researchers. It will be a luxury soon to publish dental materials research papers in general dental research publications. It is a waste already today to have to subscribe to three or four dental journals for the 5 percent or so of papers that apply to dental materials. Furthermore, when papers are prepared for publication, the authors may have to strain to connect their paper to dentistry. For example an excellent paper may be unfairly criticized for not having clinical data, when actually the information without clinical data is directly useful to dentistry, or may be a prelude to clinical work. Whether there are enough dental materials papers to have special issues devoted to this subject is still uncertain. However, this can be anticipated in the next few years, particularly since dental materials research is increasing significantly.

6. Summary

It appears that cast dental alloys arrived at their present usefulness mostly by trial and error with coordination between the dental alloy producers and the dental laboratories and dentists. The three areas of technical significance for these alloys are: alloy inertness in the oral environment, fabricability (including soldering), and alloy strengthening. One can find some basic metallurgy in the literature in these areas, but nevertheless a gap exists between the art and the documented technology. However, metallurgists are entering the field more and more, and one can expect advances in the improvement in the properties of the present alloys and in the cutting down of the precious metal content while maintaining current properties. There is a prospect of new alloy systems, mostly in the non-precious or low precious metal area. Improvements in casting technique, mostly in the direction of automatic casting can be expected. Likewise, dependence on the necessary manual skills in soldering, both of the precious metal and the base metal type, will be reduced. The trial and error method works too slowly to bring these improvements to the fore in the near future. Hence research programs should be initiated; first to acquaint the research metallurgist as to what is already good in the present-day dental alloys and techniques, and secondly to open avenues as to where improvements

can come about. Ceramic metal systems need further study. Dimensional stability of castings is also important. A most interesting long range project, and one that is important for medical materials in general, is the study of prosthetic material-human tissue reactions. Finally, it seems that certain research aids are in order to assist the new metallurgist working on basic metallurgy of dental alloys. A dental materials handbook should be compiled and revised periodically. Dental materials papers should be given special issue status in the dental journals.

Considerable assistance in the preparation of this report came from Joseph Tuccillo of the Jelenko Co., Edmund M. Wise (formerly of the International Nickel Co.), and Professor Ernest Levine of New York University. Many references were used and it is difficult to make detailed credits. The following were the ten most frequently used.

7. Bibliography

1. Asgar, K., Techow, B. O., Jacobson, J. M., A new alloy for partial dentures, *J. Prosthetic Dentistry* **23**: 36, February 1970.
2. ASM Handbook, 8th Ed. vol 1, pp. 1174-1196 (American Society for Metals, Metals Park, Ohio, 1961).
3. O'Brien, W. J., Kring, J. E., and Ryge, G., Heat treatment of alloys to be used for fused porcelain technique, *J. Prosthetic Dent.* **14**: 955 Sept-Oct, 1964.
4. Peyton, F. A., *Restorative Dental Materials*, 3rd Ed. (The C. V. Mosby Co., St. Louis, Mo. 1968).
5. Shell, J. W., *Hogden-Shell Dental Materials* (The C. V. Mosby Co. St. Louis, Mo. 1938).
6. Skinner, E. W., and Phillips, R. W., *The Science of Dental Materials*, 6th Ed. (W. B. Saunders Co., Philadelphia, Pa., 1967).
7. Souder, W., and Paffenbarger, G. C., Physical Properties of Dental Materials, *NBS Circ.* **433**, 34-80 (1942).
8. Vines, R. F., and Wise, E. M., *Platinum Metals and Their Alloys* (International Nickel Co., 1941).
9. Vines, R. F., and Wise, E. M., *Age Hardening Precious Metal Alloys*, pp. 190-230 (American Society for Metals, Metals Park, Ohio, 1940).
10. Wise, E. M., *Gold* (D. Van Nostrand Co., New York 1964).

IV. New Development in Nonmetallic Restorative Materials

Dental Porcelain

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Current research on dental porcelain has been concentrated on methods of improving fracture resistance of porcelain restorations. Enamelling of metals or dispersion strengthening of glasses offer the greatest possibilities for this purpose. The fusion of porcelain to metal copings has proved very successful under clinical conditions, but the necessity for masking the metal substructure presents difficulties in obtaining the desired aesthetic characteristics. Replacement of the metal copings by a higher strength ceramic should improve aesthetics and reduce productive costs. Dispersion strengthening of glass with high strength alumina crystals has resulted in the production of a new range of aluminous porcelains for jacket crown and bridge pontic construction.

Key words: Aluminous porcelain; ceramic materials, dental; dental materials; dental porcelain; dispersion strengthening of glass; porcelain, dental; porcelain-gold techniques and materials.

1. Introduction

The exacting aesthetic requirements of dentistry have largely dictated the composition of dental porcelain. In order to produce highly translucent enamels, dental porcelain must contain a high proportion of glassy material. Regular dental porcelain has been developed from feldspathic glasses modified by small amounts of crystalline materials and coloring pigments, and suffers from the inherent brittleness associated with all glasses.

It is hardly surprising that priority in research has been given to methods of reinforcing dental porcelain, since no other incident is more likely to frustrate the dentist in his work than the breakage of a porcelain jacket crown. The chipping or complete fracture of porcelain pin teeth or bridge pontics can also occur, involving both dentist and technician in time-consuming repair work.

2. Research Avenues to Improve Dental Porcelain Strength

In order to improve the strength of dental porcelain a number of avenues are open and future research would appear to center around five approaches.

1. Enamelling of metals.
2. Dispersion strengthening of glasses.
3. Enamelling of high strength crystalline ceramics.
4. Controlled crystallization of glasses.
5. Production of compressed surface layers in dental porcelain via ion-exchange.

2.1. Enamelling of Metals

The fusion of dental porcelain to metal copings is now widely used and has proved very successful

under clinical conditions. Providing a strong bond is achieved between the porcelain veneer and the metal, there is little chance of leakage at the interface. In addition the porcelain enamel is reinforced by the metal and is less likely to be placed under a tensile force which can cause brittle fracture.

The attachment of porcelain to gold in dental restorations has been variously ascribed to a combination of mechanical, wetting, or Van der Waals bonding. Vickery and Badinelli [1]¹ have examined the interfacial effects between porcelain and single crystal and polycrystalline gold surfaces and showed that, whereas mechanical and compressive forces played significant roles in attachment, Van der Waals forces probably do not make a meaningful contribution. The only true bonding effect derived from direct reaction of porcelain with interstitial compounds developed at grain boundaries in the metal substrate. No evidence was found for a chemical bond between porcelain and gold per se. Industrial research on metal-ceramic bonding using modern techniques such as electron microscopy or electron probe microanalysis has revealed that a glaze-body interface is always a region, sometimes very thin indeed, where diffusion of ions has been going on in both directions [2]. At the elevated temperatures employed, the ions are quite mobile and will diffuse from one material into the other. This might be termed chemical reaction but examination of the interface revealed no definite compound formation.

It therefore seems probable that the major contribution to effective bonding of dental enamels to gold is to be found in the compressive stresses developed through accurate adjusting of the thermal expansions of the gold and porcelain.

¹ Figures in brackets indicate the literature references at the end of this paper.

Whatever the exact nature of this bond the most important fact is that it has proved very effective under clinical conditions. Providing the technician takes care in degassing and cleaning his casting prior to applying the opaque porcelain the incidence of porcelain actually shearing off the metal is very low.

The somewhat doubtful aesthetics of the anterior fused porcelain to gold crown is perhaps of greater clinical significance. In order to ensure that the appearance of the crown is acceptable, the dentist is often required to remove more dentin than is biologically desirable. This heavy destruction of sound dentin has increased the risk of pulp mortality and considerable effort is now being made to reduce the thickness of metal, opaque and enamel porcelain used in the standard type fused porcelain to gold crown.

In order to mask the metal substructure effectively, the opaque porcelains are heavily loaded with opacifiers. These opaque layers will also present problems since light reflection from their surfaces can often be severe. The manufacturers are therefore restricted in the amount of light transmission they can allow through their dentin porcelains which are generally more opaque than the regular porcelains used in jacket crown work. The anterior fused porcelain to gold crown will often lack depth of translucency, and due to the increased opacity, light reflection from the surface is higher than in an all porcelain restoration fired in vacuo. This property not only exacerbates any metameric effects but can result in a deadness in the mouth, reminiscent of some of the early air-fired porcelain production teeth. Vacuum firing of the enamel and translucent porcelains can improve the incisal translucency but the cervical two-thirds of the tooth presents a formidable problem to the technician if the ultimate in aesthetics is to be achieved.

There is little doubt that the manufacturers have made considerable strides in solving some of these problems. Firstly by increasing the shade range of the opaque porcelains so that each opaque color is closely matched in hue to the dentin colors and secondly by using translucent overlay enamels to give an illusion of depth to the crown. Built-in concentrated colors can also improve appearance and greys and blues can enhance the effect of incisal translucency. Surface staining will never achieve the same effect and if natural enamel is to be simulated to perfection a ceramic crown must have depth of translucency.

This problem was particularly noticeable during the course of experiments on aluminous porcelain core materials [3]. Porcelains containing 40 percent very fine calcined alumina (specific surface area 6,000 cm²/g) were, for all practical purposes, totally opaque whereas core porcelains containing coarser grades of fused alumina (specific surface area 1,150 cm²/g) transmitted up to 20 percent light. The latter porcelains, when

veneered with translucent enamels, produced much more life-like crowns since some light was still being diffused through the core porcelain [4]. By contrast the totally opaque calcined alumina core porcelain caused much more light reflection from its surface, and crowns constructed from this material produced very similar effects to the opaque porcelain used in the fused porcelain to gold technique. It became clear that opaque porcelains must strike a fine balance between masking out cement linings or metal but at the same time not reflecting too much light. It is doubtful whether this fine balance will ever be struck with the fused porcelain to gold restoration since it is essential to use very opaque materials in order to avoid any metallic greyness showing through. For this reason it is likely that any further improvements in aesthetics will be achieved through careful control of dentin translucencies in relation to a wide range of neutral opaque tones. Unfortunately the manufacturers are placed in a dilemma in this situation since they could very easily produce dentin colors with higher translucency if these colors were used in consistent thickness. The variable thicknesses encountered in crowns made for clinical use will often mean that a body dentin color of less than 0.5 mm thickness must be used. In this situation a commercially produced porcelain powder must have a built-in safety factor, and light transmission through the porcelain must be reduced to a level where the opaque porcelain does not have a dominating influence on color. If such an influence occurs, the clinician will face serious metameric problems once the patient experiences varying artificial lighting conditions. In particular color changes of this type can often be severe in subdued tungsten light. It is obvious that these problems could be further reduced if the metal copings were made thinner, and the search for higher strength metals which also have a high rigidity modulus is continuing with accelerated interest. The stellite-type casting alloys based on chromium, cobalt, nickel and molybdenum are an obvious choice but obtaining good casting accuracy in thin section and a strong bond with dental porcelain can often prove difficult under average laboratory conditions. However the manufacturers are devising improved techniques to simplify these procedures and acceptable restorations can now be made.

Successful bonding of porcelain to these non-precious metal alloys is dependent upon the prevention of a buildup of too thick an oxide layer at the porcelain-metal interface. A clean and homogeneous casting is the basic requirement for successful work. Sprues should be attached in such a manner that a vertical or horizontal beam serves as a reservoir with short 2 mm connections to the casting itself. The casting must be thoroughly sand-blasted and cleaned with a solvent such as acetone or alcohol before applying the opaque.

After the opaque porcelain is applied, the cardinal point to bear in mind is that vitrification must be rapid and complete before a thick oxide separating layer can form and interfere with bonding. The use of metal firing trays to improve the thermal conduction, and furnace muffles with even heat distribution will assist the technician. Short firing cycles of one to two minutes are also recommended and opaque porcelains which can vitrify in this time are now available. Because of the strong oxide formation in metal areas which are not covered by porcelain it is good practice to extend the opaque layers into these transition areas and grind away any excess porcelain after the final bake.

More clinical experience is required before any assessment of the merits of nonprecious metal alloys versus gold alloys can be made. Even in the case of the precious metal alloys, the fine balance that needs to be struck in applying the various layers of porcelain taxes the skill of the most experienced ceramist. With a world-wide shortage in this skill it is hardly surprising that many fused porcelain to metal crowns do not do justice to the full potential of these materials.

However, despite these deficiencies, the fused porcelain to metal restoration has proved of enormous benefit to dentistry and has widened the aesthetic scope of both fixed and removable partial prosthesis.

2.2. Dispersion Strengthening of Glasses

The elimination of metal substructures in crown and bridge work is desirable, not only for aesthetic reasons but also because of the high cost of production.

The replacement of metal copings by a higher strength ceramic seemed to offer possibilities and a survey of high strength industrial ceramics indicated that increasing use was being made of ceramic oxide crystals as a reinforcing phase in industrial porcelains [3].

It is well known that the strength and elasticity of glass can be increased by physical interaction with an included phase of high elasticity [5, 6, 7]. Dispersion strengthening of glass utilizes this principle whereby ceramic crystals of high strength and elasticity are fused in a glassy matrix to form crystal-glass composites. These composites form a constant strain system and fracture has an equal chance of starting in either phase. In the absence of thermal expansion differences the strength and elasticity will increase, approximately, in proportion to the amount of the crystal phase. The choice of ceramic crystals is fairly wide but for dental purposes factors such as fusion temperature, bonding with dental porcelain, color and aesthetic values must be taken into account. Alumina (Al_2O_3) was found to be the most suitable ceramic for this purpose [3] and this material is receiving increasing attention from the dental manufacturers.

Alumina has been used as an additive in regular dental porcelain for many years [8] but its use has been mainly confined to making the so-called "hard core" porcelain which surrounds the pin anchorage in a vacuum-fired tooth. In order to use alumina reinforced porcelain in greater section it became necessary to prepare specialized materials in which much greater attention had to be paid to the matching of thermal expansions and the sintering characteristics of the glass matrix powders and alumina crystals.

Research indicated that if the alumina crystals were dispersed in a borosilicate glass of matched expansion to the alumina, the strength resulting from this stress-free matrix was improved [6]. Further work revealed that when fused alumina crystals of 99.5 percent purity and with a size range of 20 to 30 μm (specific surface area 1153 cm^2/g) were incorporated in a specially prepared borosilicate glass containing a high combined alumina content that "Aluminous Porcelains" could be produced with transverse strengths of over 20,000 psi (140 MN/m^2) and with a light transmission of up to 20 percent on 1 mm thick discs [3]. This improvement in strength is approximately double that of regular dental porcelain and clinical trials with these aluminous porcelains indicated that they could be used in jacket crown manufacture [9].

It may be generally stated that the strength and opacity of an alumina reinforced porcelain is a function of its crystal or particle size. The finer the crystal size the greater the strength and opacity. Research by the dental manufacturers has therefore been directed towards optimizing the crystal-glass particle size relationship to obtain improved sintering characteristics, strength and acceptable translucency.

One such study reports the results with a special borosilicate fusion, high in alumina, in which the glass was tailored to have good sintering characteristics and high strength in the sintered state [10]. Addition of a closely sized alumina aggregate in which the preferred alumina grains had fairly smooth surfaces improved the sintering behaviour of the alumina-glass composite, and high sintered densities were obtained. Modulus of rupture values in the range of 22,000 to 24,000 psi (150 to 165 MN/m^2) were obtained and in some cases ceramic bodies with strength values of over 30,000 psi (210 MN/m^2) were produced. Relationships for sintering behaviour and strength were obtained that were at least qualitatively predictable. These behaviour patterns closely followed Griffith's flow theory for strength and a viscous flow theory for sintering. Lowered strengths resulted from solid inclusions having unfavourably low thermal expansions or by reactions or diffusion resulting in unfavourable grain boundary stress. Pore structure was dependent upon particle size distribution of the initial powder and upon the time-temperature firing cycle.

The current alumina reinforced porcelains have benefited from this type of research and new types of isotropic glasses containing high combined alumina contents have been developed for veneering the aluminous porcelain cores. It is likely that further improvements in the strength of these alumina reinforced ceramics is possible but at present the aluminous porcelain jacket crown cannot be regarded as a replacement for the fused porcelain to gold crown. The dentist must still be aware that he is dealing with a brittle material and aluminous porcelain jackets must have adequate tooth support and at least 1 mm clearance on the lingual surface if the alumina reinforcement is to make a significant contribution to strength [11].

Due to the semitranslucent nature of the aluminous core porcelains and the high translucency of the enamel veneers the anterior aluminous porcelain crown is superior in aesthetics to the fused porcelain to gold crown.

Clinical experience has indicated that aluminous porcelain should be used primarily as a replacement for and to extend the use of regular dental porcelain.

2.3. Dispersion Strengthening of Glass With Alumina Whiskers

Alumina whiskers are filamentary single crystals having both high surface and crystalline perfection. Their strength at room temperature can be as high as 2×10^6 psi (14×10^3 MN/m²) with a modulus of elasticity of 70×10^6 psi (48×10^4 MN/m²).

Dispersion of these whiskers in a glass matrix may be done in several ways. The following two methods were tried in jacket crown work. The whiskers were intimately mixed with a finely ground glass powder used for making aluminous porcelain and applied to a platinum matrix by standard technique. It was found that whisker concentrations above 15 percent created difficulties with regard to sintering behaviour, and high densities could not be obtained. It became clear that if sufficient whiskers were to be incorporated in the glass powder to make a significant contribution to strength that alternative methods would have to be used. Vacuum hot pressing techniques allow high whisker concentrations to be used but such methods are not commercially viable in dentistry.

An alternative method was tried in which preformed "green" whisker tapes were incorporated in the jacket crown. These tapes were produced by using the finely ground glass powder and highly oriented whiskers held in an organic binder [12]. The tapes were incorporated in aluminous core porcelain on the lingual surface of the crown by a lamination technique. Once again problems of sintering the alumina whisker-glass composite arose, since the layers of porcelain in between the tapes tended to be very porous despite firing in vacuo. It was considered that future research

might make it possible to produce lingual alumina whisker-reinforced glass shells which could be lightly ground to fit the jacket preparation. In this case the shells could be produced by vacuum hot pressing. However it is doubtful whether this method could rival the comparative simplicity of the fused porcelain to gold technique.

The use of preformed "green" whisker-glass composites in tooth production should not be ignored since it may be possible to tailor-make the reinforcement to fit exactly in the tooth mould prior to applying the overlay dentin and enamel colors.

2.4. Enamelling of High Strength Crystalline Ceramics

The bonding of aluminous porcelain to high strength recrystallized alumina provides an alternative method of reinforcing the enamel veneers.

Recrystallized aluminas in excess of 85 percent purity are one of the strongest groups of industrial ceramics. Recrystallized or "high alumina" is a particularly attractive material from the dental standpoint since it may be colored to dentin shades by the use of high-temperature-resistant pigments such as manganese-alumina pink, vanadium-zircon blue or praeosodymium-zircon yellow. The resultant color backgrounds are very receptive to veneering with dental enamels and in addition a strong ionic bond is formed between the alumina and aluminous porcelain veneer. This chemical bonding is fairly tenacious and ion exchange at the surface of the alumina is such that diffusion of ions from the porcelain into the alumina can be demonstrated under ultraviolet light [3]. High alumina ceramics also exhibit high tensile strengths in excess of 17,000 psi (117 MN/m²), and their modulus of rupture is in the region of 50,000 psi (345 MN/m²) [3].

More recently methods of firing high purity alumina containing 0.2 percent magnesium oxide have been devised in which it is thought that a spinel is formed at the grain boundaries, slowing down grain growth, and allowing the diffusions of porosity along the grain boundaries. The resultant materials are almost pore-free which in turn produces a highly translucent ceramic body. A completely transparent recrystallised alumina has been developed by the General Electric Company and marketed under the trade name of "Lucalox". This type of material is particularly useful for making thin shells for crown facings.

High alumina can be manufactured in fairly intricate shapes to a high degree of tolerance (± 2 percent linear) and preformed high alumina reinforcements for crown and bridge construction are now available. These reinforcements are supplied in the form of rods, sheets, tubes, and dovetail veneers and a number of types of construction are available to the technician [13].

Oval alumina tubes provide strong anchorage areas for custom-built or factory-made bridge pontics and rival the fused porcelain-to-gold pontic in strength. Alumina tube pontics may be used with conventional golds and have the added advantage of replaceability. They can also extend the use of porcelain in cases of long span bridges and markedly improve the aesthetics of the anterior fixed bridge. Similar tubes can also be used to reinforce post crowns and very good clinical results have been recorded in close bite cases [14].

Sheets of high alumina, 0.8 mm thick, may also be incorporated in the lingual surfaces of aluminous porcelain jacket crowns to reinforce the critical biting area. These crowns are more aesthetic than the metal reinforced restorations and clinical trials have indicated a very comparable strength performance [4].

All-ceramic fixed bridges can also be constructed using aluminous porcelain jacket crowns connected by high alumina rods. However these bridges are better confined to single tooth replacement since on long spans there is a risk of the abutment aluminous porcelain crown being placed in tension and fracturing down the midline. The alumina reinforced fixed bridge will not replace fused porcelain to gold, but for the manufacture of small span anterior bridges, alumina is a material of great aesthetic appeal.

The construction of high alumina copings directly on to platinum matrices has also proved possible [4], but the control of firing shrinkage is still a problem. Regular dental porcelain or aluminous porcelain contains sufficient glass phase to deform and slump over the platinum matrix. By contrast, high alumina is extremely resistant to pyroplastic flow and when shrinkage takes place during sintering, cracks or fissures will open up in the alumina core powder. In some cases the platinum will be permanently distorted, as the alumina crushes it [4]. Experiments are continuing toward producing high content alumina-glass powders in order to increase pyroplasticity without seriously impairing strength.

2.5. Controlled Crystallization of Glasses

Controlled crystallization of glass was developed by Stookey [15] in the United States and new and unique properties were observed in these glass-ceramics. Not only was the strength of these materials markedly improved but very high thermal shock resistance was imparted.

Controlled crystallization of glass depends upon the fact that glass, at ordinary temperatures, is an undercooled liquid which is in an unstable state [16]. It can be made to crystallize by heating to the proper temperature with crystal seed or nuclei present. The glass is then converted to a dense mass of very tiny interlocking crystals. Titanium dioxide is an effective nucleating agent

and the starting glass must be homogeneous with qualities like optical glass. Spodumene is a suitable glass, compounded from the oxides of lithium, aluminum, and silicon and has been used extensively to make "Pyroceram" cooking ware. Normally the ware is heated to a temperature where nuclei are formed from the dissolved titanium dioxide. This happens at a temperature a little above the annealing point where the glass shows the first signs of softening. After myriads of nuclei have been formed in this way, the glass is slowly heated to higher temperatures where tiny spodumene crystals grow on the nuclei, converting the transparent glass to an opaque white mass composed chiefly of spodumene crystals.

The opacity of these glass-ceramics makes them unsuitable for dental application but more recently McCulloch [17] has reported on experiments with a glass-ceramic based on lithia-zinc oxide-silica and using metal phosphate nucleating agents. This glass was transparent and amber in color in the glassy state but became translucent and tooth-like after crystallization or ceraming for 1 hr at 600 °C. At this stage modulus of rupture figures in excess of 18,000 psi (124 MN/m²) were obtained.

This glass-ceramic was used to produce posterior teeth by moulding in a die and counterdie. These production teeth were made only in a single shade but further experiments were performed in which bars of the vitreous glass were made photosensitive by using silver as a nucleating agent. On cooling, the bars responded to ultraviolet light so that by differentially irradiating the surface, the glass, on heating to the ceraming temperature, could be made to crystallize at different rates, thus creating a polychromatic effect. It was shown that further characterisation might be accomplished by applying printed transfers, containing tooth pigments, to the surface.

These experiments have not yet reached the stage of commercialization and considerable problems in fabrication and color control must still present themselves to the tooth manufacturer. The current high standard of aesthetics in a vacuum fired anterior porcelain tooth has been created by building in concentrated colors and multiblended veneers of dental porcelain by manual application. The fact that this process has not yet lent itself to automation is indicative of the tremendous problems encountered in duplicating both the depth of translucency and color of human enamel and dentin. Dentistry still demands a high degree of artistic skill even in a mass produced porcelain tooth.

2.6. Production of Compressed Surface Layers in Dental Porcelain Via Ion-Exchange

Chemical toughening of glass is widely used in industry and these techniques may have some application in dentistry.

Isard and Lehman [18] have reported on experiments in which specimens of soda glass were heated in a bath of fused potassium nitrate to effect ion-exchange. The compressed surface layer produced by this treatment imparted considerable strength to the glass and it was claimed that the high strength was not removed by abrasion. The treatment could be applied to the complicated shapes with re-entrants such as jacket crowns and would be particularly suitable for use with aluminosilicate glasses used in dental porcelain where ion-mobilities are relatively high.

The application of this technique to clinical practice presents certain problems since any occlusal adjustments of the crown would remove the compressed surface layer. However it might be possible to toughen crowns chemically after grinding in the mouth and this area of research deserves further study. Chemical toughening of denture teeth does not appear to be a practical proposition since these teeth are generally adjusted for occlusion after processing the denture.

3. Additional Areas of Dental Porcelain Research

3.1. Silane Bonding of Acrylic Resin to Porcelain

Other areas of research on dental porcelain have been directed toward improving the bond between porcelain teeth and the acrylic denture base. It was shown that when feldspathic porcelain teeth were treated with gamma-methacryloxypropyltrimethoxysilane that a bond was formed between the porcelain and acrylic of such strength that when failure occurred, fracture took place in the porcelain [19].

Semmelman and Kulp [20] considered that this bond was not adequate in heat-cured denture bases when measured from a clinically determined standpoint and that the pin anchorage was still necessary. This evidence was in agreement with the work of Myerson [21] who considered that the unsatisfactory bond strength was produced by excessive shear stress during cooling. He showed that by reducing the temperature of processing, the cooling shear stress was reduced and concluded that the self-cure systems produced the strongest bond with the silane treated porcelain tooth. His final conclusion, which is probably most pertinent, stated that the large differential in thermal expansion represented the weak point in the silane bonded porcelain-acrylic system. This must be accounted for before the obvious advantage of silane bonding can be used.

3.2. Refractory Die Materials

The development of new types of refractory die materials for the construction of all-ceramic

alumina reinforced bridgework or for direct baking of porcelain jacket crowns has reached a stage where commercial materials are now available.

Vickery [22] has described a technique for using a castable, refractory, ceramic die composition in which it is claimed that accurate reproduction of impressions taken in silicone or polysulphide elastomers is possible. When coated with a special polyphase refractory suspension the dies may be employed for the direct construction of porcelain jacket crowns and inlays and butt-shoulder porcelain-on-gold restorations without the use of platinum foil. The die may then be removed directly from all of these preparations. No details of the composition of this refractory die material were given, and its accuracy against the platinum foil technique has yet to be established both in the laboratory and clinic.

Miller Yardley [23] has published a clinical report on the use of multiunit aluminous porcelain bridgework constructed on a refractory die material made specially for use with alumina reinforced ceramics. The ceramic refractory was used to invest the platinum matrices prior to joining the aluminous porcelain copings with high alumina rods. The fit of these bridges was clinically acceptable and case reports were presented covering an 18 months' postoperative period.

4. Summary

Current research on dental porcelain has been concentrated mainly on methods of improving the fracture resistance of porcelain restorations.

Enamelling of metals or dispersion strengthening of glasses offer the greatest possibilities at the present time and a review is given of the progress made in each field.

The significance of the role of opaque porcelains is discussed in relation to their effect on the aesthetics of enamel veneers.

The use of nonprecious metal alloys as an alternative to gold is also receiving increasing attention and methods of improving the bond at the metal-ceramic interface are described.

Dispersion strengthening of glass with high strength alumina crystals has resulted in the production of a new range of aluminous porcelains for jacket crown and bridge pontic construction.

Chemical toughening or nucleation of glasses may also provide other means of reinforcement but at the present time these methods are still in the experimental stage.

Other areas of research have been concentrated on improving the bond between acrylic resin and porcelain denture teeth by the use of silane coupling agents. The large differential in thermal expansion between acrylic and porcelain must be accounted for before these methods become commercially viable.

5. References

- [1] Vickery, R. C., and Badinelli, L. A., Nature of attachment forces in porcelain-gold systems, *J. Dental Res.* **47**, 683 (1968).
- [2] Batchelor, R. W., Harrison and Son, Stoke-upon-Trent, England. Personal communication.
- [3] McLean, J. W., and Hughes, T. H., The reinforcement of dental porcelain with ceramic oxides, *Brit. Dental J.* **119**, 251, (1965).
- [4] McLean, J. W., The development of ceramic oxide reinforced dental porcelains with an appraisal of their physical and clinical properties, MDS thesis, University of London, (1966).
- [5] Batchelor, R. W., and Dinsdale, A., Some physical properties of porcelain bodies containing corundum, Transactions of the 7th International Ceramics Congress, London, England, p. 31, (1960).
- [6] Blinn, D. B., Some physical properties of two-phase crystal-glass solids, *Science of ceramics Vol. 1*, pp. 315-334 (Academic Press, London, England, 1962).
- [7] Hasselman, D. P. H., and Fulrath, R. M., Proposed fracture theory of a dispersion-strengthened glass matrix, *J. Amer. Ceram. Soc.* **49**, 68, (1966).
- [8] Fonvielle, F. P., and Semmelman, J. O., Uses of alumina in porcelains, IADR Program of Abstracts and Papers, No. 181 (1967).
- [9] McLean, J. W., A higher strength porcelain for crown and bridge work, *Brit. Dental J.* **119**, 268, (1965).
- [10] Harman, C. G., and Wiener, I., Sintered glass-basis composites for porcelain prosthesis. IADR Program of Abstracts and Papers, No. 339 (1969).
- [11] McLean, J. W., The alumina reinforced porcelain jacket crown. *J. Am. Dental Assoc.* **75**, 621 (1967).
- [12] Wakelin, R. J., Personal communication.
- [13] McLean, J. W., High-alumina ceramics for bridge pontic construction. *Brit. Dental J.* **123**, 571 (1967).
- [14] McLean, J. W., The alumina tube post crown. *Brit. Dental J.* **123**, 87 (1967).
- [15] Stookey, S. D., Catalyzed crystallization of glass in theory and practice. *Ind. and Eng. Chem.*, **51**, 805 (1959).
- [16] Greene, C. H., Pyroceram., *The New Scientist*, p. 1708, (Dec. 1960).
- [17] MacCulloch, W. T., Advances in dental ceramics. *Brit. Dental J.* **125**, 361 (1968).
- [18] Isard, J. O., and Lehman, M. L., Letter to Editor. *Brit. Dental J.* **120**, 56 (1966).
- [19] Paffenbarger, G. C., Sweeney, W. T., and Bowen, R. L., Bonding porcelain teeth to acrylic resin denture bases. *J. Am. Dental Assoc.* **74**, 1018 (1967).
- [20] Semmelman, J. O., and Kulp, P. R., Silane bonding porcelain teeth to acrylic. *J. Am. Dental Assoc.* **76**, 69 (1968).
- [21] Myerson, R. L., Effects of silane bonding of acrylic resins to porcelain on porcelain structure. *J. Am. Dental Assoc.* **78**, 113 (1969).
- [22] Vickery, R. C., Badinelli, L. A., and Waltke, R. W., The direct fabrication of restorations without foil on a refractory die. *J. Prosthetic Dentistry*, **21**, 227 (1969).
- [23] Yardley, R. M., Multi-unit aluminous porcelain bridge work. *Brit. Dental J.* **126**, 177 (1969).

Dental Silicate Cements

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A systematic search for improvement of dental silicate cements requires detailed knowledge of their formation and structure. Experimental evidence shows the effective bonding medium in these cements is an amorphous aluminum phosphate. Physicochemical examination of a number of dental silicate powders showed them to be powdered fluorine-containing aluminosilicate glasses. The mechanism of the cement-forming reaction was studied for one cement following extraction of soluble ions by water at various time intervals after preparation. Infrared spectroscopy was used to record the changing absorption spectra of the setting cement. The microstructure of a number of fully hardened cements was studied by a variety of techniques: optical and electron microscopy, electron probe microanalysis infrared spectroscopy and x-ray diffraction. Dissolution in acidic media of aluminum phosphate bonded silicate cements is an inherent defect stemming from the fundamental chemistry of the system.

Key words: Aluminum phosphate, amorphous; dental materials; dental silicate cements; electron probe microanalysis; glass, aluminosilicate; silica gel; silicate cements, dental; silicate cements, mechanism of hardening, microstructure of, chemical nature; silicate cements, susceptibility to acid attack.

1. Introduction

In this paper the formation and structure of the dental silicate cement is described in the light of recent fundamental work much of which is as yet unpublished. This work was carried out in the U.K. at Government research stations by B. E. Kent, R. J. Mesley (Laboratory of the Government Chemist), R. P. Miller, D. Clinton (National Physical Laboratory), and K. E. Fletcher (Building Research Station) in collaboration with the author. Results obtained enable the basic limitations and future prospects of this cement to be discussed from a fundamental viewpoint.

The dental silicate cement has a long history; its successful introduction into dentistry followed from the Steinbeck patents of 1903-4 [1]¹. It remains today a popular material despite the introduction of alternative resin systems [2, 3]. What is less certain is whether it has a future; for its drawbacks—failure by erosion in the mouth, ability to irritate pulpal tissues etc.—are well known [3].

Although some research studies have been reported [4, 5, 6] there has been as yet, no basic change in formulation of commercial materials since 1907 when Schoenbeck [7] introduced the use of a fluoride flux in the preparation of the cement powder. Following this innovation there have been some 60 years of practical development which, although it has led to improvements, has not appreciably changed the character of this material. The question remains whether this cement

is capable of significant improvement. This question can only be answered with certainty from knowledge of the fundamental nature of the setting mechanism and the microstructure.

Now, although this material has been known for a considerable time, little fundamental work has been published. Undoubtedly the reason for this is that since the material is apparently amorphous the principal structural determining technique—x-ray diffraction—is not applicable.

The generally accepted view has been that the dental silicate cement is bonded by a type of silica gel [3]. This is not an unreasonable hypothesis; if there is an interaction between an acid and a silicate, silica, often in the form of silica-gel [8] must result, and indeed there are cements where the essential bonding medium is known to be silica-gel [9]. These are the industrial silicate cements formed by reacting aqueous solutions of soluble silicates with acids, and, unlike dental silicate cements, they are acid-resistant—because silica-gel is insoluble in acids.

They are also weak when compared with dental silicate cements. The dental silicate cement is one of the strongest inorganic cements known and strength values in the region of 3,000 kg/cm² (300 MN/m²) in compression have been recorded [10] which are much greater than those reported for the industrial silicate cements: 150-270 kg/cm² (15-27 MN/m²) [9].

There are therefore sound reasons for doubting that silica-gel is the essential bond in dental silicate cements, although, of course, it must be present in the cement.

¹ Figures in brackets indicate the literature references at the end of this paper.

Studies on the effect of acids on these materials have shown that disintegration is accompanied by loss of phosphates from the cements, an observation which is consistent with the presence of a cementing phosphate bond [11]. The electrical conductivity of the freshly prepared cements has been observed to drop sharply during setting [12] (fig. 1) which suggests that setting is the result of a type of precipitation process. The increase in pH which has been observed as cements age is consistent with this view [13, 14].

These problems have been largely resolved by recent research where a number of methods of structural analysis were employed.

2. Physico-Chemical Nature of the Cement Materials

Part of the explanation of the formation of the dental silicate cement follows from a consideration of the physico-chemical nature of the cement forming materials. Qualitative analysis of 16 materials and quantitative analysis of 4 materials

(table 1) have shown that these are all of the same basic type. The liquids are strong aqueous solutions of phosphoric acid-containing metals.

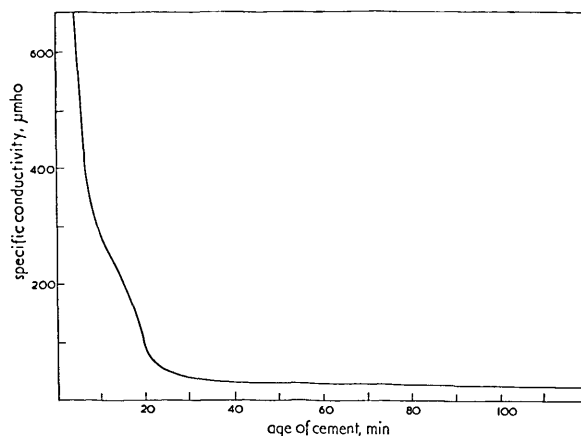


FIGURE 1. The changes in electrical conductivity of a dental silicate cement, 20 °C. (Laboratory of the Government Chemist).

TABLE 1.
Chemical Composition of Dental Silicate Cement Powders
(given as percent w/w)

Chemical species	Silicate powder			
	A	B	C	D
SiO ₂	41.6	38.8	34.5	35.9
Al ₂ O ₃	28.2	29.1	28.3	29.0
CaO.....	8.8	7.7	8.5	6.1
Na ₂ O.....	7.7	8.2	11.2	14.5
ZnO.....	.3	2.9	.1	.3
P ₂ O ₅	3.3	3.0	3.3	4.4
F.....	13.3	13.8	18.1	15.2
H ₂ O(550°C).....	2.2	1.6	1.7	1.4
MgO.....	.1	.1	.1	.1
SrO.....	.2			
Less O for F.....	105.7 5.6	105.2 5.8	105.7 7.6	106.8 6.4
Total.....	100.1	99.4	98.1	100.4

Median particle size (micrometers).....	8.6	10.6	11.5	15.5
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Chemical Composition of the Liquids
(given as percent w/w)

Chemical species	A	B	C	D
PO ₄ ³⁻	47.3	47.8	53.8	63.8
Al ³⁺	1.6	1.9	2.0	1.8
Zn ²⁺	6.1	4.2	9.1	
Mg ²⁺				1.3

The powders are unique amongst cements in that they are ground glassy bodies and not crystalline clinkers, a physical state which may account for the translucent nature of the final cement. The dental silicate glass is prepared by fusing a silica and alumina mixture in a fluoride flux containing minor amounts of phosphate. The fluoride flux is based on cryolite; the addition of fluoride lowers its fusion point.

The glasses are unusual; they are silicates, but unlike most, readily dissolve in mineral acids. They are also opal glasses of extreme composition where the fluoride content is higher than that of any other opal glass. This opacity is caused by the phase separation of two types of minute droplets approximately 4000 Å and 250 Å in diameter which can be observed under the electron microscope. This phase separation is to be expected as large amounts of fluorine in glasses weaken the continuity of the 3-dimensional network.

The other feature of interest is that these glasses are aluminosilicates with a mole ratio of Si:Al approximating unity. The structure of this type of aluminosilicate plays an important role in cement formation and requires further discussion.

A simple silicate is a macromolecule based on a continuous series of Si-O bonds, and structurally consists of chains or 3-dimensional networks of linked $[\text{SiO}_4]$ tetrahedra. Because of its atomic dimensions aluminum can replace up to half of the silicon atoms in a network which for valency reasons acquires a negative charge. These are the so-called aluminosilicates. In dental silicate glasses where the Si:Al approximates to 1:1 there are many $-\text{[SiO}_4\text{]}-\text{[AlO}_4\text{]}-$ links; the negative charge on the network being balanced by the positive charge on the glass cations, calcium and sodium.

3. Cement Formation

The dental silicate glass can be regarded as a negatively charged polymer surrounded by a cloud of cations. This type of structure is susceptible to attack by acids, since the positively charged protons can easily penetrate into the negatively charged glass network, a type of acid-base reaction. The principal sites of attack will be at the aluminum atoms which attract most of the negative charge; when there are a large number of Al-O-Si links, complete disruption of the network will result. This is exactly the situation that occurs when the dental silicate powder is mixed with the cement liquid, when infrared spectroscopy shows (fig. 2) that the aluminosilicate network is rapidly degraded to a silica or aluminosilica gel, and that H_2PO_4^- ions are formed as protons are lost from the liquid [15].

Now this process of decomposition will be accompanied by the liberation of ions locked previously in the glass lattice. As a result these ions would be expected to migrate into the cement liquid, that is

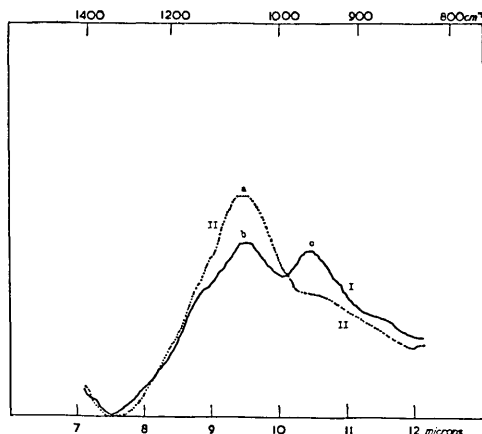


FIGURE 2. Changes in the infrared spectrums of a dental silicate cement as it sets. (Laboratory of the Government Chemist).

Curve I. Freshly prepared cement.
Curve II. Set cement.

Absorption bands (a) silica-aluminophosphate gel
(b) silica gel
(c) H_2PO_4^- ion

the aqueous phase of the cement, and be rendered water soluble.

The course of this process is illustrated by results that have been obtained from simple wet-chemical experiments. Cements of various ages were crushed and the concentration of water soluble ions determined by leaching with water. Cements were prepared using a powder-liquid ratio of 4g/ml. The chemical composition of the powder was: 18.7 percent Si, 15.0 percent Al, 6.3 percent Ca, 5.7 percent Na, 13.3 percent F, 1.0 percent P, 40.0 percent O, and that of the liquid 49 percent H_3PO_4 , 1.25 percent Al, 6.5 percent Zn. Results are shown as a plot of the concentration of leachable ions against the age of the cement (fig. 3). Now it is evident from these data that decomposition and liberation of glass ions (Al^{3+} , Ca^{2+} , Na^+ , F^-) from the powder is rapid. By the time mixing is completed (1 min) considerable amounts of sodium, calcium, and fluoride have been rendered water soluble, that is they have been liberated from the powder as a result of its decomposition.

Indeed at this point, these levels are at a maximum for calcium and fluoride because subsequently these ions are removed by precipitation and interpretation of results is obscured. For this reason the initial decomposition process is best illustrated by the curve for water extractable sodium as sodium forms no water insoluble product. By the time mixing has been completed some 10 percent of the sodium contained in the powder has been liberated; the amount increasing to a maximum of 20 percent in the following 30 min or so. If this figure corresponds to the amount of powder decomposed then the powder is in five-fold excess over the liquid.

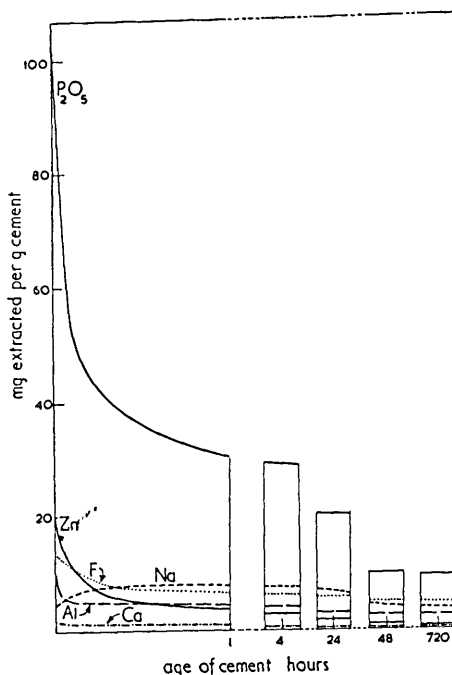


FIGURE 3. Variation of the concentration of water soluble ions contained in a dental silicate cement as it set and hardened, illustrating the liberation of ions from the glass matrix and their subsequent precipitations. (Laboratory of the Government Chemist).

The accumulation of ions in the aqueous phase of the cement paste is accompanied by a decrease in its acidity, for this is an acid-base reaction. As a result Al^{3+} , Ca^{2+} , Zn^{2+} , F^- , and the H_2PO_4^- progressively form insoluble substances causing the cement to set. This is a type of precipitation process and its correlation with setting is shown in figure 3. It is best illustrated by the curves for zinc and phosphate, since if the small amount of phosphate in the powder is neglected, these are present initially in a soluble ionic form. There is no prior extraction process to obscure interpretation of results. Inspection of this data showed that the cement sets in 6 min when 50 percent of both of these species have precipitated. The subsequent post-set hardening is due to the continuation of this process and is complete in 48 hr, for the system described.

This mechanism explains why dental silicate cements are adversely affected if exposed to moisture shortly after set and before fully hardened. Ions which would have contributed to the formation of the matrix are removed by leaching [10] and optimum strength can never be obtained. Any cement which is dependent on a precipitation set will be sensitive to moisture in this way. Unfortunately, most rapidly setting cements, and these are required for dentistry, are based on this type of mechanism. So the problem of the elimination of this drawback will not be solved easily. It is

unlikely that it will be remedied at all for the present type of dental silicate cement.

Even when the cement is fully hardened some soluble material remains; the salts of sodium with dihydrogen phosphate and aluminofluorides. This is soluble material that is eluted from cements in the specification tests for solubility and distintegration. What relationship it bears to the clinical durability of a silicate restoration is uncertain, for clinical durability will be related to the resistance of the insoluble part of the matrix towards oral fluids.

It should be noted that the setting mechanism of the dental silicate cement is totally different from that of the Portland cement. In the latter, interaction between powder and liquid is slow and is accompanied by formation of the cementing matrix. The situation for the dental silicate cement is totally different since setting and hardening are controlled by increases in pH. The interaction between powder and liquid is very rapid and most of it occurs in the initial stages, during and shortly after mixing. This process is accompanied by a relatively small change in the nominal pH of the system which only increases from an initial figure of 0.8 to 1.7 at the initial set [14]. Subsequent hardening during the next 48 hr is caused by a much larger change in pH, an increase to 5.0–5.5, which completes the precipitation process. Little further interaction between powder and liquid is required to produce this pH change; its magnitude is so small that it cannot be detected by present methods. This behavior follows from a consideration of the nature of the neutralization curve of phosphoric acid; this system has a strong buffering capacity in the region of its pK_a 's (2.1, 7.2) but little in the intermediate regions.

4. Microstructure

The set dental silicate cement has unusual and interesting features. The best examples are amongst the strongest inorganic cements known and are unique in being substantially amorphous. X-ray diffraction of seven examples showed that they contained only minor amounts of crystallites, which were however well-defined. These were identified as augelite, AlPO_4 , $\text{Al}(\text{OH})_3$ and fluorite, CaF_2 .

The appearance of polished surfaces of dental silicate cements under incident light is that of a poorly connected mosaic of highly reflecting angular grains, as a micrograph of a typical example shows (fig. 4). The grains, which appear unattacked, vary in size over a broad range, 1–100 μm in diameter. Porosity shows as black non-reflecting areas, which are more numerous in weaker cements. Under cross-polarizers and reflected light a network of birefringence is apparent in cements with strengths in compression in excess of 1,750 kg/cm^2 (170 MN/m^2) (fig. 5). This evidence taken together with the amorphous nature

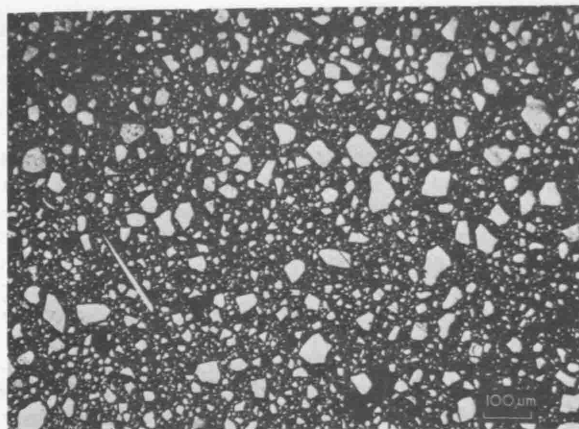


FIGURE 4. Micrograph of a polished surface of a dental silicate cement, taken by transmitted light, showing glass grains and porosity. (National Physical Laboratory).

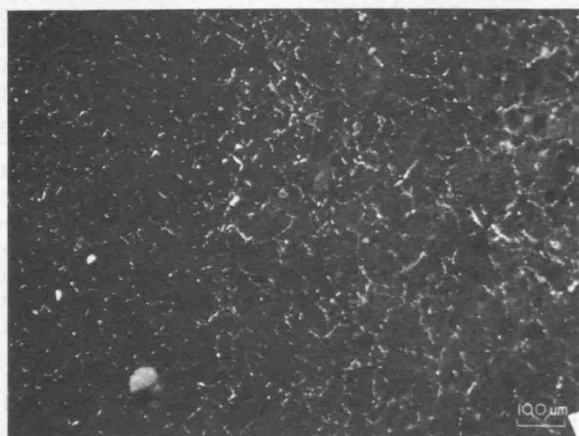


FIGURE 5. Network of birefringence shown by reflected light analysed by crossed polarizers. (National Physical Laboratory).

of the bulk of the cement matrix and the isotropic nature of the crystallites indicates that this birefringence is the result of orientation due to internal stresses.

The scanning electron microscope with its high magnification coupled to a considerable depth of focus is a powerful tool for determining the physical microstructure of materials. Fractured surfaces are normally chosen for examination. A micrograph of a typical strong cement is shown (fig. 6). The dominant feature is a glass particle about 10 μm across, which by its angular appearance is apparently unattacked. Inhomogeneities on its surface are indicative of local attack, these also serving to distinguish it from the surrounding matrix. The matrix which appears particulate in strong cements is plate-like in weaker ones (fig. 7). The appearance of the fractured surfaces suggests

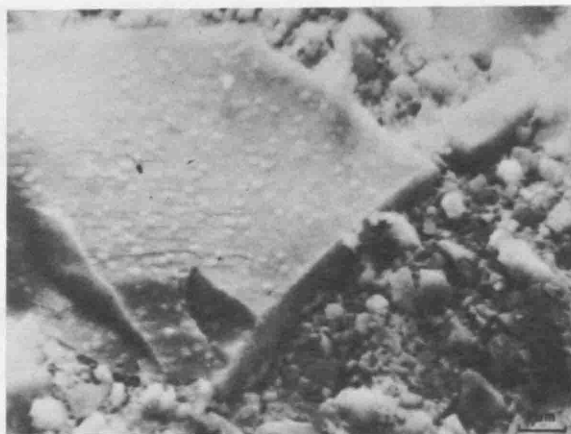


FIGURE 6. Scanning electron micrograph of a strong cement. (National Physical Laboratory).

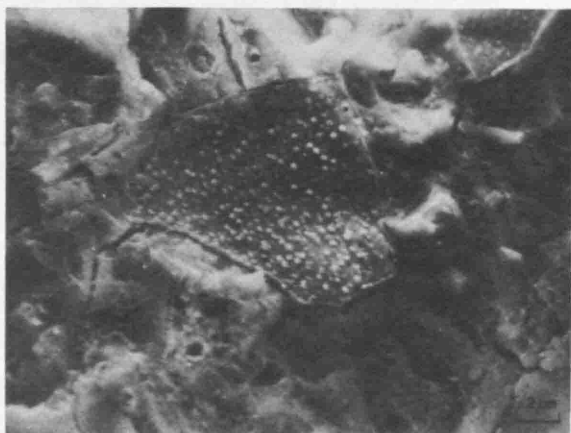


FIGURE 7. Scanning electron micrograph of a weak cement. (National Physical Laboratory).

the bonds between particles and matrix are comparatively weak.

Attempts have been made to improve the strongest properties of cements by the inclusion of fibers and other forms of inert aggregate. In our laboratories it has been found that these are ineffective. A micrograph of a fiber-containing cement shows that the matrix has shrunk from the fiber with crack initiation (fig. 8).

5. Microchemical Nature of the Matrix

Electron-probe microanalysis is an important technique for determining the chemical nature of the microstructure of amorphous materials. In this technique a narrow electron beam, some 2 μm across, scans a flat polished section and records the chemical composition of each point on the cement surface. This enables the distribution of elements to be mapped as white points on a black background.



FIGURE 8. Scanning electron micrograph of a cement containing glass fibers. (National Physical Laboratory).

In the case of dental silicate cements the element distribution can be compared with the physical positions of the particles in the matrix, as shown by the back scattering of electrons, thus enabling the chemical composition of both particles and matrix to be established.

An electron-image photograph and a set of element-distribution photographs of the same area of study for a dental silicate cement are shown in figure 9. The cement used was similar to that employed for the reaction studies, metals being omitted from the liquid to avoid confusing experimental data. From an examination of these it is apparent that phosphorus is almost entirely in the matrix. Silicon is associated with the particles, and there is none in the matrix.

Calcium and aluminum are present in both regions. Since originally both were present solely in the glassy particles, it is clear that there has been some migration into the aqueous or matrix phase. No data are shown on the diagram for sodium and fluorine because of experimental limitations; however more recent experimental results using improved techniques indicate that some sodium and fluoride also migrate from the powder grains into the liquid.

Detailed electron scans show that in fact the glass cations are displaced from the surface region of the individual particles, leaving a central unattacked core in the case of the larger particles.

This displacement of cations from the glassy particles is a result of the penetration of protons from the liquid which means that water will have entered the surface layer of each particle. Since silicon remains in this degraded surface layer it may be inferred that it is present as a type of silica gel. Infrared data confirm this deduction. It is the retention of this siliceous framework which preserves the geometry of the glassy particles thus giving them the appearance of remaining unattacked.

The association of the various cations and anions in the matrix has, as yet, not been resolved completely. The detection of minor amounts of crystallites, angelite, $\text{AlPO}_4\text{Al}(\text{OH})_3$, and fluorite, CaF_2 , in the matrix may be indicative of the association of ions in the predominant amorphous phase of the matrix. Infrared spectroscopic data are consistent with the presence of amorphous aluminum phosphate which must be considered as the major constituent of the matrix. Aluminum phosphate is known in ceramic science as a binding agent [16] and must be regarded as the effective bonding medium.

The exact nature of the polymer remains a subject for speculation. Results from other studies indicate that the function of the powder may only be to supply ions needed for the reaction at an appropriate rate. Cement strength is far more dependent on the phosphoric acid concentration of the liquid than the chemical composition of the powder (fig. 10). There are therefore good reasons for supposing that the structure of the phosphoric acid liquid is important, for it is dependent on acid concentration [17]. It is known that aluminum forms a complex with phosphate in acid solution and that as the proportion of aluminum increases, dimers and polymers are formed where both hydroxyl and phosphate act as bridges between the aluminum atoms [18]. Therefore there are grounds for supposing that the setting of the cement proceeds with the progressive formation of an aluminum-oxygen-phosphorous polymer as aluminum enters the liquid from the powder. It is plausible to suggest that a pH-dependent polymerization occurs in the cement to give a water-insoluble polynuclear species, which is the effective binding medium, and is based on phosphate and hydroxyl between aluminum ions.

The structure of the dental silicate cement is more simple than might have been supposed from the many combinations possible of elements present. For spatial reasons a combination of silicon and phosphorus is not possible. Moreover, even if it were, such a combination is unlikely; the rare Si-O-P bond is not of a strength comparable with the Si-O-Si, Al-O-Si and Al-O-P bond, and stable structures do not result [18]. Another possibility is the metal aluminophosphate of Barrer and Marshall [18] $(\text{M}_2\text{O})_{n-m}(\text{Al}_2\text{O}_3)_n(\text{P}_2\text{O}_5)_m \cdot x\text{H}_2\text{O}$. However, such bodies, at least in crystalline form, have not been identified; possibly the affinity of calcium for fluoride inhibits their formation. The indications are that the matrix is a simple mixture of a basic aluminum phosphate and calcium fluoride, a little of which has crystallized.

This structure of the dental silicate cement can be used to predict the clinical behavior of a restoration. The effective binding medium, basic aluminum phosphate, is insoluble in neutral solution, but dissolves in acidic and in neutral citrate media. A silicate restoration would, therefore, be

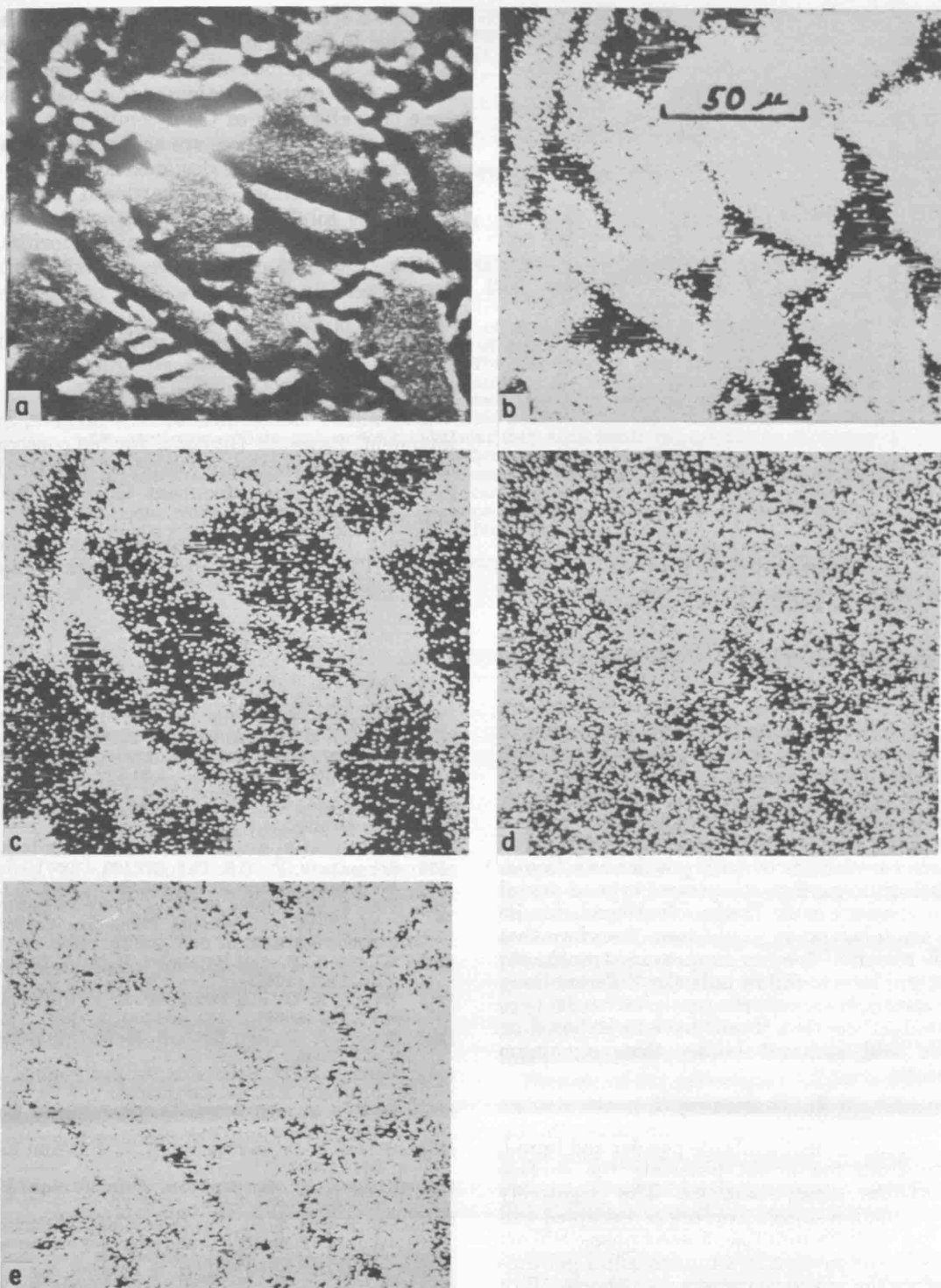


FIGURE 9. *Electron probe microanalysis showing physical microstructure and element distribution (white spots on a black background). (Building Research Station).*

(a) Electron image micrograph, (b) Silicon distribution, (c) Phosphorus distribution, (d) Calcium distribution, (e) Aluminum distribution.

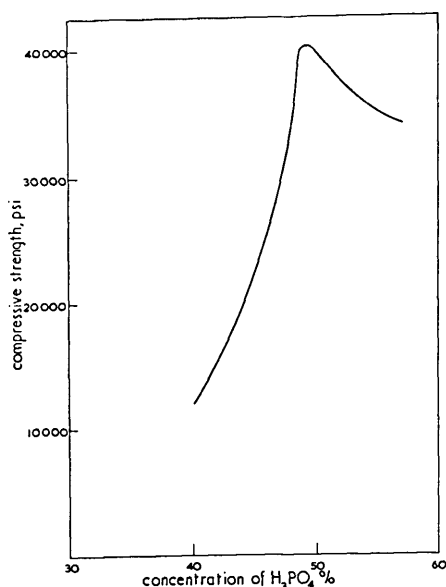


FIGURE 10. The effect of acid concentration on the compressive strength of a cement.

To convert psi (pounds per square inch) to N/m^2 (newtons per square meter) multiply by 6,895.

expected to give good service under favorable oral conditions. Saliva itself acts as a near neutral buffer, and so a silicate restoration washed by saliva should have a long life. However if sited in regions where local acidic condition can develop or if the saliva contains appreciable citrate, early failure is to be expected. This argument may be extended to any dental silicate cement as at present formulated. Whatever variation of proportions of the basic constituents of both powder and liquid, it is difficult to see how the present type of dental silicate cement can be further developed, for its faults are inherent. It would seem therefore that future research for an improved translucent cement will have to follow radically different lines. If the cement is to be of the precipitation-set type for rapid setting then it will have to be based on a more acid resistant binder than aluminum phosphate.

6. Summary

On mixing the dental silicate powder and liquid, protons from the liquid penetrate the surface layer of the glassy particles. The negatively charged aluminosilicate network is disrupted and glass ions migrate into the aqueous phase. Silicon remains in the surface as a type of silica gel thus preserving the initial shape of each particle. With the exception of Na^+ ions which have accumulated in the aqueous phase (Al^{3+} , Ca^{2+} , F^- , $H_2PO_4^-$)

undergo a type of precipitation process as the pH increases and the cement sets. The effective binding agent is amorphous aluminum phosphate; the matrix also contains calcium fluoride. There is some crystallization of these compounds.

Since these substances are acid-soluble this type of cement can never be designed to withstand adverse oral conditions. The hardened cement contains some soluble material, the sodium salts of dihydrogen phosphate and aluminofluorides. The specification test only determines these soluble constituents and therefore does not necessarily give an indication of the durability of the water-insoluble phase of the matrix under oral conditions.

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7. References

- [1] Steenbock, P., German Pat., 174557 (1903). Brit. Pat. 15,176; 15,181 (1904).
- [2] Buonocore, M. G., Int. Dental J. **13**, 406 (1968).
- [3] Skinner, E. W., and Phillips, R. W., The Science of Dental Materials, 6th Edition, p. 60 (W. B. Saunders, Philadelphia and London 1967).
- [4] Wright, J. W., J. Dental Res. **1**, 35 (1919).
- [5] Manly, R. S., Baker, C. F., Miller, P. N., and Welch, F. F., J. Dental Res. **30**, 145 (1951).
- [6] Rockett, T. J., I.A.D.R. Abstracts #433 (1968).
- [7] Schoenbeck, F., U.S. Pat. 897,160 (1907).
- [8] Murata, K. J., Bull. U.S. Geol. Surv., **950**, 25 (1946).
- [9] Vail, J. G., Soluble Silicates Their Properties and Uses, Vol. 2 (Reinhold Publishing Corporation, New York, 1952).
- [10] Wilson, A. D., and Batchelor, R. F., J. Dental Res. **46**, 1425 (1967).
- [11] Wilson, A. D., and Batchelor, R. F., J. Dental Res. **47**, 115 (1968).
- [12] Wilson, A. D., and Kent, B. E., J. Dental Res. **47**, 463 (1968).
- [13] Norman, R. D., Swartz, M. L., and Phillips, R. W., J. Dental Res. **45**, 136 (1966).
- [14] Kent, B. E., and Wilson, A. D., J. Dental Res. **48**, 412 (1969).
- [15] Wilson, A. D., and Mesley, R. J., J. Dental Res. **47**, 644 (1968).
- [16] Kingery, W. D., J. Amer. Ceramic Soc. **33**, 242 (1950).
- [17] Van Wazer, J. R., Phosphorus and its Compounds, Vol. 1, Chemistry (Interscience Publishers, New York-London, 1958).
- [18] Salmon, J. E., and Wall, J. G. L., J. Chem. Soc. 1128 (1958).
- [19] Barrer, R. M., and Marshall, D. J., J. Chem. Soc., 6616 (1965).

Composite Restorative Materials¹

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This article describes the development of dental composite materials, which have quickly established a place in the practice of dentistry because of the shortcomings of alternative esthetic direct filling materials. The goal-directed basic research in which the composite materials were developed was initiated at the National Bureau of Standards in 1956. Late in 1957, a monomer was synthesized that is suitable for use with reinforcing fillers. Commercial dental composite materials available in 1969 use this resin together with particulate fillers and various additives; they have lower polymerization shrinkage and coefficient of thermal expansion, and higher compressive strength and stiffness relative to unreinforced resins. Compared to silicate cements, the composites have lower solubility, higher tensile strength, and comparable compressive strength. Composite restorative materials, when they have been fully developed, should provide the dental profession and the public with greatly improved restorations for anterior teeth.

Key words: Biomaterials; composites; dentistry; fillers; glass; methacrylates; monomers; prostheses; resins; restorative material.

1. Historical Introduction

Although composite dental restorative materials are yet in their infancy, the roots of their development can be traced back through the scientific literature for many years. In 1843 a German chemist, Joseph Redtenbacher, reported a new acid to which he gave the name acrylic acid [1].² In the last part of the century, methacrylate esters and their polymers were discovered [1]. Probably before 1940, Schnebel had found that tertiary amines (such as Michler's ketone) would activate benzoyl peroxide to give self-hardening resins [2]. So far as can be determined, the first self-curing methyl methacrylate resin formulation for filling teeth was introduced in the United States in 1948.

There soon appeared on the market a number of direct filling resins, and many believed that these materials would be the answer to the shortcomings of the decades-old silicate cement. However, this idea was short-lived [3]. These resin restorations discolored [4], tended to shrink away

from the cavity walls [5], allowed the exchange of oral fluids around their margins [6] and were associated with pulpal inflammation [7-9] and a high incidence of recurrent decay [10-11]. Furthermore, discrimination between decalcified dentin and the unreinforced direct filling resin was difficult because they were both radiolucent. For these and other reasons, a great many practitioners returned to the use of silicate cements [3].

The shortcomings as well as the merits of silicate cements are well known. After nearly a hundred years [12] of development and use, these esthetic materials with good thermal and anticariogenic properties still have distinct disadvantages [3]. Most obvious is the susceptibility to disintegration in a decay-like manner [13-15], typically after about four years in the mouth [3, 14]. Further description is given by Wilson elsewhere in this publication.

Because of the persistent need for a permanent, esthetic direct filling material, there were continued efforts to improve the methacrylate resins. An aluminum silicate filler (about 15 percent) was part of one methyl methacrylate monomer-polymer system [16]. The use of fillers with the proper index of refraction and a low thermal expansion, and the development of adhesion in the resin were advocated [17]. Indeed, when inert fillers were incorporated into poly (methyl methacrylate), there was a reduction in the coefficient of thermal expansion and in the water sorption in proportion to the concentration of fillers [18]. However, there were limited adhesive characteristics in these and certain other resins investigated [19].

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² Figures in brackets indicate the literature references at the end of this paper.

Epoxy resins [20], developed early in the present century, had an annual production rate of about 20 million pounds by 1954. Certain formulations of these resins had intriguing properties including adhesive characteristics and the ability to harden at moderate temperatures with little shrinkage. These led numerous investigators to study epoxy resins as a binder for inorganic fillers [19, 21]. Primarily with indirect techniques, composite restorations were prepared using powdered fused silica and porcelain, bonded together with minor quantities of (heat-cured) epoxy resins. The good esthetics and other favorable properties of these composites encouraged the further investigation of this approach to dental restorative materials [21].

However, attempts to develop composite materials using epoxy resins with various hardening agents for use in direct techniques met with numerous difficulties. Although epoxy resins were initially adhesive to hard tooth tissues, the strengths of bonds to enamel or dentin after prolonged exposure to water were disappointing [19, 21, 22].

2. Early Composite Developments

The goal-directed research in which the composite dental restorative materials were developed was initiated at the National Bureau of Standards in 1956. After unsuccessful attempts to use various epoxy resins and hardening systems, a compromise between epoxy and methacrylate resins was conceived late in 1957 [23, 24]. The reaction sites (oxirane rings) of the epoxy molecule were replaced by methacrylate groups. This gave a hybrid molecule that polymerized through methacrylate groups [25]. It was suitable for use as a binder for reinforcing fillers because it was nonvolatile, had a relatively low polymerization shrinkage, and hardened rapidly under oral conditions when suitably formulated with an appropriate initiator system.

This dimethacrylate monomer (BIS-GMA) was synthesized by the reaction of bisphenol A and glycidyl methacrylate [26]. The same product is also produced by the reaction of the diglycidyl ether of bisphenol A and methacrylic acid [25]. Its structural formula [27] is shown in figure 1.

Although BIS-GMA has been referred to as an epoxy resin, this is not the case; the original epoxy (oxirane) groups disappear during the synthesis and are, in effect, replaced by methacrylate groups. Unfortunately, this dimethacrylate monomer has also been called a polyester. The well-established term "polyester" should be restricted to the polycondensation products essentially of dicarboxylic acids with dihydroxy alcohols [28].

Since the coefficients of thermal expansion of organic polymers are many times higher than that of the dental hard tooth tissues [6, 29], means for lowering this value were needed. Fillers [17] in-

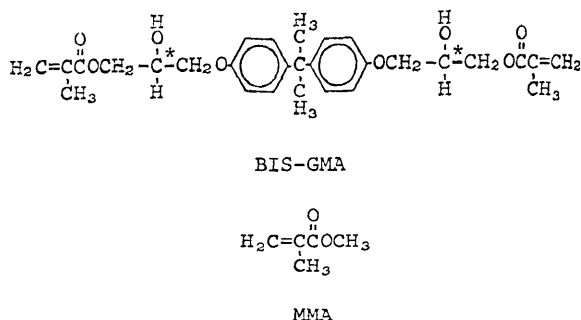


FIGURE 1. Structural formula of BIS-GMA.

The asterisks indicate asymmetric carbon atoms that give rise to a number of stereoisomers. Methyl methacrylate (MMA is shown for comparison [37].

corporated into the resin could do this [18]. Experimental composites prepared in 1953 utilized particles of fused silicon dioxide as a reinforcing filler because of the extremely low coefficient of thermal expansion of vitreous silica [21]. With the epoxy resin system, there was relatively good adhesion between the resin and the surfaces of these particles.

Later in the investigation, after the more adhesive epoxy resins had been replaced by the less adhesive dimethacrylate resins (BIS-GMA) [26], it became apparent that special means for attaining adhesive bonding between the resin matrix and the filler particle surfaces were required. At that time vinyl silane coupling agents appeared to be the most suitable means of improving this bonding [30, 31]. The more reactive γ -methacryloxypropyl silane coupling agents [32, 33] had not then become commercially available. A vinyl silane coupling agent applied to reinforcing filler gave composites that had about four times the tensile strength of composites utilizing the same filler without its being treated with the vinyl silane [34]. When the methacryloxypropyl silanes became available, their ability to promote adhesive bonding between the resin and glass was compared with that of vinyl silanes; the methacryloxypropyl silanes gave significantly stronger and hydrolytically more-stable bonding than did the vinyl silanes [35-37].

Since the strength and durability of the composites depended on the quality of the bonding between the organic matrix and the reinforcing filler particles, it was of utmost importance that the best coupling agents be used in the optimal manner. The coupling agent most widely used was γ -methacryloxypropyltrimethoxy silane, also known as 3-(trimethoxysilyl)propyl methacrylate. This organofunctional silane was hydrolyzed and condensed on the surfaces of the filler particles. It made the particles water repellent, reducing the water sorption of the composites; it also formed chemical bonds at the surface of the particles, connecting the organic polymer and the inorganic

filler [38], converting inert fillers to reinforcing fillers [39].

Although fused quartz or fused silica received a great deal of attention in experimental work [14, 21, 23, 24, 26, 34], many other filler materials were also investigated [16, 18, 19, 21, 31-34]. These included the synthetic mineral β -eucryptite and closely related materials [35, 40, 41], microcrystalline glasses [42], aluminosilicate glasses, barium-titanium glass, crystalline quartz and pyrogenic silica [36]. It has been widely held (although not universally accepted) that condensation between SiOH groups on the surfaces of these silica-containing fillers and SiOH groups of the hydrolyzed silane accounted for the bonding between the coupling agent of the filler and the filler particle itself. Copolymerization of the methacrylate groups of the silane with the methacrylate groups of the monomers comprising the organic continuous phase has been thought to complete the chemical linkage between the phases of the composites [38].

The BIS-GMA monomer was too viscous to be readily mixed with these fillers without first being thinned with some suitable monomer having a lower viscosity. Among others, methyl methacrylate and ethylene and tetraethylene glycol dimethacrylate, have been used for this purpose [23, 24].

As with antecedent methacrylates [16], stabilizers such as hydroquinone were first used to inhibit premature polymerization and give the necessary storage stability (shelf life) to the BIS-GMA formulations [23, 26]. On polymerization, less discoloration occurred with the use of the monomethyl ether of hydroquinone. Later, hydroquinone was replaced by BHT (butylated hydroxytoluene; 2,6-di-*tert*-butyl-4-methylphenol), a stabilizer that appeared to contribute no discoloring effects [43].

Other additives that contributed to color stability of the restorations were ultraviolet-absorbing compounds. While these may have contributed to the stability of the monomers during storage, their primary purpose was to reduce the amount of discoloration in the resin of the final composite material. Typical UV absorbers were 2-hydroxy-4-methoxy-benzophenone [43] and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole.

Since most of the experimental work on composite materials utilized an amine-peroxide initiating system, another important component has been the amine accelerator. The most commonly used of these was N,N-dimethyl-*p*-toluidine (DMPT). This compound interacted with peroxides to produce free radicals which brought about the polymerization of the methacrylate monomer groups and thus the hardening of the resin binder of the composite. Investigations of factors that produce discoloration in these materials led to the introduction of N,N-dimethyl-*sym-m*-xylidine (DMSX; also known as DMDA), which not only gave less discoloration but also was a more effective accel-

erator than DMPT when compared on an equimolar basis [43].

In a composite material developed in Great Britain [44], a long-chain mercaptan, together with an aliphatic peroxide, served as the hardening initiators.

Although other peroxides have been used [44], benzoyl peroxide has been the one most used in composite restorative materials. It has been dispersed either in the reinforcing filler with the aid of a solvent that is removed by evaporation, or is dissolved in one of the monomeric liquids of the composite formulation.

Sulfinic acids or their derivatives were used in the initiator systems for experimental composite materials [14].

3. Some Properties of Experimental and Commercial Composites

Before proceeding with recent and current developments, perhaps it would be well to define "composite." For this discussion, the term "composite restorative material" refers to a man-made, three dimensional combination of at least two chemically different materials with a distinct interface separating the components [39], properties are thus obtained for the restoration of the form and function of defective teeth which could not be achieved by any of the components acting alone. Thus, the use of the term "composite" distinguishes the combination of inorganic aggregates bonded together with organic polymers from unreinforced direct filling resins and from silicate cements.

It is primarily the high proportion of reinforcing filler in composite restorative materials that yields properties different from those of direct filling resins. Most of the physical properties of composite restorative materials have been improved by the incorporation of a maximum amount of reinforcing filler together with a minimum amount of a binder of cross-linking polymerizable organic resin.

The "first generation" of commercial dental composite materials used BIS-GMA resin binder, described previously, together with major portions of various particulate fillers and minor portions of various additives. Data that have been reported in the literature [45-60] and more recently obtained [61, 62] show that composites have lower polymerization shrinkages and coefficients of thermal expansion, and higher compressive strengths and stiffnesses relative to unreinforced resins. Compared to silicate cements, the composites have lower solubilities and higher tensile strengths. More detailed data are given in tables 1 and 2, including comparisons with dentin and enamel [24, 63-68]. The quantitative information presented in the tables is incomplete since the methods and conditions of measurement are not described; however, these data will serve to illus-

trate the ranges of values and order of magnitude to be expected with these materials.

The smoothness of the finished surface is comparable with that of silicate cements [36, 57, 58] but inferior to that of unreinforced resins [52] and most of the other restorative materials. The abrasion resistance of composite materials is superior to direct filling resins [36, 47, 48, 51, 56, 58].

Similar to some other dental restorative materials, problems encountered in packaging and storage include volatility of some ingredients and premature gelation of resin components [36].

4. Current Research

Current research has the goal of making improvements on this "first generation" of composite materials now available to the dental practitioner. For example, there is a degree of pulpal irritation caused by some of these materials [69, 70], and it has not yet been established which of the various ingredients contribute most to the inflammatory reactions of the dental pulp tissues. Other problems that have been encountered are incomplete color stability [62] and resistance to staining, difficulties encountered in finishing and polishing, and lack of x-ray opacity.

The recent investigations at the National Bureau of Standards have led to new dimethacrylate monomers, reinforcing fillers, accelerators, stabilizers, and adhesion-promoting coupling agents that will, hopefully, lead to an improved "second

generation" of composite materials. For example, the BIS-GMA is not completely color stable and is too viscous for use without being thinned with a monomer of lower viscosity. Furthermore, it cannot be purified by distillation or by crystallization since it is inherently a mixture of non-volatile optical isomers. To overcome these problems, three dimethacrylate monomers were synthesized that can be prepared and purified separately by recrystallization [27]. These are the condensation products of 2-hydroxyethyl methacrylate with the acid chlorides of phthalic, isophthalic and terephthalic acids, respectively. Upon combining these three crystalline products, a ternary eutectic liquid mixture is formed that has a viscosity low enough to be used without the addition of any volatile ingredients. Preliminary tests show it to be non-toxic and non-irritating [27].

Numerous other monomers [71-75] are currently being synthesized and evaluated for use in dental composite materials.

The research effort to improve polymerization accelerators [76] has led to the successful synthesis of aromatic amines having unusually high molecular weights [77] so as to minimize their solubilities in tissue fluids and thus their freedom to diffuse into the pulp or other tissues. The structure of these amines is based partly on the fact that the color stabilities of the composites have correlated better with the nature of the ring substituents than with the kind of nitrogen substituents in the amine accelerators [76, 77].

TABLE 1. *Some physical properties of esthetic direct-filling materials*

	Hardening time	Polymerization shrinkage	Water sorption	Solubility and disintegration
	<i>minutes</i>	<i>% (by volume)</i>	<i>% (by weight)</i>	<i>% (by weight)</i>
Experimental composites	4 [14] 3-8 [24, 26] 5-7 [34] 7-10 [41] 5 [61] 3. 5-5 [62]	2 [23] 2. 7-2. 8 [26]	0. 9 [26] 0. 30-0. 35 [62]	0. 00-0. 08 [23] 0. 04 [26] 0. 15-0. 22 [61]
Commercial composites	3-4 [50] 1. 5-4. 5 [52] 1-1. 5 [55] 2. 5-5 [59] 3-3. 5 [61]	1. 2-1. 5 [52]	0. 78-2. 46 [53] 1. 60-3. 68 [56] 0. 8-1. 6 [57] 1. 12 [62]	0. 01-0. 08 [53] 0. 12-0. 16 [62]
Silicate cements	4-6 [14] 4 [34]	2 [5] 3. 3 [26] 1. 3 [60]	-----	0. 4-1. 1 [14] 0. 4-1. 3 [26]
Unreinforced resin	6 [14] 6 [34] 3-3. 5 [50] 4 [52] 2-4 [59]	6-8 [5] 6. 2 [26] 5. 2 [52] 5-6 [60]	^a (1. 0-1. 5 [5]) ^b (2. 1 [26])	^b (0. 10 [26]) 0. 1 [60]

^a Volumetric expansion

^b Self-curing denture base resins.

TABLE 2. Some physical properties of esthetic direct-filling materials, dentin and enamel

	Tensile strength	Compressive strength	Modulus of elasticity	Coefficient of linear thermal expansion	Indentation resistance and recovery	
					Indentation	Recovery
Experimental composites	psi ¹ 3, 700-5, 400 [24] 4, 000 [26] 2, 000-4, 700 [34] 5, 400-7, 100 [41] 6, 000-7, 700 [45] 3, 700-6, 000 [61]	psi 27, 700 [14] 23, 000 [23, 26] 3, 600-27, 700 [34] 12, 000 [41] 12, 200-18, 600 [45] 23, 600-31, 200 [61] 26, 000-27, 000 [62]	psi $\times 10^6$ 1. 4 [14] 1. 6 [24] 1. 2-1. 7 [34] 0. 7-2. 6 [61]	ppm/°C 26:35-45°C [14] 24:30-40°C [23] 22:30-40°C [26] 18, 19, 26:28-46°C [34] 18, 19-39: 0-60°C [41] 30:24-38°C [61] 31-36:25-49°C [62]	μm^2 55 [26] 58-96 [34] 50-70 [61] 60-64 [62]	percent 77 [26] 56-72 [34] 69-74 [61] 67-70 [62]
Commercial composites ²	2, 000-5, 900 [52] 1, 800-8, 500 [57] 2, 000-5, 900 [62]	17, 400-29, 000 [52] 20, 200-33, 200 [53] 15, 900-35, 000 [57] 18, 000-28, 000 [58] 26, 800-33, 700 [62]	0. 78-1. 62 [52] 0. 75-1. 25 [53] 1. 3-2. 2 [62]	27-41:24-38°C [52] 22-44:21-49°C [53] 27-35:25-45°C [56] 20-50: 0-60°C [57] 30-45:20-50°C [59] 31-41:30-55°C [62]	65-97 [52] 50-90 [62]	62-70 [52] 48-72 [62]
Silicate cements	440-1, 010 [24] 930 [34]	24, 300-30, 000 [14] 24, 600-31, 000 [34] 23, 000 [65] 25, 600-32, 100 [66]	3. 1 [24] 2. 4 [65] 3. 2-3. 6 [66]	7. 6:20-50°C [67]	40 [26]	83 [26]
Unreinforced resin	3, 800-5, 100 [24] 3, 300 [52] 3, 100 [34]	12, 100 [14] 10, 700 [26] 11, 000 [65]	0. 3 [14] 0. 26 [24] 0. 34 [52] 0. 27 [65] 0. 27 [68]	100:35-35°C [14, 34] 92:24-88°C [52]	125 [34] 113 [52] 95-115 [68]	73 [34] 74 [52] 60-80 [68]
Dentin	7, 500 [24]	43, 100 [63] 50, 400 [64] 31, 500-44, 200 [65]	2. 8 [24] 2. 8 [26] 2. 4-2. 7 [63] 2. 2 [64] 1. 1-2. 0 [65]	8:20-50°C [67] 7:25-55°C [62]	46 [26]	85 [26]
Enamel	1, 500 [24]	19, 400-40, 200 [64] 13, 700-41, 800 [65] 53, 900-55, 700 [66]	1. 8-8. 2 [64] 1. 4-9. 1 [65] 1. 1-1. 2 [66]	12:25-55°C [62]	33 [26]	86 [26]

¹ To convert psi (pounds per square inch) to MN/m² (meganeutons per square meter) multiply by 6.895 $\times 10^{-3}$.² Micrometers (microns).³ Not all products are represented in each range of values shown.

Color stability is also profoundly affected by the characteristics of the stabilizers that are used. Significant advances are being made in the synthesis and utilization of stabilizers that are non-toxic and that do not cause discolorization of composites. [43, 76, 77].

In the instance where there has been evidence of greater surface staining of composite restorations relative to the adjacent tooth enamel, it has not yet been determined to what extent this accretion of discolored material is due to inadequate hydrolytic stability of the adhesive bond between individual particles and the resin matrix, the chemical nature of the reinforcing filler materials, the chemical nature and degree of polymerization of the resin formulations, the roughness of the surface after the restoration is finished [78], or some combination of these factors. These factors are currently being studied.

Until recently, there has been little or no effort to prepare special materials to serve as reinforcing fillers for dental composite materials, rather, materials already available were selected for this application. However, the unique demands on this kind of composite material warrant the development and use of the most suitable fillers as well as other ingredients.

One experimental composite [79] contained a mixture of two reinforcing fillers: spherical particles of fused silica made up about two-thirds of the filler and smaller particles of an x-ray opaque glass made up about one-third of the filler. The smaller particles were composed of a special barium fluoride-containing glass that was developed for this purpose [80]. Radiopacity is desirable so that dentists can distinguish between the filling material and any carious dentin that underlies the filling.

The most recent investigations are involved with the preparation and evaluation of a single glass filler material containing silica and only enough barium to give the desired refractive index and x-ray opacity [81]. Preliminary indications are that it will be suitable for converting into spherical particles utilizing conventional techniques while retaining the appropriate refractive index, and will have a low coefficient of thermal expansion. Chemically, the glass is formulated to have, at least in theory, hydrolytic stability in its bonding with the silane coupling agents.

Since these composite materials are not intrinsically adhesive to the prepared tooth surface, special coupling agents have been developed which improve bonding between such composite filler materials and dentin and enamel. The chemical design of these special coupling agents was based on empirical observations of the types of groups that could displace water from the surfaces of powdered human enamel and dentin, thereby making the surface organophilic rather than hydrophilic [82].

One of the coupling agents, NPG-GMA (the reaction product of N-phenylglycine and glycidyl methacrylate), has two functions in the same molecule. One function is that of a chelate group that can form multiple bonds with calcium in the tooth surface. The other function is that of a methacrylate group, which can copolymerize with the hardening organic matrix of the composite material [83]. A solution of the coupling agent placed on the prepared tooth surface with the excess solution being wiped away leaves an invisible film. Following this, the freshly mixed (but not yet hardened) composite material is placed on top of this treated surface and the subsequent polymerization apparently includes the methacrylate groups of the coupling agent. The coupling agent has presumably also formed ionic and coordinate bonds with the tooth surface. Laboratory data on tensile adhesion tests clearly demonstrate that the use of the coupling agent significantly improved the adhesion between composite materials and tooth surfaces [83, 84]. Clinical evaluations are under way [79].

There is a rapidly-expanding wealth of experience and information regarding composite dental materials, not only of the kind described here, but also of a wide diversity of materials and techniques [85]. Composite restorative materials, when they have been developed to their best potentialities, should eventually provide the dental profession and the public with greatly improved restorations for anterior teeth.

5. References

- [1] Luskin, L. S., Milestones in the History of Acrylic Products, *Or-Chem Topics* No. 23, Summer 1967, Philadelphia, Rohm & Haas Co.
- [2] Schnebel, *Dentistische Reforme* 4 and 5, 1942; Blumenthal, L., Recent German developments in the field of dental resins, fiat final report no. 1185, Field Information Agency, Technical, Office of Military Government for Germany (US) (27 May 1947).
- [3] Paffenbarger, G. C., Dental cements, direct filling resins, composite and adhesive restorative materials: A Resume, *Proceedings of the Engineering Foundation Research Conference on Engineering in Medicine-Bioceramics*, J. Biomed. Mater. Res. (Special Issue 1972).
- [4] Caul, H. J., and Schoonover, I. C., Color stability of direct filling resins, *J. Am. Dental Assoc.* 47, 448-452 (Oct 1953).
- [5] Smith, D. L., and Schoonover, I. C., Direct filling resins: Dimensional changes resulting from polymerization shrinkage and water sorption, *J. Am. Dental Assoc.* 46, 540-544 (May 1953).
- [6] Nelsen, R. J.; Wolcott, R. B., and Paffenbarger, G. C., Fluid exchange at the margins of dental restorations, *J. Am. Dental Assoc.* 44, 288-295 (March 1952).
- [7] Kramer, I. R. H., and McLean, J. W., The response of the human pulp to self-polymerizing acrylic restorations, *Brit. Dental J.* 92, 255-261, 281-287, 311-315 (May-June 1952).
- [8] Grossman, L. I., Pulp reaction to the insertion of self-curing acrylic resin filling materials, *J. Am. Dental Assoc.* 46, 265-269 (March 1953).

- [9] Kramer, I. R. H., The relationship between pain and changes in the dental pulp following the insertion of fillings, *Brit. Dental J.* **96**, 9-13 (Jan 1954).
- [10] Hedegård, B., Cold-polymerizing resins as restorative materials, *Odontol. Tidskr.* **65**, 169-212 (June 1957).
- [11] Hedegård, B., Co-Report, Synthetic Plastics, *Intern. Dental J.* **3**, 249-250 (June 1958).
- [12] Fletcher, T., British Patent No. 3028, 1878, Fletcher, T., Silicate of lime and alumina, *Brit. Dental J. Science* **22**, 74, (1879).
- [13] Henschel, C. J., Observations concerning in vivo disintegration of silicate cement restorations, *J. Dental Res.* **28**, 528-529 (Oct 1949).
- [14] Bowen, R. L., Paffenbarger, G. C., and Mullineaux, A. L., A laboratory and clinical comparison of silicate cements and a direct filling resin, A Progress Report, *J. Prosthetic Dentistry* **20**, 426-437 (Nov 1968).
- [15] Norman, R. D., Swartz, M. L., Phillips, R. W., and Virmani, R., A comparison of the intraoral disintegration of three dental cements, *J. Am. Dental Assoc.* **78**, 777-782 (April 1969).
- [16] Knock, F. E., and Glenn, J. F., Dental Material and Method, U.S. Patent No. 2,558,139 (June 26, 1951).
- [17] Paffenbarger, G. C., Nelsen, R. J., and Sweeney, W. T., Direct and indirect filling resins: A review of some physical and chemical properties, *J. Am. Dental Assoc.* **47**, 516-524 (Nov 1953).
- [18] Rose, E. E., Lal, J., Green, R., and Cornell, J., Direct resin filling materials: Coefficient of thermal expansion and water sorption of polymethyl methacrylate, *J. Dental Res.* **34**, 589-596 (Aug 1955).
- [19] Rose, E. E., Lal, J., Williams, N. B., and Falcetti, J. P., The screening of materials for adhesion to human tooth structure, *J. Dental Res.* **34**, 577-588 (Aug 1955).
- [20] Lee, H., and Neville, K., *Handbook of Epoxy Resins* (McGraw-Hill Book Co., New York, 1967).
- [21] Bowen, R. L., Use of epoxy resins in restorative materials, *J. Dental Res.* **35**, 360-369 (June 1956).
- [22] Bowen, R. L., and Mullineaux, A. L., Adhesive restorative materials, *Dental Abstracts* **14**, 80-82 (Feb 1969).
- [23] Bowen, R. L., Dental Filling Material Comprising Vinyl Silane Treated Fused Silica and a Binder Consisting of the Reaction Product of Bisphenol and Glycidyl Acrylate, U.S. Patent No. 3,066,112 (Nov 1962).
- [24] Bowen, R. L., and Rodriguez, M. S., Tensile strength and modulus of elasticity of tooth structure and several restorative materials, *J. Am. Dental Assoc.* **64**, 378-387 (March 1962).
- [25] Bowen, R. L., A Method of Preparing a Monomer having Phenoxy and Methacrylate Groups Linked by Hydroxy Glyceryl Groups, U.S. Patent No. 3,179,623 (April 1965).
- [26] Bowen, R. L., Properties of a silica-reinforced polymer for dental restorations, *J. Am. Dental Assoc.* **66**, 57-64 (Jan 1963).
- [27] Bowen, R. L., Crystalline dimethacrylate monomers, *J. Dental Res.* **49**, 810-815 (July-Aug 1970).
- [28] Bjorksten, J., Tovey, H., Harker, B., and Henning, J., *Polymesters and Their Applications*, p. 11 (Reinhold Publishing Corp., New York 1956).
- [29] Guide to Dental Materials and Devices (5th ed), pp 51, 98 (Am. Dental Assoc., Chicago, 1970-71).
- [30] Vanderbilt, B. M., and Simko, J. P., Jr., Silane coupling agents in glass-reinforced plastics, *Modern Plastics* **38**, 135-217 (Dec 1960).
- [31] Vanderbilt, B. M., and Jaruzelski, J. J., The bonding of fillers to thermosetting resins, *Ind. and Eng. Chem., Prod. Res. and Dev.* **1**, 188-194 (Sept 1962).
- [32] Sterman, S., and Marsden, J. G., Filler-silane interactions, *Modern Plastics* **41**, 254-266 (Oct 1963).
- [33] Sterman, S., and Marsden, J. G., Silane coupling agents as integral blends in resin-filler systems, *Modern Plastics* **40**, 125-177 (July 1963).
- [34] Bowen, R. L., Effect of particle shape and size distribution in a reinforced polymer, *J. Am. Dental Assoc.* **69**, 481-495 (Oct 1964).
- [35] Bowen, R. L., Development of an Adhesive Restorative Material, *Adhesive Restorative Dental Materials—II* (Public Health Service Publication No. 1494, p. 225, Washington, D.C., 1966).
- [36] Bowen, R. L., Unpublished data.
- [37] Holliday, L. (ed), *Composite Materials*, p. 153 (Elsevier Publishing Co., New York 1966).
- [38] Johansson, O. K., Stark, F. O., Vogel, G. E., and Fleischmann, R. M., Evidence for chemical bonding formation at silane coupling agent interfaces, *J. Comp. Materials* **1**, 278-292 (Jan 1967).
- [39] Broutman, L. J., and Krock, R. H. (eds.), *Modern Composite Materials*, pp. 501, 7 (Addison-Wesley Publishing Co., Reading, Massachusetts, 1967).
- [40] Hatch, R. A., Phase equilibrium in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$, *The American Mineralogist* **28**, 471-496 (Sept-Oct 1943).
- [41] Boyd, R. N., Collin, L., and Kaufman, E. G., Dental Filling Composition of a Coefficient of Thermal Expansion Approximating that of Natural Tooth Enamel, U.S. Patent 3,503,128 (March 31, 1970).
- [42] Smoke, E. J., Ceramic compositions having negative linear thermal expansion, *J. Amer. Ceramic Soc.* **34**, 87-90 (March 1951).
- [43] Bowen, R. L., and Argentar, H., Diminishing discoloration in methacrylate accelerator systems, *J. Am. Dental Assoc.* **75**, 918-923 (Oct 1967).
- [44] McLean, J. W., and Short, I. G., Composite anterior filling materials, *Brit Dental J.* **127**, 9-18 (July 1969).
- [45] Hirasawa, T., Self-curing resins containing inorganic fillers for dental restorations. II. Effect of surface treatment of glass fillers on mechanical properties, *Shika Zairyo Kenkyusho Hokoku* **2**, 629-643, 644-655 (March 1965).
- [46] Going, R. E., and Sawinski, V. J., Microleakage of a new restorative material, *J. Am. Dental Assoc.* **73**, 107-115 (July 1966).
- [47] Buonocore, M. G., Matsui, A., and Yamaki, M., Abrasion of restorative materials, *N.Y. State Dental J.* **32**, 395-400 (Nov 1966).
- [48] Peterson, E. A., Phillips, R. W., and Swartz, M. L., A comparison of the physical properties of four restorative resins, *J. Am. Dental Assoc.* **73**, 1324-1336 (Dec 1966).
- [49] Bowen, R. L., Adhesive bonding of various materials to hard tooth tissues. VI. Forces developing in direct-filling materials during hardening, *J. Am. Dental Assoc.* **74**, 439-445 (Feb 1967).
- [50] Matsui, A., Buonocore, M., and Yamaki, M., Heat of polymerization of certain new and conventional restorative materials, *J. Dental Res.* **46**, 1106 (Sept-Oct 1967).
- [51] Gotfredsen, C., Addent® Investigations of a plastic filling material, *Tandlaegebladet* **72**, 407-429 (May 1968).
- [52] Macchi, R. L., and Craig, R. G., Physical and mechanical properties of composite restorative materials, *J. Am. Dental Assoc.* **78**, 328-334 (Feb 1969).
- [53] Freeman, F. H., Composite restorative materials. Presented before the Dental Materials Group, IADR, Mar 21, 1969, Houston, Texas.

- [54] Tani, Y., and Buonocore, M., Marginal leakage and penetration of basic fuchsin dye in anterior restorative materials, *J. Am. Dental Assoc.* **78**, 542-548 (March 1969).
- [55] Lee, H. L., Swartz, M. L., and Smith, F. F., Epoxy resins in dentistry, presented at the ACS National Meeting, April 1969, Minneapolis, Minnesota (in press).
- [56] Gottfredsen, C., Physical properties of a plastic filling material (Addent®), *Acta Odontol. Scand.* **27**, No. 6, 595-615 (1969).
- [57] Lee, H. L., Swartz, M. L., and Smith, F. F., Physical properties of four thermosetting dental restorative resins, *J. Dental Res.* **48**, 526-535 (July-Aug 1969).
- [58] Phillips, R. W., Swartz, M. L., and Norman, R. D., Materials for the Practicing Dentist, chapter 59, pp. 182-191 (The C. V. Mosby Co., St. Louis, Mo., 1969).
- [59] Docking, A. R., Modern materials in dental practice, *Australian Dental J.* **15**, 303-309 (Aug 1970).
- [60] Schouboe, P. J., Paffenbarger, G. C., and Sweeney, W. T., Resin cements and posterior-type direct filling resins, *J. Am. Dental Assoc.* **52**, 584-600 (May 1956).
- [61] Barton, J. A., Jr., Burns, C. L., Chandler, H. H., and Bowen, R. L., An experimental, intermediate-restorative composite material (To be published in *J. Dental Res.*).
- [62] Barton, J. A., Jr. et al., Unpublished data.
- [63] Craig, R. G., and Peyton, F. A., Elastic and mechanical properties of human dentin, *J. Dental Res.* **37**, 710-718 (Aug 1958).
- [64] Stanford, J. W., Paffenbarger, G. C., Kumpula, J. W., and Sweeney, W. T., Determination of some compressive properties of human enamel and dentin, *J. Am. Dental Assoc.* **57**, 487-495 (Oct 1958).
- [65] Stanford, J. W., Weigel, K. V., Paffenbarger, G. C., and Sweeney, W. T., Compressive properties of hard tooth tissues and some restorative materials, *J. Am. Dental Assoc.* **60**, 746-756 (June 1960).
- [66] Craig, R. G., Peyton, F. A., and Johnson, D. W., Compressive properties of enamel, dental cements, and gold, *J. Dental Res.* **40**, 936-945 (Oct 1961).
- [67] Souder, W., and Paffenbarger, G. C., Physical Properties of Dental Materials, NBS Circ. 433, 222 pages (1942).
- [68] Sweeney, W. T., Sheehan, W. D., and Yost, E. L., Mechanical properties of direct filling resins, *J. Am. Dental Assoc.* **49**, 513-521 (Nov 1954).
- [69] Stanley, H. R., Swerdlow, H., and Buonocore, M. G., Pulp reactions to anterior restorative materials, *J. Am. Dental Assoc.* **75**, 132-141 (July 1967).
- [70] Langeland, L. K., Guttuso, J., Jerome, D. R., and Langeland, K., Histologic and clinical comparison of Addent with silicate cements and cold-curing materials, *J. Am. Dental Assoc.* **72**, 373-385 (Feb 1966).
- [71] French Patent No. 2,008,541 (Jan 23, 1970).
- [72] Mihailov, M., and Boudevska H., Synthesis and polymerization of polyester methacrylates and terephthalic and furane-2, 5-dicarboxylic acid, *Compt. Rend. Acad. Bulgare Sci.* **18**, 31-34 (1965).
- [73] French Patent No. 2,010,896.
- [74] French Patent No. 2,010,905.
- [75] Atsuta, M., Nakabayashi, N., and Masuhara, E., Hard methacrylic polymers, II., copolymers of methyl methacrylate and 2,2-Di(4-methacryloxyphenyl)propane, *J. Biomed. Mat. Res.* **5**, 183-196 (May 1971).
- [76] Bowen, R. L., and Argentar, H., Amine accelerators for methacrylate resin systems, *J. Dental Res.* **50**, 923-928 (July-Aug 1971).
- [77] Bowen, R. L., and Argentar, H., Tertiary aromatic amine accelerators with molecular weights above 400, *J. Dental Res.* **51**, 473-482 (Mar.-Apr. 1972).
- [78] Chandler, H. H., Bowen, R. L., and Paffenbarger, G. C., A method for finishing composite restorative materials, *J. Am. Dental Assoc.* **83**, 344-348 (Aug 1971).
- [79] Chandler, H. H., Bowen, R. L., Paffenbarger, G. C., and Mullineaux, A. L., Clinical investigation of a radiopaque composite material, *J. Am. Dental Assoc.* **81**, 935-940 (Oct 1970).
- [80] Bowen, R. L., and Cleek, G. W., X-ray-opaque reinforcing fillers for composite materials, *J. Dental Res.* **48**, 79-82 (Jan-Feb 1969).
- [81] Bowen, R. L., and Cleek, G. W., A new series of X-ray-opaque reinforcing fillers for composite materials, *J. Dental Res.* **51**, 171-182 (Jan-Feb 1972).
- [82] Bowen, R. L., Investigation of the surfaces of hard tooth tissues by a surface activity test. Proceedings of the Workshop on Adhesive Restorative Dental Materials at Indiana University, Owen Litho Service, Spencer, Indiana-Publishers Sept 1961; National Technical Information Service, U.S. Dept. Commerce, Springfield, Va. 22151, PB 173009, Phillips and Ryge (ed.).
- [83] Bowen, R. L., Surface-Active Comonomer and Method of Preparation, U.S. Patent No. 3,200,142 (Aug 10, 1965).
- [84] Bowen, R. L., Adhesive bonding of various materials to hard tooth tissues (Parts I-V), *J. Dental Res.* **44**, 690-695, 895-902, 903-905, 906-911, 1369-1373 (July-Dec 1965).
- [85] Craig, G. G., The placement of composite resin restorations, *Australian Dental J.* **15**:277-280 (Aug 1970).

Cements Containing *o*-Ethoxybenzoic Acid (EBA)

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Cements containing *o*-ethoxybenzoic acid (EBA) are reviewed. Studies of the mechanism of hardening of zinc oxide-eugenol cements indicated the potential usefulness of other chelating agents in dental cements. Products with greatly enhanced physical and mechanical properties are obtained by the partial substitution of EBA for eugenol. Similar to zinc oxide-eugenol cements, these materials are well tolerated by the tissues, but they also stimulate the formation of reparative dentin. Physical properties of the EBA-containing cements approach those of the biologically and physiologically less desirable zinc phosphate cements. The EBA cements have become commercially available and have been well accepted as luting agents for fixed restorations and as insulating bases. They appear to be the materials of choice for indirect pulp capping. Resin modified EBA restoratives show good stress-bearing characteristics and should find applications as an intermediate restorative. Possible studies to further improve these versatile materials are discussed.

Key words: Crown and bridge cements; dental cements; EBA cements; EBA sedative bases; intermediate restorative; *o*-ethoxybenzoic acid cements; pulp capping materials; zinc oxide-EBA-eugenol cements.

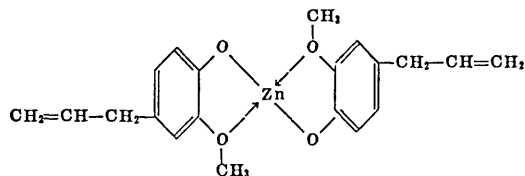
1. Introduction

Cements containing *o*-ethoxybenzoic acid (EBA) are an outgrowth of studies to improve zinc oxide-eugenol (ZOE) cements which were first reported in the dental literature about one hundred years ago [1-3].¹ Over the years ZOE cements have found a wide range of applications in dentistry: as temporary restoratives, sedative bases, cementing media, for crown and bridge work, in pulp capping, as soft tissue packs in oral surgery and periodontics, as root canal sealers in endodontics and with modifying agents as impression pastes. The ZOE cements possess much better compatibility than most dental materials with both the hard and soft tissues of the mouth [4-7]. They have excellent sealing properties [8] and their sterilizing effectiveness [9] has been demonstrated. ZOE cement also acts as a palliative or anodyne and as a mild non-irritant antiseptic. Their low strength which may not be large enough to resist forces of mastication and their lack of resistance to wear and disintegration deter more extensive use in temporary restorations.

2. Setting Mechanism of ZOE Cements

A number of studies have shown that the set mass resulting from mixes containing the proper proportion of zinc oxide and eugenol consists of zinc oxide embedded in a matrix of zinc eugenolate

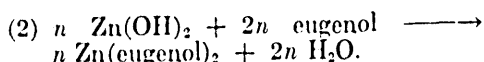
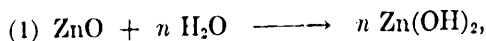
chelate with any excess eugenol being sorbed by both zinc eugenolate and the unreacted zinc oxide [10-11]. More detailed studies of the infrared spectra have confirmed the bisdioxachelate structure of zinc eugenolate [12].



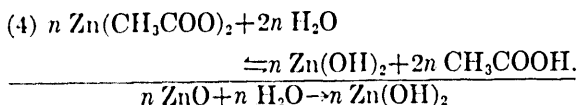
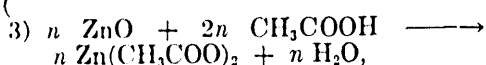
The crystal structure of this compound has been investigated by Douglas [13] and Cartz [14]. X-ray diffraction of commercial ZOE products or experimentally prepared formulations which also have a large excess of zinc oxide yield extremely small values for the relative intensity ratios of the principal peaks of zinc eugenolate to ZnO. This suggests that in these cements the zinc eugenolate reaction product is formed below the 2% level resolvable in standard preparations [15-16]. High resolution microscopy also indicates that the zinc eugenolate product in commercial formulations is small and is confined to the reaction interface [17]. These formulations also contain about 5% free eugenol after hardening [18].

The setting reaction is speeded up by the presence of an accelerator such as zinc acetate. Presence of water or a decrease in the pH of the reaction mixture also reduces setting time. Water reacts with zinc oxide to form the hydroxide which in turn reacts with eugenol [19].

¹ Figures in brackets indicate the literature references at the end of this paper.



The formation of the hydroxide is slow, but acid speeds up the reaction.



Since the zinc hydroxide reacts with eugenol, reaction (4) goes to the right. Obviously, zinc acetate can be substituted for acetic acid, but to start the reaction a trace of water must be present. Commercial formulations generally contain zinc acetate dihydrate as accelerator which furnishes the water to initiate the reaction.

3. Modified ZOE and EBA Cements

Low strength is unquestionably the main disadvantage of ZOE cements. A number of studies have been undertaken during the last decade to upgrade the properties of the cements. The following approaches have been taken:

1. Replacement of zinc oxide by other metal oxides.
2. Incorporation of fillers, reinforcing or modifying agents.
3. Substitution of eugenol by other chelating agents.

Only limited studies have been made to substitute other metal oxides for zinc oxide [11]. Cupric eugenolate can be prepared by a procedure similar to that used in the synthesis of zinc eugenolate. A slight excess of a methanolic solution of cupric acetate monohydrate is reacted with eugenol at 60° C for one hour [16]. Employing the same reaction conditions, that is, refluxing methanolic solutions of eugenol with mercuric-, lead-, nickelous- or calcium-acetate did not yield the respective metal eugenolates. Attempts to synthesize the cupric or nickel isoeugenolates also were unsuccessful.

Addition of rosin or hydrogenated rosin improves the working properties of the mixes. Hydrogenated rosin is commonly used since it is stable to oxidation and yields cements with good color stability. Incorporation of up to 20 percent polymer dissolved in eugenol to improve the physical properties was first suggested by Curtis [20]. An experimental cement containing surface-treated zinc oxide (80%) and poly(methyl methacrylate) (20%) powder and a liquid consisting of 99 percent eugenol and 1 percent acetic acid had a compressive strength of 54.0 MN/m² (550 kg/cm², 7,820 psi), a tensile strength of 4.1 MN/m² (42 kg/

cm², 600 psi) and a solubility and disintegration value of 0.008 g/cm² [21]. A clinical evaluation of this cement as an intermediate restorative material at intervals of 60 days for a period of 12 months showed this formulation to be superior to three other experimental cements with regard to the maintenance of anatomical form and marginal integrity [22]. Products incorporating poly(methyl methacrylate) in the powder have become commercially available both as luting agents and intermediate restoratives.

The knowledge gained from the characterization of the reaction products led to extensive investigations with the ultimate aim of obtaining improved cements by substitution of other complexing agents for eugenol. Eugenol isomers capable of forming chelates were synthesized [23] and the effect of the position of substituents on the behavior of the isomers as evidenced by their ionization constants and reactivity with zinc oxide was determined [24]. In the reaction of eugenol isomers with zinc oxide, the 1,2,3-trisubstituted isomers do not react readily compared to the unsymmetrically 1,2,4- or 1,2,5-trisubstituted ones, indicating that the chelation reaction is greatly influenced by steric hindrance of the bulky neighboring allyl groups. The chelation reaction may also depend to some degree on the ionization constants since the more acidic chavibetol reacts somewhat faster than eugenol.

Zinc oxide will react with many chelate-forming compounds to yield coherent products [25]. Mixes containing *o*-ethoxybenzoic acid (EBA), salicylaldehyde, acetylacetone, *o*-ethoxyacetic acid or lactic acid form hard products within one hour at room temperature. Some of these products disintegrate in water.

Cements obtained from *o*-ethoxybenzoic acid (EBA) and metal oxides of group II of the periodic table or lead oxide have been studied in considerable detail [26]. Products formed from zinc oxide and EBA-eugenol solutions in the absence of an accelerator harden more rapidly and have higher strength and lower solubility and disintegration values than those made with EBA alone (figs. 1 and 2). Most useful properties are obtained with liquids containing between 50 to 70 percent EBA. However, these cements have a high water solubility. Substitution of 2-propoxy-5-methylbenzoic acid, a higher, more hydrophobic homologue for EBA, yields cements with unexpectedly high water solubility and disintegration [26, 27]. On incorporation of rosin or hydrogenated rosin the water solubility is greatly reduced [26]. Addition of a reinforcing agent such as monocalcium phosphate, heat-treated fused quartz or aluminum oxide gives products with compressive, shear and tensile strengths that are three to four times those of conventional ZOE formulations. Thus, these EBA containing products have mechanical properties similar to those of zinc phosphate cements.

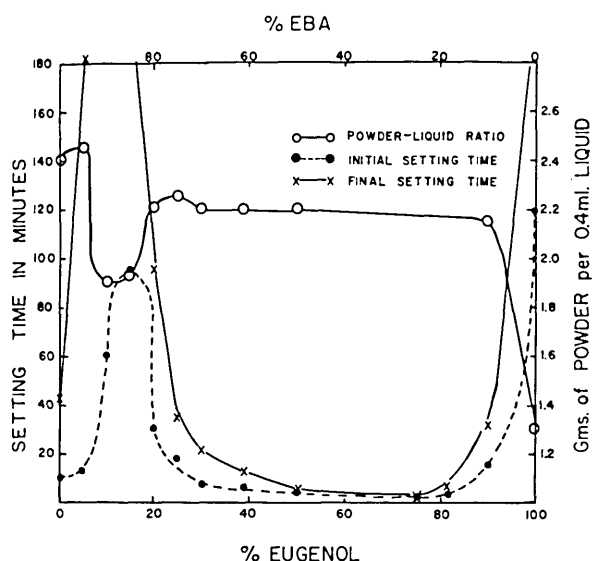


FIGURE 1. Effect of composition of the liquid on setting time and standard consistency powder-liquid ratio of ZnO-EBA-eugenol mixes [25].

The properties of cements, based on zinc oxide, hydrogenated rosin, EBA, and eugenol have been studied in detail [28]. The strength of the cements is nearly independent of the particle size of zinc oxide and fused quartz. The carbon dioxide and water content of the zinc oxide also have little effect on the physical properties of the hardened product [28-30]. Alumina reinforced EBA cements have physical properties superior to those of cements reinforced with fused quartz [31]. The preferred composition contained 64 percent zinc oxide, 30 percent tabular Al_2O_3 and 6 percent hydrogenated rosin. A slurry prepared from 1.7 g of powder per 0.2 ml of liquid can be mixed easily and will harden in less than 10 minutes. The resulting product has a compressive strength of 93 MN/m^2 (950 kg/cm^2 , 13,500 psi) and a film thickness of 26 μm (table 1). With one-surface inlays, these cements adhere at least as well as commercial zinc phosphate cements and give much higher tensile

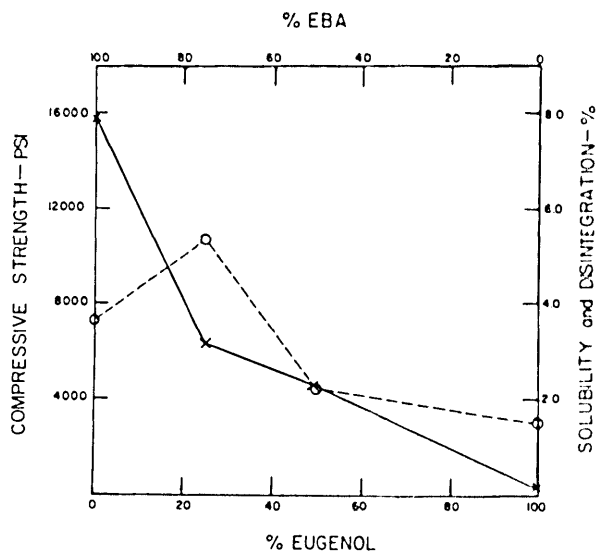


FIGURE 2. Effect of composition of the liquid on compressive strength and solubility and disintegration of ZnO-EBA-eugenol cements.

x—x solubility and disintegration. o-----o compressive strength [25].

adhesion values than ZOE products. Similar formulations have become commercially available and have been well accepted as luting agents in crown and bridge cementation. On incorporation of more powder into the mix, excellent base materials can be obtained. Especially desirable is their high ten-minute compressive strength of 46.1 MN/m^2 (470 kg/cm^2 , 6,680 psi) which can easily withstand the forces encountered in condensing an amalgam.

The brittleness of these luting agents limits their use for temporary restorations of multiple surface carious lesions in areas subject to heavy masticatory forces [32]. Stress bearing characteristics of EBA cements can be improved through the incorporation of powdered polymers of relatively low elastic moduli [30]. The most suitable resins are methacrylate copolymers, although vinyl copolymers may also be potentially useful. Other resins, because of their resilient nature are difficult to obtain

TABLE 1. Physical properties of dental cements¹

	Powder-liquid quantities	Setting time	Tensile strength ²		Compressive strength ²		Solubility and disintegration
	gm/ml	min	MN/m^2	kg/cm^2	MN/m^2	kg/cm^2	Percent
Zinc oxide-eugenol (ZOE)-----	1. 0-2. 2/ 4	3-8	1. 4-2. 5	14-25	16. 7-38. 3	170-390	0. 02-0. 20
Reinforced ZOE-----	. 6-1. 1/ 3	3-8	1. 5-6. 9	15-70	39. 2-75. 5	400-770	. 05- . 80
EBA (Al_2O_3 reinforced)-----	1. 6-2. 0/ 2	7-9	3. 9-7. 4	40-75	58. 9-93. 1	600-950	. 05- . 13
EBA (plastic-modified)-----	1. 1-1. 3/ 2	7-8	6. 6-9. 8	66-99	50. 0-78. 5	510-800	. 13- . 94
Zinc phosphate cement-----	1. 4/ 5	7-8	3. 2-4. 6	33-46	68. 7-147. 1	700-1, 500	. 10- . 20

¹ Some of the data given in this table are taken from the results of the collaborative test program—Zinc oxide—Eugenol Dental Cements ISO Technical Committee 106/WG1—Filling Materials.

² One day.

in powdered form. A cement made from powder containing 58.2 percent ZnO, 27.3 percent Al₂O₃, 5.4 percent rosin and 9.1 percent methyl methacrylate copolymer and liquid containing 62.5 percent EBA and 37.5 percent eugenol had, after one week, tensile and compressive strengths of 11.5 MN/m² (117 kg/cm², 1,660 psi) and 65.1 MN/m² (664 kg/cm², 9,430 psi) respectively. Thus, the addition of the polymer greatly increases the tensile strength of the hardened cement. These markedly higher tensile strength values are probably more important than the somewhat lower compressive strength; the clinical results described later bear out this point.

Cements containing rosin have somewhat higher tensile strength, but are more soluble and set more slowly than those to which hydrogenated rosin has been added [30]. Improvement in the physical properties of a formulation containing 58.2 percent ZnO, 27.3 percent Al₂O₃, 5.4 percent hydrogenated rosin and 9.1 percent methyl methacrylate copolymer in the powder and 62.5 percent EBA-37.5 percent eugenol in the liquid was not obtained on increasing the (1) hydrogenated rosin content, (2) percentage of eugenol, and (3) ratio of zinc oxide to aluminum oxide reinforcing agent. Addition of 0.5 percent aluminum sulfate decreases very slightly the solubility and disintegration of cements containing rosin or hydrogenated rosin. A vinyl chloride-vinyl acetate copolymer-containing cement had one-week tensile and compressive strength of 9.8 MN/m² (100 kg/cm², 1,420 psi) and 91.5 MN/m² (933 kg/cm², 13,300 psi), respectively. Incorporation of an acrylonitrile-butadiene-styrene terpolymer, a polyacetal resin, or various grades of commercial polycarbonate molding powders produced materials with physical properties somewhat lower than those containing acrylic copolymer. A summary of the physical properties of conventional and reinforced ZOE cements, alumina-reinforced, plastic-modified EBA cements, and zinc phosphate cements is given in table 1.

A comparison of the first commercially available EBA crown and bridge cements has been made by Phillips and coworkers [33]. Properties investigated were compressive and tensile strength, film thickness, solubility and disintegration in both water and acid and retentive characteristics as determined by the amount of tensile force required to remove one-surface inlays from prepared cavities following cementation with the various agents. Physical properties of an experimental alumina-reinforced EBA cement and commercial EBA cements of unknown composition have also been studied by Custer and Anderson [34]. The properties of typical commercial EBA cements have been measured in a collaborative test program which had as its aim the development of a specification for ZOE and EBA type cements [35].

4. Mechanism of Setting of EBA Cements

The products formed on hardening of commercial EBA cements have not been completely characterized [16]. Cements made up of zinc oxide and a liquid consisting of either EBA or 62.5 percent EBA-37.5% eugenol were pulverized. The powder was extracted by shaking with 50 ml of methanol for 6 hr. After centrifuging, the methanol layer was decanted and the remaining powder was dried at 110 °C and weighed. From cements containing EBA, the original liquid was removed quantitatively (table 2). Cements containing EBA and eugenol lost 60 to 70 percent of their liquid component on extraction. Probably all the EBA was removed by the methanol extraction. The results were confirmed by heating the dried unextracted solid residue in a crucible to remove any remaining organic matter. There was no loss in weight on heating the residue of the cement prepared with EBA liquid. The EBA-eugenol containing cement showed a 30 to 40 percent loss in weight which accounted for all the unextracted liquid. Thus, eugenol is much less readily extracted, and hence more firmly bound than EBA in the hardened cements.

TABLE 2. Weight loss of cements on solvent extraction

Cement containing zinc oxide and	Extraction with CH ₃ OH	Loss of liquid on heating CH ₃ OH insoluble residue	Extraction with CHCl ₃
Eugenol.....	Percent 10-12	Percent 80-90	Percent ~80
EBA.....	100	0	*119
EBA and eugenol.....	60-70	30-40	*102

*Including some solid extracted with CHCl₃.

To study the reaction product, zinc oxide (2 g, 0.0246 mole) and *o*-ethoxybenzoic acid (8 g, 0.048 mole) were stirred together and set aside. After two months at room temperature, the mixture consisted of a soft layer on top of a hard layer. X-ray diffraction did not give any peaks. The product was partially soluble in hot water, insoluble in methanol, ethanol, chloroform, or dimethylformamide.

The reaction products were added to warm acetone and filtered. On evaporation of the solvent an amorphous material separated from the filtrate. The solid residue, insoluble in warm acetone, could be dissolved by boiling in acetone for 10 min. A solid (mp 92-100 °C) crystallized on cooling to 0 °C. After drying in a vacuum, analysis for carbon and hydrogen indicated that the compound was zinc *o*-ethoxybenzoate (Anal: Calcd. for C₁₈H₁₈O₆Zn: C, 54.63, H, 4.58. Found: C, 54.8; H, 4.6) Absence of an infrared absorption peak around 1,750 cm⁻¹ indicated that no unreacted

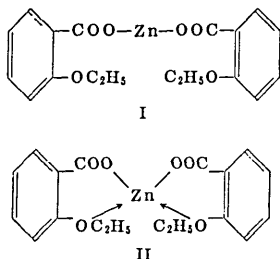
COOH is present. The broad absorption band of *o*-ethoxybenzoic acid around $1,230\text{ cm}^{-1}$ which can be attributed to the ethoxy group [36] is present in the zinc derivative as a sharp band at $1,240\text{ cm}^{-1}$. The spectrum of *o*-ethoxybenzoic acid has absorptions at $1,745\text{ cm}^{-1}$ and also carbonyl absorptions at $1,594$ and $1,609\text{ cm}^{-1}$. For the primarily ionic-bonded zinc *o*-ethoxybenzoate, the absorption peak of the $-\text{COO}^- \text{Zn}/2$ group falls in the same region at $1,600\text{ cm}^{-1}$. Since the uncoordinated $-\text{COO}^-$ group also absorbs in the same region [37], it was not possible to establish from the infrared spectrum whether the *o*-ethoxybenzoate possesses a chelate structure.

The same compound was obtained on heating 20 g (0.12 mole) of EBA, 5 g (0.061 mole) of zinc oxide, and 20 ml of methanol on a steam bath until most of the solvent had evaporated. On cooling in a refrigerator, a white solid crystallized which, on recrystallization from chloroform, had a melting point of $90\text{--}103^\circ\text{C}$. The infrared absorption spectrum was identical with the spectrum of zinc *o*-ethoxybenzoate obtained by the procedure described above. (Anal: Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Zn}$: C, 54.63, H, 4.58. Found: C, 54.3; H, 4.6).

The zinc *o*-ethoxybenzoate could also be synthesized in 20 percent yield from 12.3 g (0.075 mole) EBA dissolved in 20 ml methanol and 8.8 g (0.04 mole) zinc acetate by heating for 6 hr on a steam bath, filtering and dissolving the residue in hot chloroform.

Slurries using powder-liquid ratios of 10:1, 5:1, and 1:1 of zinc oxide powder and EBA or 62.5 percent EBA-37.5 percent eugenol liquid were prepared and allowed to harden at 37°C . and 100 percent relative humidity. X-ray diffraction patterns showed only minor changes on varying the powder-liquid ratio with all patterns resembling closely those of zinc oxide.

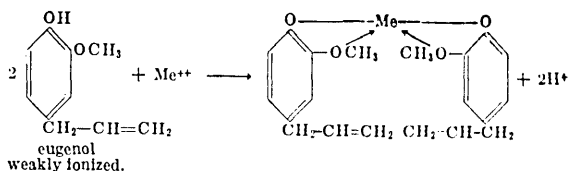
On addition of EBA to zinc oxide, either a salt (I) or chelate complex (II) can form:



Possible formation of a chelate was studied [16] by titration of an aqueous solution of EBA with base in the presence of zinc ions and Job's spectrophotometric method of continuous variation [38].

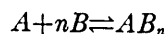
The first procedure depends on the fact that most metal chelates may be considered as formed by the displacement of a weak acidic portion of the chelating agent by a metal ion [39]. Thus, the addition of metal ion causes a drop in pH and the

greater the tendency for metals to combine with a given chelating agent, the greater the drop in pH.



This simple technique of checking for chelate or complex formation is not very sensitive for EBA since it is a moderately strong acid. Hence, there is little decrease in pH if chelation occurs. Results of the titration of EBA with base in the presence and absence of Zn^{++} were inconclusive.

The composition of chelates can often be determined by a simple colorimetric technique introduced by Job [38]. For the chelating reaction:



$$K = \frac{[AB_n]}{[A][B]^n}$$

where $[A]$ is the concentration of the metallic ion and $[B]$ that of the chelating agent. If $[A] + [B] = \text{constant}$, it can be shown that when concentration $[AB_n]$ is a maximum

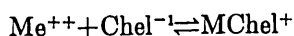
$$[B]/[A] = n;$$

that is, for a constant total concentration of metal and chelating agent, the concentration of chelate with respect to unreacted metal or chelating agent is greatest when the metal and chelating agent are brought together in the same ratio in which they exist in the chelate. If the chelate absorbs light in the visible or ultraviolet region, a plot of optical density versus composition of the solution under the restriction imposed above will give a curve with a maximum at the composition corresponding to the formula of the chelate. If substances are present that absorb light in the same region as does the chelate, the difference in optical densities between the chelate and the estimated amounts of unchelated absorbing substances may be plotted as a function of concentration.

The absorption of aqueous EBA and eugenol solutions as well as of solution of these compounds containing zinc sulfate were measured in the ultraviolet (250–360 nm). EBA and eugenol solutions follow Beer's law. They show an absorption peak around 292 nm, whereas ZnSO_4 does not absorb at this wave length. Job's method of continuous variation was applied to EBA-ZnSO_4 solutions having a total concentration of $4 \times 10^{-4}\text{ M}$. No maximum was observed by plotting optical density versus composition of the solution. This result does not necessarily indicate that no chelate formation takes place since some chelates have absorption spectra that do not differ significantly from those of the chelating agent. McKenzie and

coworkers [40] have shown that ionic chelates have nearly the same absorption spectra as their chelating agent, but that the absorption spectra for covalent bonded chelates contained strong absorption bands characteristic of the chelate, and hence of the metal-donor bond. Since EBA is a moderately strong acid, its anion should be a fairly strong conjugate base. Formation of an ionic complex with a divalent metal ion such as Zn^{++} is likely to occur, especially since oxygen donors favor ionic bonds.

Eugenol forms a five-membered chelate whereas EBA may give a six-membered ring. Measurement of the chelate stability constants K as well as the formation constants k_1 and k_2 for the reaction



$$K = k_1 \times k_2 = \frac{[MChel_2]}{[Me^{++}][Chel^{-1}]_2}$$

would yield valuable information since these constants would show the relative stability of the two ring systems.

5. Clinical Studies

The main purpose of a temporary restoration is sedation and protection of the tooth from irritants and decay. The ZOE cement is essentially neutral and, therefore, offers unusual pulpal protection. The EBA-containing cements have the same mild tissue reaction of unmodified ZOE cements, which are much superior in this respect to zinc phosphate cements [41-43].

Unset cements caused some necrosis and a moderately severe inflammatory reaction when they were first inserted into rat muscle [42]. Granulation tissue formed in the region and healing proceeded rapidly, producing a fibrous capsule to the implant. When set materials were used as implants, the EBA-containing cement was always less irritating than zinc oxide-eugenol cements. Bhaskar and coworkers [43] investigated the pulpal response of four types of restorative materials. Class V cavities were prepared in 78 teeth of three miniature swine. The animals were killed after 1, 2, and 3 weeks and the teeth were examined microscopically. A powder containing 57 percent ZnO, 28 percent aluminum oxide, 9.5 percent poly (methyl methacrylate) copolymer and 5.5 percent rosin and liquid made up from 66.7 percent EBA and 33.3 percent eugenol was used. The restorative material appeared to be biologically acceptable to the dental pulp. No irreversible pulp damage was observed. Odontoblastic disruption and inflammatory infiltrate were not severe. They were least pronounced in the ZOE restoration, very slightly more marked in a commercial, resin-modified ZOE and the EBA formulation, and most prominent in

teeth restored with cyanoacrylate-containing restorative material. The layer of reparative dentin formed in response to the filling materials was proportional to the degree of odontoblastic disruption and the inflammatory infiltrate. It was much more pronounced in the teeth that were restored with cyanoacrylate and EBA than in teeth filled with ZOE cements. Thus, in cases in which the therapeutic aim is to require a thick layer of reparative dentin, a cavity base with either the EBA or cyanoacrylate is preferable.

It would be of interest to study if the reparative and secondary dentin formation produced by EBA cements is as rapid as that formed after the use of calcium hydroxide. Coleman and Kirk [42] filled cavities scheduled for extraction for orthodontic reasons with ZOE and EBA cements. The teeth were extracted after periods ranging from 24 hr to 3 weeks. The teeth were fixed in 10 percent formol saline, decalcified, and examined histologically. Little or no pulpal reaction could be attributed to either the ZOE or the EBA materials. The odontoblast layer was usually intact. Although some vacuolation was present in this region, this was also seen in the control teeth where no cavities had been prepared.

There has long been a deep interest in an improved ZOE cement that would be suitable for permanent cementation of cast restorations. The modified ZOE or reinforced EBA cements have been employed successfully as crown and bridge cements and appear to be well suited for this purpose. The absence of irritation on the dentine-pulp complex and the resulting freedom from post-cementation symptoms gives them a big advantage over zinc phosphate cements. Since their compressive strength is much higher than that of unmodified ZOE cements, their retentive properties are improved and approximate those of zinc phosphate cements [33, 44, 45]. A clinical study using 186 full cast crown bridge retainers and 205 full cast crowns has been reported by Horn [46]. The span of the bridges cemented with this material was limited to a maximum of two consecutive pontics of bicuspid width. Nineteen of the full cast crown bridge retainers were of the cantilever type. Resin veneers were protected from the excess EBA cement by coating them with silicone grease. No cavity liners or medicaments were applied. The crowns were not completely filled with cement, but a coating was applied to the internal surfaces and a small amount was allowed to flow into any crevices or depressions on the teeth prior to insertions. Dryness was not maintained after the restorations had been seated by applying pressure for two or three minutes. After cementation, abutment teeth were not painful, and the marginal relationships were not unduly distorted. In selected cases, tests with ice-cold water seemed to indicate excellent insulation. This effect may be caused by the ability of the cement to obtund pain.

A number of crown and bridge cements incorporating EBA have become commercially available in the United States and in Europe. Many products have film thickness of less than 25 μm . They may be used for the final cementation of metal crowns and bridges retained by metal crown, porcelain or plastic jackets, porcelain-over-metal restorations, and gold-veneered-with-resin restorations.

No clinical data are available regarding the retention of orthodontic bands cemented with EBA cements. Bands cemented with an experimental cement containing 90 percent ZnO and 10 percent hydrogenated rosin powder and 62.5 percent EBA and 37.5 percent eugenol required three times as much force to accomplish removal as bands cemented with ZOE, but the retention values were considerably lower than those obtained for phosphate or silicate cements [47].

Zinc phosphate cement has been the preferred material for use as an intermediary base beneath metallic restorations. Zinc phosphate is preferred over conventional ZOE and calcium hydroxide because of its superior strength, despite its inferior biological and slightly poorer thermal diffusion characteristics. When ZOE or calcium hydroxide bases are used, it is often recommended that they be overlaid with the stronger zinc phosphate cement [48-50].

The clinical significance of the compressive strength of a base material has not been defined. It is obvious, nevertheless, that when amalgam is condensed into the cavity preparation, the base must have sufficient strength to support the forces of condensation. If the base does not have sufficient strength, fracture or displacement of the base could permit the amalgam to contact the underlying tooth structure and thus negate the thermal protection afforded by the base.

Furthermore, in deep cavity preparation, the amalgam could be forced through microscopic exposures in the floor of the cavity and into the pulp [51-52]. Chang, Swartz and Phillips [53], in experiments conducted under laboratory conditions, showed that with ZOE materials a minimum strength capable of supporting amalgam condensation ranges from 0.7 to 1.2 MN/m^2 (7 to 12 kg/cm^2 , 100 to 170 psi).

Interest has increased in recent years in using zinc oxide-eugenol type cements as bases under amalgam and inlay restorations. These bases are nonirritating to the pulp and thus eliminate the need to protect the pulp with subbase materials when the zinc phosphate cements are used. The procedure is simplified, time is saved and the danger of pulp irritation is further controlled. The now available reinforced ZOE cements and especially the EBA cements, because of their increased early strength, are capable of withstanding the forces developed during condensation of amalgam and those forces which may subsequently be transmitted through the restoration.

EBA cements, employed as cement bases, usually utilize a higher powder-liquid ratio than when employed as luting agents. It is good practice to incorporate the maximum amount of powder into the liquid consistent with a usable consistency so that the powder will be in large excess in the hardened cement. EBA cements, because of their greater strength, seem to be well suited as a one-step base in deep cavities for gold, silicate cement and amalgam fillings [32]. When this cement was placed in 32 vital but symptomatic teeth, symptoms subsided within two days. The cavity preparations were then completed and permanent restorations placed, leaving part of the EBA cement as a base. The teeth remained vital and non-symptomatic.

An alumina reinforced EBA cement was placed as a base under a series of amalgam restorations that were packed with a calibrated spring plugger at a pressure of 140 kg/cm^2 . When the teeth were sectioned after 48 hr, the base was still intact (fig. 3), whereas ZOE bases fractured at the pulpal-proximal line angle [31].

ZOE-type cements have been the preferred material for use over recently injured pulps caused by deep and extensive operating procedures. This is especially true in the teeth of children in whom secondary dentin has not yet formed a protecting barrier within the pulp chamber. The materials are radiopaque [54], seal a cavity better than other restorative materials [8, 55] and thus prevent organisms or moisture from the oral cavity gaining access to the cavity floor. This may be the reason for the higher percentage of negative cultures obtained when lining with ZOE instead of calcium

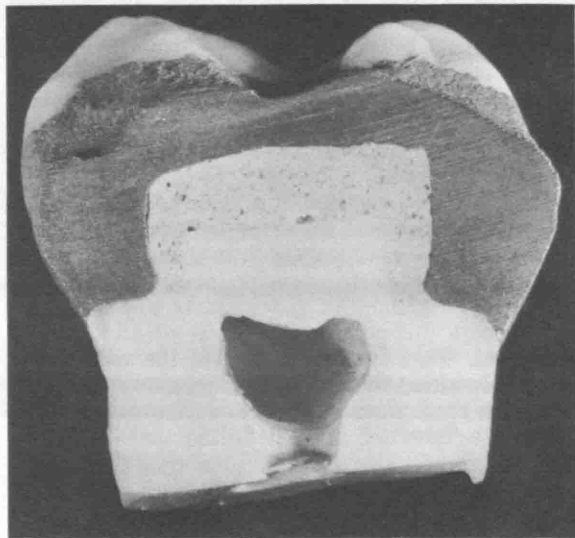


FIGURE 3. Section through an amalgam restoration condensed under 140 kg/cm^2 (13.8 MN/m^2) packing pressure against an Al_2O_3 reinforced EBA base with a ten-minute compressive strength of 470 kg/cm^2 (46.2 MN/m^2) [31].

hydroxide. Any residual organism probably remains in a latent form under sound restorations, because the environment has been altered and conditions for growth have become unfavorable. These organisms could become reactivated if saliva were to gain access to them through a leak in the restoration. Such leakage is much less likely if a ZOE or EBA lining is used. Thus, EBA cement, because of its excellent sealing characteristics [42], will assist in decreasing the number of organisms remaining in the dentin and, furthermore, will promote remineralization of decalcified dentine at the base of the cavity [43]. These properties should make EBA cements the material of choice, especially in indirect pulp capping procedures since calcium hydroxide does not possess the excellent sealing characteristics, whereas ZOE or modified ZOE cement does not stimulate the formation of reparative dentin to any appreciable extent.

Human pulps which had been exposed in the course of normal operative procedures in five non-symptomatic teeth were capped using an EBA containing cement and the cavities were filled [32]. Within a week part of the material was removed and permanent restorations placed, leaving part of the previous cement filling as a base. None of the patients reported any symptomatology. None of the teeth showed any radiographic changes and all responded normally to vitality tests within the two to ten months observation period.

Studies of the possible use of EBA cements in root canal therapy and for gingival dressing are not available. Requirements for an improved root canal sealer would include (1) a suitable consistency at the time of insertion into the canal, (2) good dimensional stability to avoid fissures resulting from shrinkage, (3) good adhesion, and (4) high degree of insolubility to body fluids [56]. ZOE yields a fairly satisfactory hermetic seal, but is only slightly adherent to the cavity walls. Furthermore, according to Erausquin and Muruzabal, ZOE can be irritating to the periapical tissues [57], although the response is reduced by addition of acrylic polymer spherules [58].

In many patients it is desirable to treat dental restorative problems for extended periods of time with a long-term temporary or intermediate restorative material. Such occasion arises in teeth in highly carious mouths, particularly those of children where immediate excavation of all caries is indicated. This treatment arrests the caries and favorably alters the oral flora. Temporary restorations are then placed and the permanent restorations are inserted as scheduling permits. The Armed Forces also have unique dental requirements such as emergencies at remote sites or in combat zones that preclude the insertion of permanent restorations. Criteria for an acceptable "intermediate" restorative include [22]: (1) a satisfactory seal between the cavity preparation and the material, (2) biologic compatibility with the pulp, (3) easy removal from the cavity prepara-

tion, (4) resistance to abrasion and attrition for an extended time, (5) ease of manipulation and placement, and (6) a longer service life than conventional ZOE temporary fillings.

Polymer reinforced ZOE cements because of their greatly improved physical properties [21], show a high degree of clinical acceptability after a 12-month observation period [22]. On the other hand, fused quartz [32] or titanium dioxide [22] reinforced EBA cements, despite their improved strength, proved unsuitable as temporary restoratives. Contrary to their low solubility and disintegration in water and dilute acids, the fused quartz reinforced EBA restoratives disintegrated rapidly under oral conditions [59]. Thus, a low in vitro solubility value may be useful in comparing the relative solubility of products of similar composition, but is not necessarily an indication of the success of such restorations in the mouth. Comparisons have been made of the in vivo intraoral disintegration of cements using specially designed partial dentures so that cements are exposed to the oral environment [60]. Results of these tests showed considerable patient variation in the rate and amount of cement lost. Abrasion played an important role in the loss of material with the greatest loss invariably occurring in those regions most subject to abrasion by the tongue. Thus, the in vivo disintegration appears to be an effect of the interaction of solubility and abrasion.

The resin-modified alumina-reinforced EBA cement, because of its demonstrated mechanical and palliative properties, especially its much higher tensile strength, appears to be very desirable for use as a long-duration temporary restorative.

In a limited clinical study [30], approximately 50 restorations, including complex restorations subject to heavy occlusal stresses, were placed using one formulation. Its powder component contained 58.2 percent ZnO, 27.3 percent Al_2O_3 , 5.4 percent rosin and 9.1 percent methyl methacrylate copolymer.

A powder-liquid ratio of 1.2 g powder per 0.2 ml of liquid was used. The material was usually mixed on a glass slab, but could also be prepared by mixing in a capsule employing a mechanical mixer. The unreacted eugenol was removed by blotting or by squeezing the mixed mass in an amalgam squeeze cloth. The material presented good manipulative properties and could be readily adapted to cavity walls and margins. Patients were recalled and observed periodically during the nine-month observation period. The restorative did not dissolve or disintegrate in the oral fluids. All restorations remained serviceable and showed only minimal signs of wear over the nine-month observation period. All teeth restored with this cement remained asymptomatic for the entire period of observation.

The formulation selected had a relatively high tensile strength, but the in vitro solubility and dis-

integration values were considerably higher (one week solubility and disintegration 0.94 percent) than those of other promising mixes. Since all restorations remained serviceable over the nine-month observation period, the *in vivo* solubility did not appear to be of any significance. Unreacted liquid in the clinical mixes was removed by blotting. It is conceivable that lower *in vitro* solubility and disintegration values would have been obtained if this procedure had been followed in the preparation of laboratory test specimens.

6. Direction of Future Work

The EBA cements, largely as a result of the extensive studies conducted during the last few years, have passed from their infancy to a state of incipient maturity. Further enhancement in physical and mechanical properties of EBA and other chelate-type cements for use as semipermanent "intermediate" restoratives would be desirable to make use of their excellent biological properties. However, progress in improving these materials may not be as rapid as one has become accustomed to during the last few years.

Basic investigations that would lead the way to the development of improved products should include pinpointing the exact mechanism of the setting of EBA cements. Determination of the chelate stability constants of potentially useful chelates as well as measurement of their hydrolytic stability would be most useful. Synthesis of prospective chelating agents and evaluating of the resulting cements would be desirable.

The existing fundamental knowledge makes it possible to conduct development of better EBA materials along many lines. Modest improvements may be obtainable by judicious selection of reinforcing agents such as treated or spherical glass powders or the partial replacement of zinc oxide by another reactive metal oxide, such as mercuric oxide. Upgrading of formulations by whisker reinforcement does not look promising. Incorporation of slightly soluble fluorides that leach from the EBA cements at a controlled rate should be studied with the aim of reducing the solubility of the components of tooth structure and thereby bestowing anticariogenic properties to these cements. Further studies of novel chelating agents to partially or wholly replace EBA in cementitious compositions, especially those that yield a strong bond at the tooth-restorative interface, are a potentially fertile field for developing a greatly superior product. Even if such a breakthrough is realized, clinical application of such compositions would be entirely dependent on the results of histological, pathological and clinical studies in order to prove beyond a doubt that such a product has the desirable biological properties that have made ZOE and EBA cements so desirable as dental restorative materials.

Besides the enhancement of properties of EBA cements resulting from successful research efforts, it is anticipated that a major advance in the near future will be the availability of many new commercial products of this type, tailor-made to the wide spectrum of specific applications needed by the practicing dentist.

The product of the future will combine convenience with versatility. It will possess excellent manipulative properties, will mix with ease to a predetermined, carefully controlled powder-liquid ratio, will have a setting time that will be relatively unaffected by environmental parameters such as temperature and humidity, will have a low film thickness when required, and if desired, can be color coded to indicate the stage of treatment of the tooth.

The findings obtained on pulp capping and on using EBA cements as sedative restorations and bases point, however, to avenues for further clinical research. Such studies should establish more clearly any potential advantages of EBA cements as bases under silicate cement or metallic fillings, as pulp capping or cementing media and as intermediate restoratives.

7. Summary

During the last few years considerable interest has been generated in improving zinc oxide-eugenol cements. A better understanding of the setting mechanism of these cements has become available which has led to the development of products with enhanced physical and mechanical properties usually containing *o*-ethoxybenzoic acid (EBA). These materials show the mild reactions to the tissues including the dental pulp similar to ZOE cements, but also stimulate the formation of reparative dentin. Physical properties of the EBA-containing cements approach those of the biological and physiological less desirable zinc phosphate cements. The EBA cements have been well accepted as luting agents for fixed restorations and as insulating bases. They appear to be the material of choice for indirect pulp capping. Resin modified EBA restoratives show good stress-bearing characteristics and should find applications as an "intermediate" restorative.

8. References

- [1] Molnar, E. J., Cloves, oil of cloves and eugenol. The medico-dental history. *Dent. Items of Interest* 64, 521, 663, 745, 876, 971 (June-Oct. 1912).
- [2] Brauer, G. M., A review of zinc-oxide eugenol type filling materials. *Rev. Belg. Med. Dent.* 20, No. 3, 323 (1965).
- [3] Brauer, G. M., New developments in zinc oxide-eugenol cement. *Ann. Dent.* 26, No. 2, 44 (1967).
- [4] Mitchell, D. F., The irrational qualities of dental materials. *J. Am. Dental Assoc.* 59, 954 (1959).
- [5] Manley, E. B., A review of pulp reactions to chemical irritations. *Intern. Dental. J.* 1, 36 (1950).
- [6] Stanley, H. R., Swerdlow, H., and Buonocore, M. G. *J. Am. Dental Assoc.* 75, No. 1, 132 (July 1967).

- [7] Massler, M., Effects of filling materials on the pulp. *N.Y. J. Dent.* **26**, 183 (1956).
- [8] Massler, M. and Ostrovsky, A., Sealing qualities of various filling materials. *J. Dent. Children* **21**, 228 (1954).
- [9] Turkheim, H. J., In vitro experiments on the bactericidal effects of zinc-oxide eugenol cement on bacteria containing dentin. *J. Dental Res.* **34**, 295 (1955).
- [10] Copeland Jr., H. I., Brauer, G. M., Sweeney, W. T., and Forziati, A. F., Setting reaction of zinc oxide and eugenol. *J. Research NBS* **55**, 133 (1955) RP 2611.
- [11] Viellefosse, R., Vayson de Pradenne, H., and Zumburn, J. P., A study of combinations of types of oxides of zinc-eugenol cements and phenol plastics. *Rev. Franc. Odontostomat* **5**, 488 (1958).
- [12] Gerner, M. M., Zadorozhnyi, B. A., Ryabina, L. V., Batovskii, V. N., and Sharchilev, V. I., Infrared spectra of eugenol and zinc eugenolate. *Russ. J. Phys. Chem.* **40**, No. 1, 122 (1966).
- [13] Douglas, W. H., Studies of crystal structure of zinc and magnesium eugenolates. (Abstract) *J. Dental Res.* **42**, 1,108 (1963).
- [14] Natarajan, S., Gopalakrishna, and Kartz, L., Program and Abstracts of Papers, 50th General Session, International Association for Dental Research, No. 386 (1972).
- [15] Norling, B. K., and Greener, E. H., X-ray diffraction studies of the ZnO-eugenol reaction. International Association for Dental Research, 46th General Meeting. Abstracts of papers. No. 430, San Francisco (March 1968).
- [16] Brauer, G. M., and Wiedeman, W. H., Unpublished results.
- [17] Grant, A. A., Greener, E. H., and Meshil, M., High resolution microscopy of dental cements. *Australian Dental J.* **13**, No. 4, 295 (Aug. 1968).
- [18] Molnar, E. J., Residual eugenol from zinc oxide-eugenol compounds. *J. Dental. Res.* **46**, 645 (1967).
- [19] Viellefosse, R., Hanegraaf, Ch., and Chastagner, N., *Rev. Franc. Odontostomat.* **15**, 467 (1968).
- [20] Curtis, D., U.S. Patent 2,413,294 (Dec. 1946).
- [21] Jendresen, M. D., Phillips, R. W., Swartz, M. L., and Norman, R. D., A comparative study of four zinc oxide and eugenol formulations as restorative materials. Part I. *J. Prosthetic Dentistry* **21**, No. 2, 176 (1969).
- [22] Jendresen, M. D., and Phillips, R. W., A comparative study of four zinc oxide and eugenol formulations as restorative materials. Part II. *J. Prosthetic Dentistry* **21**, No. 3, 300 (1969).
- [23] Brauer, G. M., Morris, R. W. and Howe, W. B. Synthesis of isomers of eugenol. *J. Res. Nat. Bur. Stand. (U.S.)*, **67A** (3) 253-259 (1963).
- [24] Brauer, G. M., Argentar, H., and Durany, G., Ionization constants and reactivity of isomers of eugenol. *J. Res. Nat. Bur. Stand. (U.S.)*, **68A**(6) 619-625 (1964).
- [25] Brauer, G. M., White, E. E. Jr., and Mashonas, M. G., The reaction of metal oxides with o-ethoxybenzoic acid and other chelating agents. *J. Dental Res.* **37**, 547 (1958).
- [26] Brauer, G. M., Simon, L., and Sangermano, L., Improved zinc oxide-eugenol type cements. *J. Dental Res.* **41**, 1096 (1962).
- [27] Brauer, G. M., and Simon, L., Synthesis of 2-propoxy-5-methylbenzoic acid. *J. Res. Nat. Bur. Stand. (U.S.)* **66A**, (4) 313-317 (1962).
- [28] Civjan, S., and Brauer, G. M., Physical properties of cements based on zinc-oxide, hydrogenated rosin, o-ethoxybenzoic acid and eugenol. *J. Dental Res.* **43**, 281 (1964).
- [29] Norman, R. D., Phillips, R. W., Swartz, M. L., and Frankiewicz, T., The effect of particle size on the physical properties of zinc oxide-eugenol mixtures. *J. Dental Res.* **43**, 252 (1964).
- [30] Brauer, G. M., Huget, E. F., and Termini, D. J., Plastic modified EBA cements as temporary restorative materials, *J. Dental Res.* **49**, 1487 (1970).
- [31] Brauer, G. M., McLaughlin, R., and Huget, E. F., Aluminum oxide as a reinforcing agent for zinc oxide-eugenol-o-ethoxybenzoic acid cements. *J. Dental Res.* **47**, 622 (1968).
- [32] Civjan, S., and Brauer, G. M., Clinical behavior of o-ethoxybenzoic acid-eugenol-zinc oxide cements. *J. Dental Res.* **44**, 80 (1965).
- [33] Phillips, R. W., Swartz, M. L., Norman, R. D., Schell, R. S., and Niblack, B. F., Zinc oxide and eugenol cements for permanent cementation. *J. Prosthetic Dentistry* **19**, No. 2, 144 (1968).
- [34] Custer, F., and Anderson, R. A., A comparison of o-ethoxybenzoic acid cements. *Fortn. Rev. Chicago Dent. Soc.* **56**, No. 3, 9 (1968).
- [35] ISO/TC 106 WG 1. (Filling materials). Draft specification for dental zinc oxide-eugenol cements.
- [36] Bellamy, L. J., *The Infrared Spectra of Complex Molecules*. 2nd ed. (Wiley and Son, New York, 1958).
- [37] Sievers, R. E., and Baylor, John C. Jr., Some metal chelates of ethylenediamine tetraacetic acid, diethylenetriaminepentaacetic acid, and triethylenetetraminehexaacetic acid. *Inorg. Chem.* **1**, 174 (1962).
- [38] Job, P., Formation and stability of inorganic complexes in solutions. *Ann. Chim.* [10] **9**, 113 (1928); Concerning hydrochloric acid and hydrobromic acid solutions of salts of cobalt, copper and bivalent nickel, *ibid* [11] **6**, 97 (1936).
- [39] Martell, A. E., and Calvin, M., *Chemistry of Metal Chelate Compounds*, p. 39 (Prentice-Hall, Inc. New York, 1952).
- [40] McKenzie, H. A., Mellor, D. P., Mills, J. E., and Short, L. N., Light absorption and magnetic properties of nickel complexes. *J. Proc. Roy. Soc. N. S. Wales* **78**, 70 (1944).
- [41] Phillips, R. W., and Love, D. R., The effect of certain additive agents on the physical properties of zinc oxide-eugenol mixtures. *J. Dental Res.* **40**, 294 (1961).
- [42] Coleman, J. M., and Kirk, E. E. J., An assessment of a modified zinc oxide-eugenol cement. *Brit. Dental J.* **118**, 482 (1965).
- [43] Bhaskar, S. N., Cutright, D. E., Beasley, J. D., and Boyers, R. C., Pulpal response to four restorative materials. *Oral Surg. Oral Med. and Oral Path.* **28**, No. 1, 126 (1969).
- [44] Jørgensen, K. D., and Holst, K., The relationship between the retention of cemented veneer crowns and the crushing strengths of cements. *Acta Odont. Scand.* **25**, No. 4, 355 (1967).
- [45] Oldham, D. F., Swartz, M. L., and Phillips, R. W., Retentive properties of dental cements. *J. Prosthetic Dentistry* **14**, 760 (1964).
- [46] Horn, H. R., The cementation of crowns and fixed partial dentures. *The Dental Clinics of North America*, pp. 65-81, (W. B. Saunders Co., Philadelphia, Pa., 1965).
- [47] Williams, J. D., Swartz, M. L., and Phillips, R. W., Retention of orthodontic bands as influenced by cementing media. *Angle Orthodontia* **35**, No. 4, 278 (1965).
- [48] Mosteller, J. H. An evaluation of intermediate base materials. *J. Am. Dental Assoc.* **43**, 571 (1951).
- [49] Messing, J. J., Linings and their manipulation. *Dent. Pract.* **8**, 336 (1958).

- [50] Hoppenstand, D. C., and McConnell, D., Mechanical failure of amalgam restorations with zinc phosphate and zinc oxide-eugenol cement bases. *J. Dental Res.* **39**, 899 (1960).
- [51] Lyell, J. S., Base forming materials for restorations of silver amalgam. *Australian Dental J.* **5**, 132 (1960).
- [52] Phillips, R. W. Cavity varnishes and base materials. *The Dental Clinics of North America*, p. 159, (1958).
- [53] Chong, W. F., Swartz, M. L. and Phillips, R. W., Displacement of cement bases by amalgam condensation. *J. Am. Dental Assoc.* **74**, No. 1, 97 (1967).
- [54] Sahs, E., Radiopacity of pulp capping materials. *Northwest Dent.* **46**, No. 2, 113 (1967).
- [55] Nichols, E., *Endodontics* (John Wright and Sons Ltd. Bristol, England, 1967).
- [56] Erausquin, J., and Muruzabal, M., Root canal fillings with zinc oxide-eugenol cement in the rat molar. *Oral Surg.* **24**, No. 4, 547 (1967).
- [57] Erausquin, J., and Muruzabal, M., Tissue reaction to root canal cements in the rat molar. *Oral Surg.* **26**, No. 2, 360 (1968).
- [58] Erausquin, J., and Muruzabal, M., Periapical tissue response to root canal cements with the addition of acrylic polymer spherules. *Oral Surg.* **26**, No. 4, 523 (1968).
- [59] Brauer, G. M., The relationship between laboratory tests on solubility of zinc oxide-eugenol type cement and their behavior in the mouth. *N.Y. J. Dent.* **37**, No. 4, 146 (1967).
- [60] Norman, R. D., Swartz, M. L., Phillips, R. W., and Virmani, R., A comparison of the intraoral disintegration of three dental cements. *J. Am. Dental Assoc.* **78**, No. 4, 777 (1969).

Organic Adhesives

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The materials and means for improving joint strengths in a wet environment between dentin or enamel and restoration or cavity liner are reviewed. Critical surface tension, γ_c , a descriptive property of surfaces, offers a basis to evaluate capacity of adhesives to wet tooth surfaces. Used as a pretreatment, an adhesive may function by displacing water. Attachment to tooth surface through hydrogen bonding may also occur. Adhesion may be improved by use of liners, coupling agents, fillers and tooth surface treatments such as etching processes. Dental adhesive materials include acrylics, cyanoacrylates, epoxy resins and polyurethanes, the latter having apparently good promise as a dental adhesive of the future.

Key words: Critical surface tension; dental adhesion improvement through liners, coupling agents, fillers, and surface treatment; dental adhesives to include acrylates, cyanoacrylates, epoxy resins and polyurethanes; dental materials; polyurethane.

1. Introduction

Perhaps this review should have been entitled "Organic Structural Adhesives," or yet more confining, "Synthetic Organic Structural Dental Adhesives." A more confining title would not only better indicate the scope of the discussion to follow, but also would help deliver the important message that dental adhesives are something special; the requirements for their application and performance probably impose greater constraints than for any other adhesive application. Certainly, in no other technology would the designer of an adhesive joint want to be restricted to a medically acceptable, low temperature and fast setting, high strength adhesive, which at the time of application and over the long term, must be resistant to water. Indeed, some adhesive experts, for example in the coatings or aerospace fields, may well doubt that such requirements could ever be met.

But certainly many of the requirements have been met. Organic polymeric restoratives are now used in clinical practice, and many truly adhesive dental polymeric materials are currently under investigation. This review is intended to cover some of the more promising approaches of research in new adhesive systems, and to discuss means for enhancing joint strength with these materials. Regretfully, the scope of this review must be limited and cannot include all of the pertinent published work, the recent information on biological adhesives (such as from the barnacle), nor delve into differences among dental adhesives, adhesive restoratives, and cavity liners. This review is restricted to materials and means for improving the joint strength of bonds between dentin or enamel and another member (which may be the adhesive

itself), in a wet environment, no matter if the material is to be applied as a restoration, adhesive, or cavity liner.

2. Some Surface Chemical Considerations

The function of an organic dental adhesive is obviously to bond to the tooth substance, whether the tooth surface be mineral, protein, or otherwise in nature. So before discussing adhesives, per se, it is worth considering some aspects of the chemistry of the tooth adherend surface.

Like other surfaces, tooth—either dentin or enamel—may be described in terms of its critical surface tension, i.e., the maximum surface tension of a liquid which will wet or form a zero contact angle. The now familiar critical surface tension, or γ_c , concept has been developed by Zisman and co-workers [1]¹ and has been related to adhesion and abhesion [2]. The γ_c value of an adherend solid then teaches what the surface tension of an adhesive must be to wet and spread. Also, the γ_c values are useful for ranking solids as high or low energy surfaces. For example, table 1 following, from Zisman [1], ranks some polymer surfaces, a low value of γ_c indicating a low energy surface.

It is generally believed that metals, minerals, and certain other inorganic solids have high energy surfaces, i.e., most liquids will spread on them. Apparently, this is not true for tooth surfaces; Uy and Chang [3] measured γ_c of dentin and enamel surfaces at 50 and 100 percent relative humidity (RH). Their results are given in table 2.

On comparing table 2 with table 1, the γ_c of tooth surfaces at 23 °C and 50 percent RH is

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. Critical surface tensions of various polymeric solids [1]

Polymeric solid	Dynes/cm. at 20 °C.
Polymethacrylic ester of ϕ' -octanol.....	10.6
Polyhexafluoropropylene.....	16.2
Polytetrafluoroethylene.....	18.5
Polytrifluoroethylene.....	22
Poly(vinylidene fluoride).....	25
Poly(vinyl fluoride).....	28
Polyethylene.....	31
Polytrifluorochloroethylene.....	31
Polystyrene.....	33
Poly(vinyl alcohol).....	37
Poly(methyl methacrylate).....	39
Poly(vinyl chloride).....	39
Poly(vinylidene chloride).....	40
Poly(ethylene terephthalate).....	43
Poly(hexamethylene adipamide).....	46

TABLE 2. Critical surface tensions, dynes/cm [3]

Surface	37 °C. (100 percent R.H.)	23 °C. (50 percent R.H.)
Human dentin.....	39.5	39-49
Human enamel.....	31.5	38.5-40
Bovine dentin.....	28-31	38-40.5
Bovine enamel.....	24-49	38-42.5

about the value of polyvinyl chloride. Looking at the lower numbers for γ_c at 37 °C and 100 percent RH, the tooth surface appears to be like that of polyethylene or lower surface energy polymer. At the time of publication, such conclusions were difficult to understand. Although Uy and Chang may be criticized for using many H-bonding liquids in making the measurements, the final γ_c values are nonetheless an experimental result which today, because of more recent publications by others can be interpreted.

Other workers have examined supposedly high energy surfaces at high humidities. Shafrin and Zisman [4] found that the effect of water on the spreading of organic liquids on glass was to cause an apparent change in the critical surface tension from about 46 dynes/cm at 1 percent RH to 30 dynes/cm at 95 percent for the same glass surface. Essentially similar results were found by Burnett and Zisman [5] for borosilicate glass, quartz, and sapphire surfaces (again, all supposedly high energy surfaces) and by Alter and Cook [6] for keratin fiber surfaces. In the latter study it was found that the γ_c of native and oxidized hair fibers ranged from 34 to 25 dynes/cm from 1 percent to 95 percent RH, respectively. The higher γ_c is about what may be expected for a protein surface [6]. The lower values, 25 to 30 dynes/cm, are interpreted as measures of the critical surface tension for wetting a condensed water layer, whether the water layer is on glass, sapphire, keratin, or now,

tooth surfaces. Thus, a nonmiscible, nonhydrogen bonding adhesive (or adhesive solution) applied to tooth substance must wet and spread on a low energy surface of condensed water, as measured by Uy and Chang [3], and as might be expected to occur in the high humidity oral environment.

Alternatively, the adhesive may displace the water from the surface. Such displacement is accomplished largely by surface-chemical action, rather than merely dissolving away the water layer. The mechanism of water displacement by an organic liquid has recently been analyzed by Zisman and co-workers [7]. It may be summarized as follows.

The "initial spreading coefficient," S_{ba} , of liquid b displacing liquid a , is related to the surface and interfacial tensions γ by:

$$S_{ba} = \gamma_a - (\gamma_b + \gamma_{ab})$$

Generally, when liquid a is water, for any homologous series of b liquids, S_{ba} increases as the solubility in water increases and as the boiling point decreases. A high value of S_{ba} is desirable. This is summarized in figure 1, taken from reference 7. Note the high values, corresponding to effective water displacement for some familiar liquids such as ethyl ether and ethyl acetate.

The displacement of water from a surface is also facilitated by having the liquid partially miscible with water. For example, in figure 2 (also taken from reference 7), high values of initial spreading coefficient are associated with the solubility in water for a series of alcohols. The area of effective water displacement is clearly marked and corresponds to compounds such as 1-butanol, 2-methyl-1-propanol, 1-pentanol, and 2-methyl-2-butanol.

Thus, in order to wet the tooth surface, the surface tension of the adhesive must be lower than γ_c , which may be as low as 24 dynes/cm, the γ_c of a condensed water layer. This is true only if the

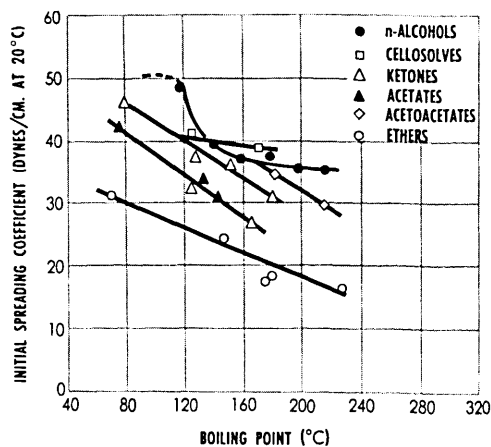


FIGURE 1. Initial spreading coefficient versus boiling point for various aliphatic water-displacing compounds [7].

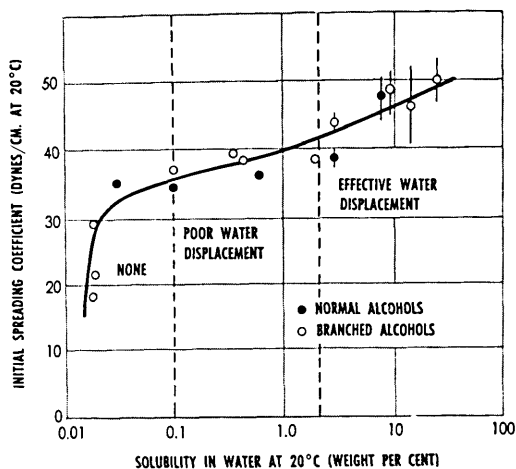


FIGURE 2. Relation of water solubility to initial spreading coefficient and water displacing ability of simple monohydric alcohols.

The vertical lines through points in the region of strong displacement are proportional in length to the areas of a 2-mm water film displaced by the respective alcohols [7].

adhesive is not hydrogen bonding. Alternatively, the adhesive (as a pretreatment for the surface) may displace the water layer. A third alternative is that the adhesive is hydrogen bonding, such as an epoxy or polyurethane. These types of adhesives are discussed in later sections.

3. Dental Adhesive Materials

3.1. Acrylics

Acrylic polymers, such as poly(methyl methacrylate), have long been used as restoratives [8] and much careful study has been devoted to these materials, particularly at the National Bureau of Standards and by the group this symposium honors [9, 10]. The attributes and deficiencies of this class of materials are well known and it is generally recognized that for all their merit in clinical practice, they do not adhere to tooth substance. Some improvement in their adhesion can be obtained, at least qualitatively, by appropriate copolymerization [11].

The acrylics are usually applied as a mixture of polymer, monomer, and polymerization catalyst. One reason for the widespread use of acrylics is that such mixtures can polymerize in place quickly, particularly when an accelerator is included [12]. The polymerization of such mixtures to polymer is usually accomplished by considerable shrinkage, 6 percent or more by volume [13], an intolerable level for adhesive bonding under any circumstances. Means of avoiding the shrinkage are the common practices of incorporating particulate filler, dissolving polymer in the monomer before polymerization, and using the "brush" technique.

Although the conventional acrylate dental materials do not adhere well to tooth substance, they illustrate a general means of applying adhesive, viz., permitting the adhesive to polymerize in place to give monomer and polymer an opportunity to absorb, and thus produce higher bond strengths. The importance of polymerizing the adhesive in place has been demonstrated at least for amine cured epoxy adhesives [14]; the importance of adsorption as an early and necessary step in the adhesion process is generally accepted.

An improved dental restorative material based on an acrylic copolymer has been one of the major contributions from the dental research at the National Bureau of Standards. Bowen [15-18] has described a composite restorative system based on acrylic copolymers and their further improvement by attention to tooth surface preparation, mode of filling, and adhesion of the restorative to the filler particles. The resultant materials appear to be improved restoratives, rather than new adhesives [19].

3.2. Cyanoacrylates

A relatively new class of acrylates, the alkyl α -cyanoacrylates, is being investigated as a possible restorative [20]. This class of adhesives is of interest because the monomers polymerize readily with the aid of a weak base or water as an initiator. Interestingly, a general precaution in applying the cyanoacrylates as adhesives is to dry the adherend surfaces, relying on only trace water vapor as an initiator, and to avoid acidic surfaces. Long exposure to water, or water vapor, can have a deleterious effect on the bond strength [21].

The polymerization of the alkyl α -cyanoacrylates is highly exothermic, resulting in a peak polymerization temperature which may be uncomfortable *in vivo*. This peak temperature, and the ability of the monomers to displace blood (and probably water), as well as certain of the properties of the polymerized mass, such as mechanical strength, rate of hydrolysis, and histotoxicity, depend on the length of the alkyl side chain [20, 22, 23]. The chemistry of this class of adhesive has been discussed in the context of use as tissue adhesive in surgical procedures and for hemostasis [22, 23]. Use in dentistry has been described by Bhaskar and Frisch [24] and by Collito [25].

3.3. Epoxy Adhesives

The use of epoxy resins as dental restoratives was described early by Bowen [26]. Later, Lee [27] reported additional experimental work directed at an epoxy material for clinical dental use. Also, Lee and co-workers [28, 29] have synthesized new resins with the aim of achieving high bond strengths. They found that a bulk restorative resin could be made from the triglycidyl ether of tri-

hydroxybiphenyl cured with cyclohexane bis-(methylamine) and that the cured material had a good balance of properties for a restorative material. The resin sets moderately slowly and requires mixing on a hot plate prior to insertion to achieve clinically feasible set times.

Lee and co-workers [28] have synthesized and investigated many types of epoxy resins as well as several different types of curing systems. None seem feasible at this time for various reasons. Promising results were obtained by blending epoxy resins with polyurethanes; the latter are reviewed in the next section.

The most promising of the epoxy restorative resins, one based on the triglycidyl ether of trihydroxybiphenyl cured with cyclohexane bis-(methylamine), was used in limited clinical trials [29]. This resin system, filled with alumina, maintained adhesion to human dentin *in vivo* when placed in restorations prepared without undercuts for at least three months [29].

The clinical results were obtained with Epoxylite resin NIH-27. If this material must be applied in a manner similar to Epoxylite resin NIH-7, then prior to inserting the restoration the epoxy resin and its hardener must be mixed on a temperature-controlled hot plate for 60–90 s, and this mixing must be well controlled. Then, the finishing should not be attempted for at least 30 min after mixing and preferably on a subsequent visit by the patient to the dentist [29]. No adhesion test data are given trying to relate the laboratory procedures with the clinical trials [28, 29].

Epoxy resins have also been used for bonding orthodontic attachments to teeth [30]. The bond strengths of commercial epoxy adhesives under laboratory conditions were reported to be in excess of the forces judged to be exerted on the orthodontic attachment during treatment, and this finding was verified in limited clinical trials. This report [30] is brief and qualitative; it is impossible to tell from it exactly what was done.

Although epoxy resins are useful structural adhesives for many applications, and despite the large amount of research performed relative to their use in dentistry, such use seems severely limited. The reason for this is that generally, high bond strengths are obtained only after high temperature bakes and/or mixing of resin and hardener at elevated temperature. Typical curing agents are polyfunctional amines, of questionable utility in contact with tissue of any sort [31]. Even the so-called room temperature curing formulations of epoxy adhesives require several hours to develop their maximum strength, well beyond reasonable clinical practice times. In our laboratory we experimented briefly with epoxy dental adhesives which would cure hard in a few minutes at room temperature, even in the presence of water. These formulations were catalyzed by BF_3 and its complexes, compounds not to come in contact with epidermis, let alone other tissue, and the

work was dropped [32]. In short, epoxy resins, for all of their attributes in adhesives technology, do not appear to be broadly suited to dental practice.

3.4. Polyurethanes

As used for dental adhesives, the term polyurethane refers generally to the condensation polymer between a polyol (derived e.g. from a polyester or polyether), and a polyfunctional isocyanate. Polyurethane formation may be summarized as in figure 3.

The condensation reaction can be rapid at room temperature and may be catalyzed to take place in a few minutes by weak bases such as tin octoate or tertiary amines. The isocyanates are applied as adhesives similar to acrylics or epoxies in that mixture of the monomers or prepolymers and the cross-linking agent (TDI in the example in figure 3) are applied to the joint and permitted to polymerize in place.

An interesting aspect of the chemistry is that organic isocyanates will react with water to generate CO_2 . (This is the basis of some urethane foam production.) The reaction between tolylene diisocyanate (TDI) and water, is shown in figure 4. This reaction scheme provides for excess isocyanate in a urethane adhesive formulation acting as a water scavenger for water on the tooth surface. In this way, the polyurethane adhesive may bond to a dry (or temporarily dry) surface. The CO_2 generated should be able to escape from thin sections, such as a cavity liner. The water scavenging action and any effect it may have on dental adhesions are speculative at this point.

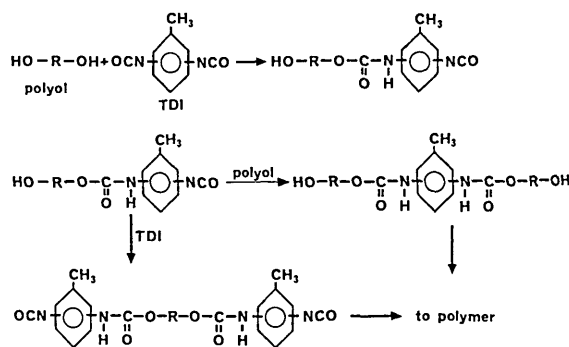


FIGURE 3. Polyurethane formation.

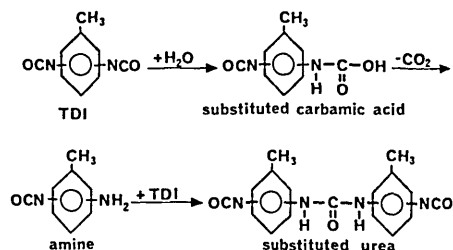


FIGURE 4. Behavior of TDI in the presence of water.

The first description of polyurethane adhesives for dental applications was by Galligan, Schwartz and Minor [33] who investigated adhesive liners based on equal parts by weight of TDI and a poly(propylene glycol) of 2,000 nominal molecular weight. This composition contained a tenfold excess of isocyanate groups; 0.01 percent tripropylamine was in some instances added as a catalyst. The composition was tested as an adhesive liner for conventional restorations in freshly extracted, sound human premolars in conical cavities. (The cavities were "dried" with a blast of air for 5 s before the liner was applied.) A summary of the data is given in tables 3 and 4. (The reader is referred to reference 33 for the experimental methods.) In every case, including when the urethane was used as a restoration, an improvement in properties was obtained with the test composition compared to the results for the conventional restorative materials. Noteworthy, the joint strengths of the acrylic restorations were increased above zero, the value for the acrylic alone. The liners were adhesive to teeth, and to the restora-

tions, and prevented water from entering the restoration margin [33].

The adhesion of the polyurethane can be improved by other choices of polyol and isocyanate. At the present time in our laboratory, we generally obtain higher bond strengths with the polyurethane from castor oil (triglyceride of ricinoleic acid) cross-linked with PAPI² (a polyphenylene isocyanate from Upjohn) than with the polyurethane reported by Galligan et al. [33]. However, the joint strength can be increased even more by choice of filler, other additives, coupling agents, and means of preparing the tooth surface, than by making small changes in the choice of reactants in the adhesive. Such means to increase adhesion are discussed in the next section.

4. Means to Improve Adhesion

Several means have been proposed to improve dental adhesives by bonding the adhesive chemically to the mineral or protein portion of teeth. For example, Buonocore [34] investigated the inclusion of glycerophosphoric acid dimethacrylate in an acrylic restorative with generally encouraging results and obtained evidence to suggest that there may be some chemical reaction between the components of the adhesive and the organic matter of dentin. Similarly, Lee et al. [28] suggested cross-linking the collagen portion of dentin with zirconium acetate to render it hydrophobic and thus improve bond strengths. Brauer et al. have suggested using chelating agents [35] between the adhesive and mineral portion of the tooth as well as the ceric ion induced grafting of synthetic polymers to the protein portion [36]. Other suggestions have been the use of rubbery liners, coupling agents (such as silanes), proper choice of fillers, and acid and enzyme debridement of the prepared tooth surface to improve adhesion or bond strength. These latter suggestions are reviewed in some detail below.

4.1. Rubbery Liners

The adhesive failure of a joint means that the joint strength was exceeded by the applied stress. In practice, this stress may be tensile, compressive, or shear, and usually is a complex mode which often involves a shear component. (See for example, reference 37.) Dental adhesive joints are usually tested in tension [38] and there have been no reports of a stress analysis of any dental adhesive test. Patrick et al. [39, 40] have suggested that tests of dental adhesive joints include a shear

TABLE 3. Adhesion of restorations to teeth [33]

Restoration	Strength		Com- pres- sion	Thermal Shock
	lb	N	Cycles	Cycles
Acrylic.....	0. 0	0	0	1
Urethane-lined* acrylic.....	8. 3	37	>400	>40
Amalgam.....	0. 3	1	0	1
Urethane-lined* amalgam.....	8. 6	38	240	>40
Silicate.....	5. 5	24	>400	15
Zinc phosphate.....	5. 1	23	220	11
Urethane*.....	3. 0	13	>400	>40

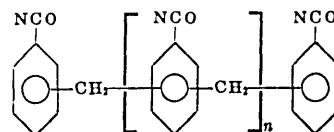
*The urethane was the product obtained by curing a 1:1 mixture of tolylene diisocyanate and polypropylene glycol¹

TABLE 4. Tensile strength of urethane-lined acrylic restorations [33]

Urethane liner		Tensile strength	
Iso- cya- nate*	Polyglycol	lb	N
TDI	Polypropylene glycol ("2010").....	8. 3	37
TDI	Ethylenediamine-based polyethylene-propylene glycol.....	9. 1	40
PAPI	Polypropylene glycol ("1010").....	4. 3	19
PAPI	Polypropylene glycol ("2010").....	13. 4	60
PAPI	Polyethylene-propylene glycol.....	6. 6	29
PAPI	Trimethylolpropane based polypropylene glycol.....	8. 9	40

*TDI, tolylene diisocyanate; PAPI, polymethylene polyphenylisocyanate.

²PAPI is:



where n is approximately 1.

component, as well, and have devised a punch test for this purpose. Also, they pointed out that a joint between high modulus dental tissue and a relatively brittle (although having a 20 times lower modulus) resin produces a mechanical situation which enhances joint failure close to the interface. Therefore, they proposed using a rubbery liner between dental tissue and restorative, to provide a zone to absorb stress. Obviously, the rubbery liner must be adherent to the restorative and to the tissue.

Patrick et al. [39, 40] used a rubbery liner of partially saponified poly(acrylonitrile-co-butyl acrylate) and tested composite joints of bovine dentin (or enamel)-rubbery liner-epoxy resin by their shear-punch test. These composite joints had an average test strength of 3415 ± 198 psi (23.6 ± 1.4 MN/m²) without the rubbery liner and 4300 ± 254 psi (29.7 ± 1.8 MN/m²) with the liner. In addition, the strength of the joint with liner was less affected by thermocycling (4 °C, 10s; 65 °C, 10s; for each cycle) than similar joints without liner [40].

4.2. Coupling Agents

The term coupling agent usually refers to a compound which can form a bond between the adhesive and adherend. Frequently, such agents are substituted silanes and are applied to the adherend surface before applying the adhesive. Such coupling agents are frequently used in glass-polymer composites; one of their principal functions is to reduce the moisture sensitivity of the composite [41]. Presumably, they will have the same function for dental restoratives. Noteworthy, coupling agents need not be silanes, although, silanes are used most often.

The extension of coupling agent technology to dental practice is a logical one, and many workers have done so (e.g., references 27, 39, 40, 42); perhaps the earliest use was by Bowen [15, 43]. There is little question that coupling agents, particularly silanes, improve the adhesion of joints with dental materials. Two examples are worth citing.

Patrick et al. [39], using the shear punch test described earlier, demonstrated the value of a silane coupling agent with the rubbery liner. Some of their data, reproduced in figure 5, illustrate the higher bond strengths and greater resistance to water immersion (in this case, synthetic saliva at 37 °C) for joints prepared with silane coupling agent, compared to those without. Each point on this figure represents the average test result of from 15 to 120 specimens.

In our laboratory, we have demonstrated that improved bond strengths are obtained (tested after 3 days immersion in water) for acrylic restorations bonded to either bovine enamel or human dentin when a selected coupling agent is incorporated in either the acrylic or the polyurethane liner used in this work [44]. Some selected results are shown in table 5.

The joint strengths were measured by the butt test of Lee et al. [38]. The polyurethane liner was based on PAPI and castor oil and filled with titania. The PMMA (poly(methyl methacrylate)) was applied as preformed rod wetted with monomer, to simulate an acrylic restorative. The rationale behind the choice of coupling agent was to chose compounds with reactive moieties which will incorporate with both the acrylic and urethane polymers on polymerization. The compounds were mixed in the polyurethane before applying and curing; their effect was to near double the joint strength of the cured system. (The formic acid

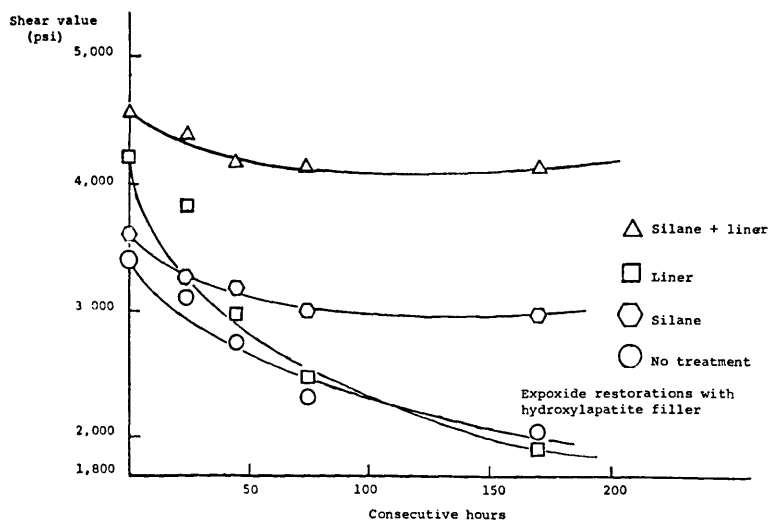


FIGURE 5. Effect of exposure time in 37 °C saliva on shear values as determined from model bovine restorations [39].

To convert shear value in psi to MN/m² multiply by 0.006895.

TABLE 5. *Effect of coupling agents on adhesion of PMMA to formic acid treated bovine enamel [44]*

Amount coupling agent, phr*	Joint strength with coupling agents							
	a		b		c		d	
	psi	MN/m ²	psi	MN/m ²	psi	MN/m ²	psi	MN/m ²
0	700	4.8	700	4.8	700	4.8	700	4.8
2	1270	8.8	1070	7.4	1160	8.0	1190	8.2
5	1125	7.8	1380	9.5	1000	6.9	1340	9.2

a. 2-hydroxyethyl methacrylate; b. 2-hydroxypropyl methacrylate; c. 2-t-butylaminoethyl methacrylate; d. 1, 3-di(allyloxy)-2-hydroxymethyl propane.

*Parts per hundred parts of resin.

treatment is explained in a later section.) Similar results have been obtained with other coupling agents, including silanes, and will be reported later [44].

4.3. Fillers

Particulate fillers are usually incorporated in an adhesive for several reasons, such as to better match the thermal expansion coefficients of adherend and adhesive and thus improve bond performance. Bowen has shown that the strength of dental restoratives can be improved by proper attention to filler particle size and distribution and, interestingly, the importance of using a silane coupling agent to improve the bond between filler and resin [15]. Related to this, Alter has shown [45] that thermoplastic polymers and rubbers are reinforced by certain particulate mineral fillers, depending very much on their particle size. Reinforced thermoplastic polymers, especially using fillers pretreated with silane coupling, are articles of commerce [46].

The effect of fillers on the adhesion of polyurethanes to dental tissue was demonstrated by Fookson and Ellison [42]. Table 6 shows some of their data for the large increase (as much as four-fold) in the force to remove the filled polyurethane restoratives from a conical cavity in human dentin after 3 days water immersion. Additional data illustrating the importance of proper choice and amount of filler in polyurethane dental materials will be reported later [44].

4.4. Surface Preparation

In 1955 Buonocore [47] reported that a phosphoric acid and phosphomolybdate-oxalic acid treatment of dental enamel increased the adhesion of acrylic filling materials. More recently, Newman and Sharpe [48] showed that one effect of such a treatment is to make the tooth surface more wettable.

In 1956, Bowen [26] reported an improvement in the adhesive strength and moisture resistance of epoxy resins to dental tissue by washing the cut surface of tooth with a solution of ammonium triacetic acid or ethylenediamine tetra-acetic acid,

which are known chelating agents for Ca ion. Since then, several other workers have reported the use of acids, sequestering agents, and enzymes for the etching or debridement of tooth surfaces prior to applying an adhesive or restorative (for example, references 28, 34, 36, 42, 44). This appears to be a highly effective general means for improving the adhesion of dental adhesives. Also, the recent widespread use of the scanning electron microscope (SEM) for examination of the treated dental surfaces has provided a clear understanding of what these debridement treatments are achieving. This is illustrated below with examples from our own work. The use of the SEM in studying dental anatomy was recently reported [49].

Figure 6 shows a series of SEM photographs tracing the appearance of bovine enamel ground wet with successively finer grit polishing paper,

TABLE 6. *Increase in adhesive joint strength of PAPI-castor oil polyurethane due to addition of fillers [42]*

Filler	Amount	Average force to break	
		lbs	N
None.....	phr*	7	31
ZnO, USP.....	50	12	53
ZnO, USP.....	100	19	84
TiO ₂ , reagent grade.....	50	18	80
TiO ₂ , reagent grade.....	100	25	111
Super Floss ^a	50	18	80
Snow Floss ^b	37	27	120
Adsorption alumina.....	50	31	138
ZrO ₂ , electronic grade.....	100	10	44
ZrO ₂ , electronic grade.....	150	9	40
Asbestos, crude.....	12½	14	62
Asbestos, crude.....	25	15	67

^a A calcined diatomaceous earth—Johns-Manville Company, Incorporated.

^b An uncalcined diatomaceous earth—Johns-Manville Company, Incorporated.

*Parts per hundred parts of resin.

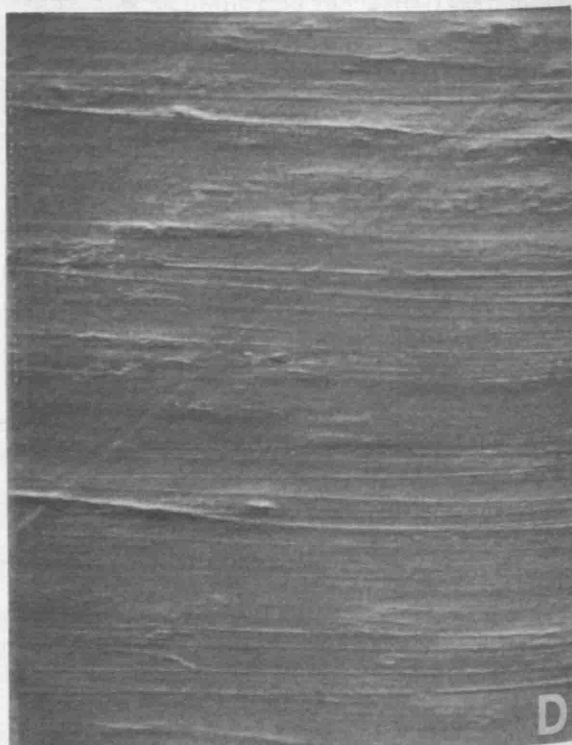
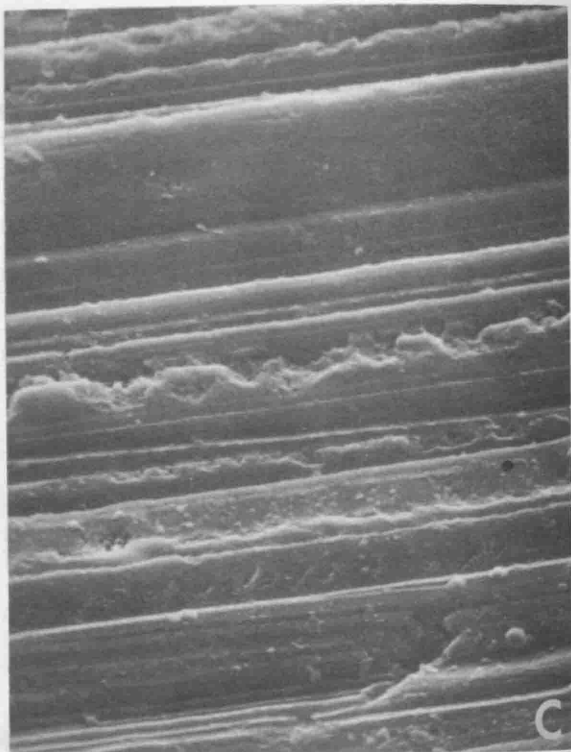
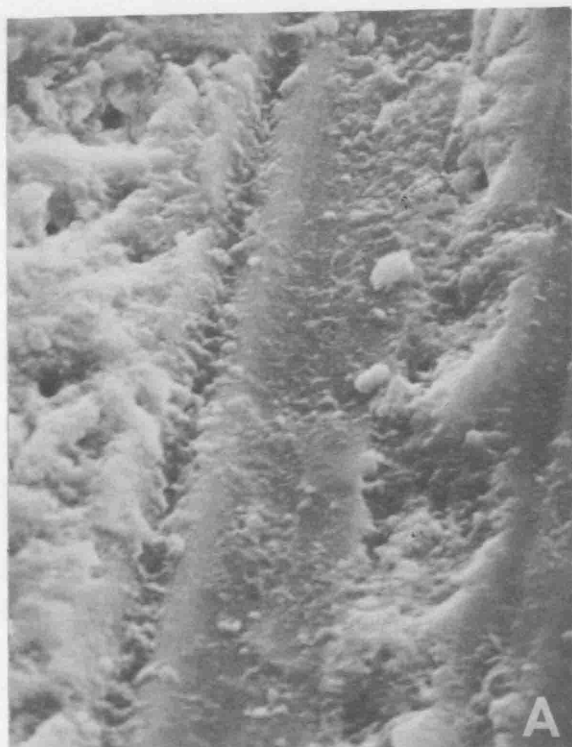


FIGURE 6. Bovine enamel polished with various abrasives (Magnification 3000 \times).
A: 220 grit paper; B: 440 grit paper; C: 600 grit paper; D: γ -alumina.

and finally with γ -alumina (Buhler), a very fine particle size polishing compound. Although this successive finer and finer polishing removes much of the debris from cutting, and although the specimen in the final photo appeared to be highly polished to the eye, the final specimen can still be considered rough and the enamel anatomy is not visible. Figure 7 shows the effect of treating the polished enamel with dilute acids for a brief time. The final polishing debris is removed and the rod structure of the enamel is clearly evident.

Figure 8 shows a similar effect on dentin where the sample polished with γ -alumina shows a rough surface and it is difficult to distinguish the familiar tubular structure of the dentin. Figure 9 shows that a brief etch with dilute acid again removed the debris and the tubular structure is clearly evident. Similar results have been obtained with human tooth tissue. It is possible to etch too far, as shown in figure 10. Here, a good deal of the surface tooth tissue was removed, exposing the delicate tubular labyrinth structure. Such a surface, as an adherend, could have a weak boundary layer (there is insufficient mineral to support the bond) and the joint shows a low strength.

Surfaces of the types shown in the SEM photographs were used to make adhesive joints with a polyurethane adhesive and were tested by the butt joint method. Some selected results are given in tables 7 and 8.

Work currently in progress in our laboratory extends these observations. There is every indication that bond strengths of polyurethane adhesives to dental tissue can be greatly increased by short

treatment with dilute acids and other agents, some undoubtedly physiologically acceptable.

5. Some Directions for the Future

Some of the state of the art reviewed here leads to possible future directions for research in organic dental adhesives. So, we may gaze into a very

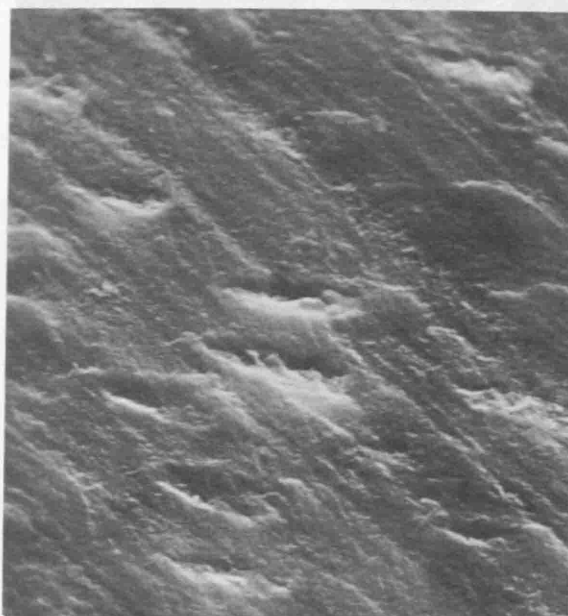


FIGURE 8. Bovine, dentin polished with γ -alumina (Magnification: 3000 \times).

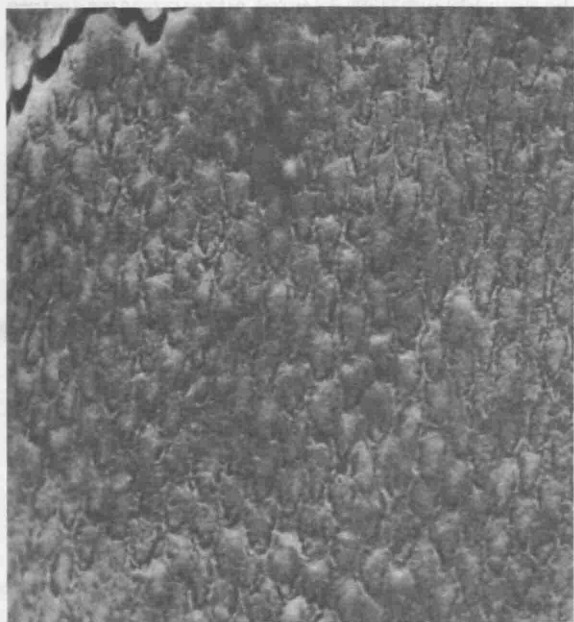


FIGURE 7. Bovine enamel etched with 50 percent aqueous formic acid for one minute (Magnification: 3000 \times).

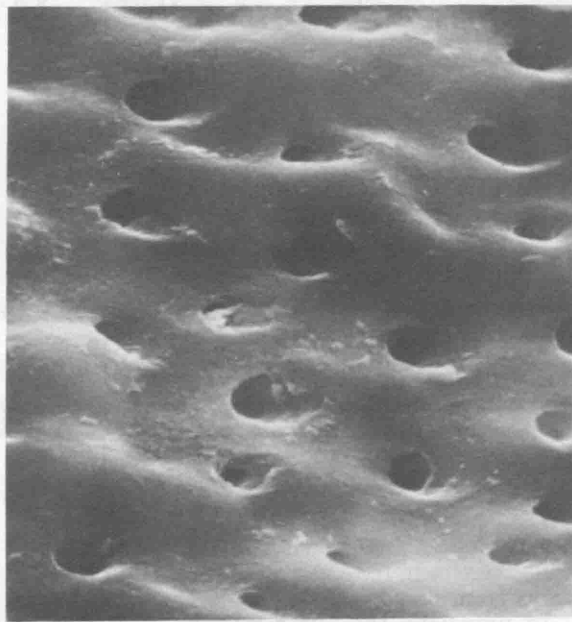


FIGURE 9. Bovine dentin treated with 50 percent aqueous formic acid for one minute (Magnification: 3000 \times).

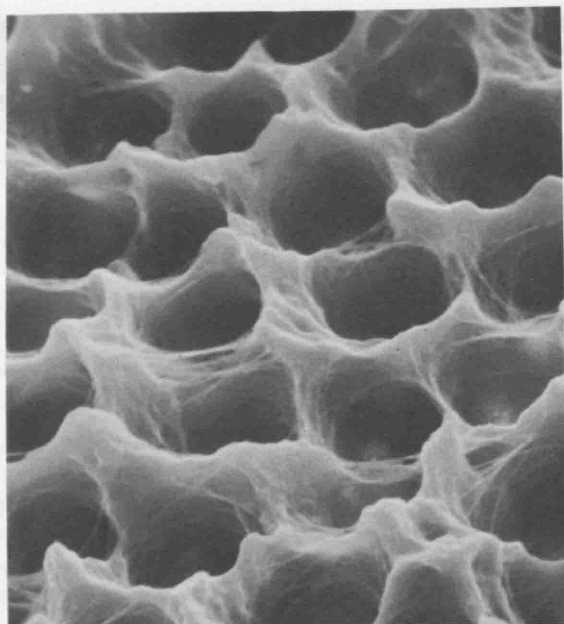


FIGURE 10. Excessively etched bovine dentin (Magnification: 3000X).

TABLE 7. Adhesion of filled PAPI-castor oil resin to untreated and formic acid etched bovine tooth tissue

Surface	Treatment	Joint strength	
		psi	MN/m ²
Dentin-----	None-----	173	1.2
	Formic acid ^a -----	228	1.6
Enamel-----	None-----	373	2.6
	Formic acid ^a -----	^b 705	4.9

^a 50 percent acid for one minute, then wash.

^b Cohesive failure.

TABLE 8. Adhesion of filled PAPI-castor oil resin to citric acid treated bovine enamel

Treatment time	Joint strength			
	25% aq. acid		50% aq. acid	
minutes	psi	MN/m ²	psi	MN/m ²
0	410	2.8	410	2.8
1/2	940	6.5	1420	9.8
1	1230	8.5	1360	9.4
5	970	6.7	1410	9.7

cloudy crystal ball and speculate what an ideal adhesive system for clinical practice might be some years from now.

In preparing the restoration, no undercutting will be necessary, the freshly cut tooth surface will be etched with a dilute acid (such as citric) and/or

maybe an enzyme or sequestrant. The etched surface will be dried, maybe by surface-chemical displacement, and then a coupling agent, most likely a silane, applied. Alternatively, the coupling agent will be incorporated in the adhesive.

Today, it appears that the most likely adhesive to be used will be a polyurethane. The reason for this is that the polyurethanes have the right balance of properties: low toxicity (judged from the literature), controlled and short cure times within clinical practice, and apparently adequate mechanical and adhesive strength. The polyurethane of the future will probably be one based on PAPI, which is the isocyanate of least toxicity [50], so far, and the polyol will be derived from a polyether, because polyester derived ones have poor long-term hydrolytic stability in other applications [51]. The polyurethanes we have been using can be cured in clinically feasible times, controlled from 5 to 20 min.

The polyurethane will be filled and the filler may well be pretreated with a silane coupling agent. In addition, the particle size and size distribution of the filler will be carefully controlled.

The filled polyurethane may well be the restorative itself, although, this seems unnecessary. There now exist many good restorative materials; it is just that they are not adhesive. We have found that polyurethanes are adhesive not only to dental tissue, but also to acrylics (especially with the right coupling agent) and, in preliminary work, to dental amalgam.

Much research has yet to be done before this type of dental restoration can be clinically tested. Indeed, much of the above speculation is based on the assumption that *in vitro* adhesive joint testing is translatable to the *in vivo* situation. This assumption will be tested soon in our laboratory in animals. Hopefully, other laboratories will do similar work in the near future.

The work reviewed here, the new results reported from our own research, and indeed the speculation as to the future, are all in large part possible because of the pioneering and active dental research program carried out these past 50 years at the National Bureau of Standards. Our thanks to this group, for making it possible, and best wishes for continued contributions to dental research.

6. References

- [1] Zisman, W. A., *Advan. Chem. Ser.*, **43**, 1 (1964).
- [2] Zisman, W. A., *NRL Report* 5699, November 29, (1961).
- [3] Uy, K. C., and Chang, R., *Adhesive Restorative Materials—II*, *Proc. 2nd Workshop, Bio-materials Res. Advisory Committee, Nat. Inst. Dental Res.*, (1965).
- [4] Shafrin, E. G., and Zisman, W. A., *J. Am. Ceramic Soc.*, **50**, 478 (1967).

- [5] Bennett, M. K. and Zisman, W. A., *J. Colloid and Interf. Sci.*, **29**, 413 (1969).
- [6] Alter H., and Cook, H., *J. Colloid and Interf. Sci.*, **29**, 439 (1969).
- [7] Baker, H. R., Leach, P. B., Singleterry, C. R., and Zisman, W. A., *Ind. and Eng. Chem.*, **59** (No. 6), 29 (1967).
- [8] Skinner, E. W. and Phillips, R. W., *The Science of Dental Materials*, Chps. 11 and 14 (W. B. Saunders Co., Philadelphia, 6th ed., 1967).
- [9] Paffenbarger, G. C., Nelson, R. J., and Sweeney, W. T., *J. Am. Dental Assoc.* **47**, 516 (1953).
- [10] Coy, H. D., *J. Am. Dental Assoc.* **47**, 532 (1953).
- [11] Schwartz, A. M., and Galligan, J. D., *Adhesive Restorative Materials—II*, Proc. 2nd Workshop of the Bio-materials Research Advisory Committee, Nat. Inst. Dental Res., (1965).
- [12] Brauer, G. M., Davenport, R. M., and Hansen, W. C., *Modern Plastics*, **34** (No. 3), 153 (1956); Brauer, G. M. and Burns, F. R., *J. Poly. Sci.*, **19**, 311 (1956).
- [13] Brauer, G. M., *J. Am. Dental Assoc.* **72**, 1151 (1966). See also reference 8, p. 225.
- [14] Alter, H. and Soller, W., *Ind. Eng. Chem.*, **50**, 922 (1958).
- [15] Bowen, R. L., *J. Am. Dental Assoc.* **69**, 481 (1964).
- [16] Bowen, R. L., *J. Am. Dental Assoc.* **74**, 439 (1967).
- [17] Bowen, R. L., *J. Dental Res.*, **44**, 895, 903, 906 (1965).
- [18] Bowen, R. L., U.S. Patents 3,194,783 and 3,194,784 (1965).
- [19] Lee, H. L. and Swartz, M. L., *J. Dental Res.*, **49**, 149 (1970).
- [20] Civjan, S., Margetis, P. M., and Reddick, R. L., *J. Dental Res.*, **48**, 536 (1969).
- [21] Coover, H. W., Jr., Ch. 31 in *Handbook of Adhesives*, I. Skeist, ed., (Reinhold Pub. Co., New York, 1962).
- [22] Lehman, R. A., Hayes, G. J. and Leonard, F., *Arch. Surg.*, **93**, 441 (1966).
- [23] Woodward, S. C., Herrmann, J. B., Cameron, J. L., Brandes G., Pulaski, E. J., and Leonard, F., *Ann. Surg.* **162**, 113 (1965).
- [24] Bhaskar, S. N. and Frisch, J., *J. Am. Dental Assoc.* **77**, 831 (1968).
- [25] Collito, M. B., U.S. Patent 3,250,002 (1966).
- [26] Bowen, R. L., *J. Dental Res.*, **35**, 360 (1956).
- [27] Lee, H. L., *Adhesive Restorative Materials—II*, Proceedings 2nd Workshop, Bio-materials Res. Advisory Committee, Nat. Inst. Dental Res. (1965).
- [28] Lee, H. L., Cupples, A. L. and Swartz, M. L., *Annual Comprehensive Report No. 68-140 to Nat. Inst. Dental Res.*, June (1968).
- [29] Lee, H. L., Cupples, A. L., and Swartz, M. L., *Comprehensive Report No. 67-112 to Nat. Inst. Dental Res.*, June (1967).
- [30] Retief, O. H., and Dreyer, D. J., *J. Dent. Assoc. South Africa*, **22**, 338 (1967).
- [31] Skeist, I., Ch. 25 in *Handbook of Adhesives*, I. Skeist, ed., (Reinhold Pub. Co., New York, 1962).
- [32] Alter, H., Unpublished.
- [33] Galligan, J. D., Schwartz, A. M., and Minor, F. W., *J. Dental Res.*, **47**, 629 (1968).
- [34] Buonocore, M. J., *Adhesive Restorative Dental Materials—I*, Proc. 1st Workshop, Bio-Materials Res. Advisory Committee, Nat. Inst. Dental Res. 1961.
- [35] Driessens, F. C. M., Brauer, G. M., and Termini, D. J., *IADR Program of Abstracts and Papers*, No. 137 (1969).
- [36] Brauer, G. M., and Termini, D. J., *IADR Program of Abstracts and Papers*, No. 404 (1970).
- [37] Patrick, R. L., ed., *Treatise on Adhesion and Adhesives*, Vol. 1 (M. Dekker, New York, 1967).
- [38] Lee, H. L., Swartz, M. L., and Culp, G., *J. Dental Res.*, **48**, 211 (1969).
- [39] Patrick, R. L., Kaplan, C. M. and Beaver, E. R., *J. Dental Res.*, **47**, 12 (1968).
- [40] Patrick, R. L., and Kaplan, C. M., *Adhesive Restorative Materials—II*, Proc. 2nd Workshop, Bio-materials Res. Advisory Committee, Nat. Inst. Dental Res., (1965).
- [41] Brelant, S., in *Treatise on Adhesion and Adhesives*, Vol. 2, R. L. Patrick, ed., (M. Dekker, New York, 1969).
- [42] Fookson, A., and Ellison, A. H., *IADR Program of Abstracts and Papers No. 136* (1969).
- [43] Bowen, R. L., *Adhesive Restorative Dental Materials—I*, Proc. 1st Workshop, Bio-materials Res. Advisory Committee, Nat. Inst. Dental Res., (1961).
- [44] Ellison, A. H., and Fookson, A., *Annual Comprehensive Report to Nat. Inst. Dental Res. for 1968-1969*.
- [45] Alter, H., *J. Applied Poly. Sci.*, **9**, 1525 (1965).
- [46] Sterman, S., and Marsden, J. G., *Modern Plastics*, **43**, (No. 7), 133 (July, 1966).
- [47] Buonocore, M. G., *J. Dental Res.*, **34**, 849 (1955).
- [48] Newman, G. V., and Sharpe, L. H., *J. New Jersey State Dental Soc.*, **37**, 289 (1966).
- [49] Hoffman, S., McEwan, W. S., and Drew, C. M., *J. Dental Res.*, **48**, 242 (1969).
- [50] Anon., *Tech. Bulletin 105, Engineering, Mechanical Control and Toxicological Considerations—Urethanes*, The Upjohn Co., Kalamazoo, Mich. (July, 1968).
- [51] Gahimer, F. H. and Nieski, F. W., *Insulation*, p. 39, August, (1968).

V. Mechanical Behavior

Viscoelastic Behavior

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Since the mechanical responses of many dental materials are functions of time as well as of applied stress, viscoelastic theory, and experimental methods should be used in describing and characterizing these materials. Both static and dynamic methods may be used. Viscoelastic theory useful for characterization of dental materials and for interrelation of responses under different types of static and dynamic tests includes the Boltzmann superposition principle for linear materials and as modified and extended for non-linear materials, the time-temperature superposition principle and approximation methods for calculation of relaxation and retardation spectra. Methods which have been applied to dental materials such as amalgam, polymeric restorative materials, elastic impression materials and natural tooth structure include creep, stress relaxation, indentation and forced vibration methods.

Key words: Amalgam, dental; creep; dental materials; denture base reins; indentation test method; mechanical properties, dental materials; rocking beam oscillator; stress relaxation; torsion pendulum; viscoelastic methods.

1. Introduction

Since many restorative as well as natural dental materials have deformation characteristics which are time-dependent as well as stress-dependent, viscoelastic theory and methods offer the most advantageous means for description and characterization of their mechanical behavior. However, even though well established procedures for viscoelastic characterization are available, their application to dental materials has not been extensive. To encourage further work in this area, theory and methods described in various publications (references below) are brought together in this paper and discussed with particular attention to their potential utilization in dental research. Several examples of the application of such methods to dental materials are described.

The viscoelastic description has numerous advantages: (1) it enables researchers to describe analytically and to predict the mechanical behavior of these materials both in laboratory experiments and in the mouth; (2) it enables one to separate and quantitatively describe the relative contribution of the various time-dependent and non-time-dependent mechanical responses occurring simultaneously in a material; (3) it furnishes a unified theory whereby the mechanical behavior of materials with time-dependent responses can be compared with the behavior of materials with non-time-dependent responses used for the same purpose, such as the different types of anterior restorative materials; (4) it enables one to compare mechanical response of a material under one test condition to that under another test condi-

tion in a quantitative manner by appropriate transformation equations; (5) it enables one to select a test or group of mechanical tests that will fully measure the various mechanical phenomena occurring in the material and evaluate the mechanical parameters of each; and (6) it isolates individual mechanical phenomena and their parameters at the macroscale level and together with microviscoelastic theory, permits better description of the relation of mechanical response to microstructure.

Both static and dynamic test methods have been used to investigate the viscoelastic properties of dental materials. Commonly employed static tests are classified as: (1) a constant stress test, such as a creep test, (2) a constant strain test, such as a stress relaxation test, or, (3) a test where the stress and strain are both varied slowly and in some cases cycled;¹ an example is the classical stress-strain test. All of the above types of static testing have been employed in dental research and testing. Dynamic test methods may be generally classified as follows: (1) free vibrational methods, (2) forced vibrational methods, both resonance and nonresonance, and (3) propagation methods using either pulses or continuous waves. In many cases, the same dynamic apparatus may be used to determine the viscoelastic properties of a material by two or more of the above methods. Whether the method be static or dynamic, the following factors should be considered when testing a material:

- (1) The specific mechanical characteristics of the material to be investigated;

¹It becomes difficult to make a distinction between static stress-strain testing and dynamic testing when cycling occurs.

- (2) how this information on the material may be interrelated to that obtained for the material using other methods; and
- (3) how the mechanical phenomena and their parameters obtained for the material may be directly or indirectly related to the microstructure of the material.

2. Creep of Linear Viscoelastic Materials

The creep test as a method of investigation of the viscoelasticity of a material has the advantage of simple instrumentation, and is preferred for the long testing time required for those materials having retardation times that extend over a long time scale, but has the disadvantage of insensitivity to the retardation behavior of the material in the initial short portion of the experimental time scale. A creep test is normally conducted on the material in the form of a specimen having a uniform cross sectional area. A constant load is applied either in tension, compression, or shear, and the deformation is measured in the direction of load application as a function of time. The deformation, detected by such devices as a cathetometer, strain gage, or differential transformer, may be measured as a function of time for periods of less than one second to many years, if necessary. Creep curves for the material are obtained for different stresses, and then deformation behavior of the material as a function of time and stress is extracted from the family of creep curves.

The creep curve of a strain-hardened specimen consists commonly of one or more of three phenomena, each of which may or may not be a linear function of the applied stress; while as a function of time, one is independent, one linear, and one nonlinear. The three deformation or strain phenomena are:

- (1) Instantaneous elastic strain ϵ_i , described by analogy to a spring having a compliance J_0 , or a modulus G_0 , where $J_0 = 1/G_0$,
- (2) viscous strain ϵ_v , which may be described as analogous to a dashpot when linear, having a coefficient of viscosity η equal to the applied stress divided by the strain rate, and
- (3) retarded elastic strain ϵ_r , usually described by analogy to the so-called Voigt element or series of Voigt elements, the components of which consist of a spring of compliance J_R , or modulus G_R in parallel with a dashpot having a coefficient of viscosity η_R , where the retardation time τ of the Voigt element is defined as $\tau = \eta_R J_R$.

If a material exhibits a linear combination of all three types of strain, $\epsilon = \epsilon_i + \epsilon_v + \epsilon_r$, it may be

represented by a spring of compliance J_0 (instantaneous behavior) and a dashpot having a coefficient of viscosity η (viscous behavior) in series with one or more Voigt elements (retarded elastic strain). The graphical behavior of each of the three types of strain and their combination, along with its accompanying model and corresponding analytical strain function, may be seen in figure 1 where the strain is assumed to be a linear function of the stress σ . When the strain is a linear function of the stress, the data obtained at different stresses may be reduced to a single creep curve by plotting the creep compliance $[J(t) = \epsilon(t)/\sigma_0]$ as a function of time or logarithmic time. The creep compliance $J(t)$ of the combination of the three types of phenomena versus time and the logarithm of time may be seen in figure 2. When the retarded elastic creep compliance has a continuous distribution of retardation times τ_r , the combination creep compliance $J(t) = J_I + J_v + J_R$ may be described by the following analytical equation:

$$J(t) = J_0 + t/\eta + \int_0^\infty J(\tau)[1 - e^{-t/\tau}]d\tau \quad (1)$$

as shown graphically in figure 2a. Substitution of $L(\tau)/\tau$ for $J(\tau)$ in eq (1), gives:

$$J(t) = J_0 + t/\eta + \int_{-\infty}^{+\infty} L(\tau)[1 - e^{-t/\tau}]d \ln \tau. \quad (2a)$$

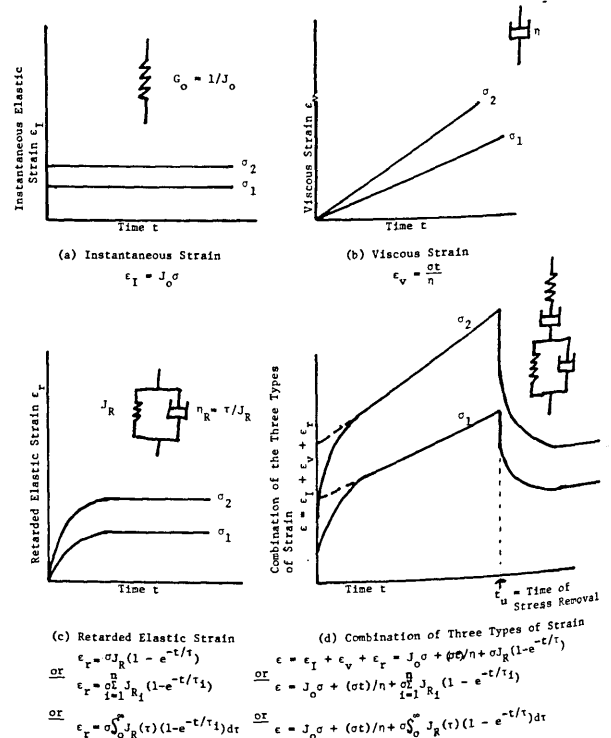


FIGURE 1.

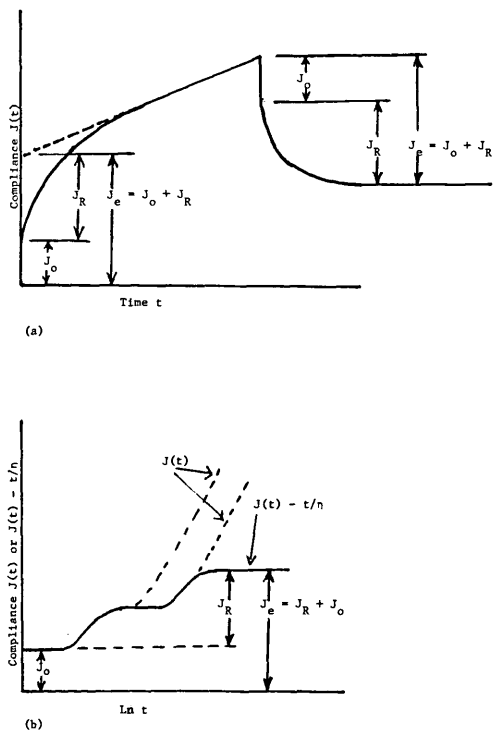


FIGURE 2.

The subtraction of t/η from both sides of eq (2a) results in

$$J(t) - t/\eta = J_0 + \int_{-\infty}^{+\infty} L(\tau)[1 - e^{-t/\tau}]d \ln \tau \quad (2b)$$

where

$J(t)$ is the creep compliance

J_0 is the instantaneous elastic compliance

t/η is the viscous response where t is the time after application of the stress, σ , and η is the coefficient of viscosity

$$\int_0^{\infty} J(\tau)(1 - e^{-t/\tau})d\tau \text{ or } \int_{-\infty}^{+\infty} L(\tau)[1 - e^{-t/\tau}]d \ln \tau$$

are analytical forms of the retarded elastic response with $J(\tau)$ and $L(\tau)$ being forms of the retardation spectrum of the material.

The graphical representation of eqs (2a) and (2b) is seen in figure 2b. It might be mentioned that $J(t) - t/\eta$ represents the elastic portion (instantaneous plus retarded) of the creep compliance curve in a constant stress experiment and also represents, after appropriate transformation, the recovery portion of the curve in figure 2a when the stress has been removed. Plots of creep compliance $J(t)$ or $(J(t) - t/\eta)$ versus $\ln t$ rather than versus t for a linear viscoelastic material, have the advantages of more direct utilization—(1) in calculating the retardation spectrum $L(\tau)$ by various

approximation methods as well as giving a better visual picture of the distribution of retardation times τ , for the material, and (2) in application of the time-temperature superposition principle [1, 2, 3]² to a linear viscoelastic material to obtain its creep compliance behavior at a given temperature that otherwise would require experimental data over many decades at that temperature. Therefore, a creep curve may be obtained at a specific temperature T for times outside the range of practical observation at this temperature by obtaining creep curves at higher and lower temperatures within the time scale of the creep experiment, and then shifting the higher and lower temperature creep curves for the linear material along the axis of the logarithmic time scale until they all join into a continuous master curve for the temperature T . Before the experimental creep curves can be shifted to make the master curve at temperature T , the compliance values should in theory have a density (or specific volume) correction, but, in practice, the density changes with temperature are often small enough to be neglected. The amount the curves are shifted along the \ln time axis is described by the equation:

$$(\ln t - \ln t_0) = \ln t/t_0 = \ln A_T,$$

where the shift is said to be positive when the curve is shifted to shorter times (to the left on the \ln time scale) in forming the master curve. The time-temperature superposition principle is applicable not only to creep data, but also to stress relaxation data and to dynamic mechanical testing data. The A_T values obtained from the shift on the \ln time scale, or $\ln 1/\omega$ (reciprocal frequency) scale in the case of dynamic measurement, for these different methods of testing are equivalent. The theory and application of the time-temperature superposition principle to a linear viscoelastic material, as well as the theoretical significance of A_T for the material, will be discussed in a later part of this paper.

3. Stress Relaxation of Linear Viscoelastic Materials

Stress relaxation behavior is observed in viscoelastic materials; that is, the stress in the material relaxes or decreases with time when the material is deformed quickly and the deformation is held constant. Stress-relaxation tests require slightly more complex instrumentation than creep tests in that, in addition to requiring a device for detecting deformation, a load measuring device is required in order to follow the force change with time. Like the creep test, the stress-relaxation test is the preferred method for the long test time required for some materials, but has the disadvantage of the lack of sensitivity to relaxation

² Figures in brackets indicate the literature references at the end of this paper.

behavior exhibited by the material in the initial short portion of the time scale. Stress-relaxation data are generally more directly interpreted in terms of viscoelastic theory than are creep data. A tensile stress-relaxation device often consists simply of two clamps between which the specimen is attached; the upper clamp is usually attached to a load detecting cell which is rigidly attached to a frame; the lower clamp can be adjusted up or down in respect to the fixed upper clamp to obtain various deformations in the specimen. Once the lower clamp has been adjusted to obtain the desired deformation in the specimen, the clamp is held fixed in respect to the frame. The amount of deformation in the specimen can be detected by means of a strain gage, differential transformer or cathetometer.

The stress-relaxation curves are obtained at different deformation levels, thus the stress-relaxation as a function of time and deformation is obtained for the material from the family of stress-relaxation curves at different deformations. The stress is plotted as a function of linear time or of logarithmic time. If stress is plotted as function of strain for a common time value from the family of curves, the stress-strain curves for the fixed time values will yield the functional relationship between the stress and the strain. With materials exhibiting a linear stress-strain relationship, dividing the stress values for each curve by the corresponding fixed strain value gives relaxation modulus $G(t) = \sigma(t)/\epsilon_0$ and the family of stress-relaxation curves reduces to a single master modulus relaxation curve. If the material is linear in its stress-strain behavior at a fixed time, the usual curves plotted are relaxation modulus curves either as a function of linear time or logarithmic time.

The simplest analog to describe stress-relaxation behavior is the Maxwell model which is a series combination of a spring of modulus G_0 and a linear dashpot having a coefficient of viscosity η which has the differential equation of motion:

$$\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} + \frac{1}{G_0} \frac{d\sigma}{dt} \quad (3)$$

In the normal stress relaxation test as mentioned previously, the strain is held constant after initial rapid deformation. Hence, $\frac{d\epsilon}{dt}$ becomes zero and the solution is:

$$\sigma(t) = \sigma_0 e^{-\frac{G_0 t}{\eta}} = \sigma_0 e^{-t/\tau} \quad (3a)$$

A material that can be described by a Maxwell model is said to have a single relaxation time defined as $\tau = \eta/G_0$. Such a material is shown graphically by a plot of stress as a function of linear and logarithmic time and also by a plot of relaxation modulus (stiffness) $G(t) = \sigma(t)/\epsilon$ as a function of logarithmic time in figure 3. As

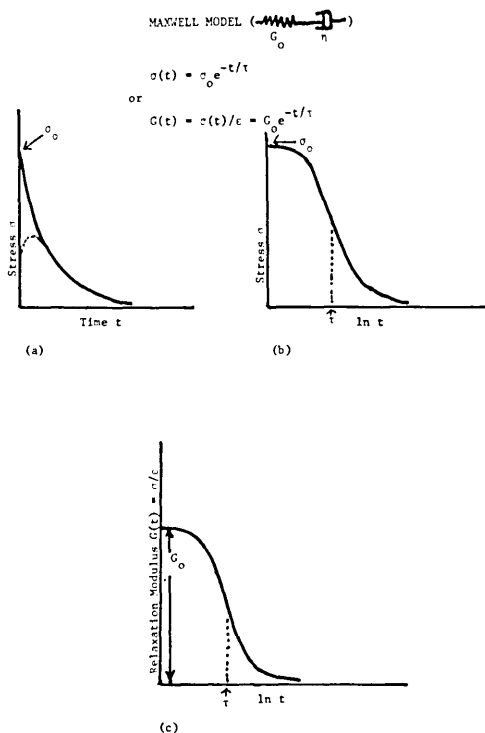


FIGURE 3.

previously mentioned, there is the lack of initial sensitivity to stress-relaxation behavior of certain materials as a consequence of the finite time required for application of the fixed strain (rather than idealized instantaneous application of the strain). This lack of initial stress-relaxation sensitivity can be discussed in terms of a material which can be represented by a single Maxwell element. If such a material has a short relaxation time, τ , or expressed another way, the stress-relaxation time scale is short compared with the time required for application of the strain, the instantaneous maximum stress and corresponding limiting modulus $G_0 = \sigma_0/\epsilon$ are indeterminate. The result of this can be seen for a simple Maxwell material represented by the dotted line in figure 3(a).

Most materials, including dental materials, cannot be characterized by a single Maxwell model having a single relaxation time. These materials have more than one relaxation time and, in many cases, so numerous are the relaxation times that they can be treated as continuous in their distribution, the continuous function $H(\tau)$ being called the relaxation spectrum. When the relaxation modulus $G(t)$ for a linear viscoelastic material is plotted against logarithmic time (over an extended time range), most often a decreasing sigmoidal shape curve is obtained, as illustrated in figure 4. In figure 4, the limiting short time value of the relaxation modulus is called the glass modulus G_0 , while the value of $G(t)$ at infinite times approaches an

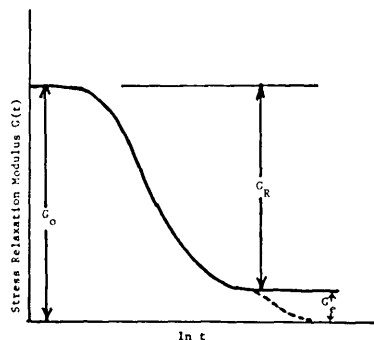


FIGURE 4.

equilibrium modulus value G_e or zero, depending on the microstructure of the material. The difference between the glass modulus G_0 and the equilibrium modulus G_e is defined as the decay modulus $G_R = G_0 - G_e$. For example, in the case of amorphous polymer, the value of G_e would depend on whether the polymer was crosslinked or not. The crosslinked polymer would exhibit a value G_e at infinite time, but the noncrosslinked would approach zero at infinite time. Commonly, even though $G_e = 0$ for noncrosslinked polymers, an intermediate plateau is observed, the length of which is molecular weight dependent. Since most materials must be described by a finite number of relaxation times or a continuous relaxation spectrum, the modulus-relaxation behavior shown in figure 4 may be described by one of the following equations. In the case of a finite number of relaxation times, the relaxation modulus equation takes the form

$$G(t) = \sum_i G_i e^{-t/\tau_i} + G_e \quad (4)$$

In the case of continuous distribution of relaxation times, the relaxation modulus equation takes the form for a linear material

$$G(t) = \int_0^\infty G(\tau) e^{-t/\tau} d\tau + G_e \quad (5)$$

or, upon substituting $G(\tau) = H(\tau)/\tau$, the equation becomes

$$G(t) = \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d \ln \tau + G_e \quad (6)$$

The monotonic decrease of $G(t)$ from G_0 to G_e , as shown in figure 4, can be described by eq (6). It is noted that the sigmoidal relaxation modulus $G(t)$ curve in figure 4 roughly approximates the mirror image of the creep compliance $J(t)$ plot shown in figure 2, both plots being on a logarithmic time scale. As recalled from earlier discussion, the glass modulus and glass compliances are related as $G_0 = 1/J_0$. Also, the equilibrium modulus G_e and steady-state compliance J_e are reciprocally related. However, the relaxation modulus $G(t)$

and the creep compliance function $J(t)$ are reciprocally related only at the limiting values, and, therefore, their curves on a logarithmic time scale are not true mirror images for a given linear viscoelastic material. It has been shown by Gross [4], and more specifically by Leaderman [5], that the two functions $G(t)$ and $J(t)$ are related by a reciprocal relationship between their respective Laplace transforms:

$$pL[J(t)] = 1/pL[G(t)] \quad (7)$$

where the Laplace transform is defined as follows:

$$L[f(t)] = \int_0^\infty e^{-pt} f(t) dt$$

While equation (7) relates the two functions $J(t)$ and $G(t)$, there is difficulty in obtaining one function from the other by means of equation (7) due to the obstacles involved in the inversion of the Laplace transform. More often the functions $G(t)$ or $J(t)$ are given as empirically determined data and numerical inversion is required. One of the most severe drawbacks in using the above equation is that usually one function has been determined only over a limited time scale and the entire time scale is required to make the inversion.

The logarithmic time plot for relaxation modulus $G(t)$ illustrated in figure 4 has the same advantages of direct use as in the case of creep compliance versus $\ln t$: (1) in determining the relaxation spectrum $H(\tau)$ by approximation methods and giving a qualitative visual picture of the distribution of relaxation times τ_i , and (2) in applying the time temperature superposition principle to the relaxation modulus data for a linear material. Again, as in the case of creep compliance data, if the relaxation modulus $G(t)$ data are obtained at various temperatures above and below some reference temperature T , these higher and lower temperature modulus curves may be shifted along the $\ln t$ time axis until they form a master curve at the reference temperature T . The amount of shift again being described by $(\ln t - \ln t_0) = \ln t/t_0 = \ln A_T$, where the A_T values obtained by the shifts of the relaxation data are equivalent to those obtained from the shift of the creep compliance data on the same linear material—this result is encompassed in the theory of the time-temperature superposition principle.

4. Boltzmann Superposition Principle—Relation to Stress-Strain Behavior

According to Boltzmann's superposition principle, if a series of stresses have been applied to a specimen at various times, the deformation at any subsequent time is simply the summation of the deformations which would have been observed at that time if each of the stresses had been applied independently.

Recalling the definition of creep compliance, $J(t) = \epsilon(t)/\sigma$ discussed earlier, it has been noted that in a linear viscoelastic material, when a single stress σ is applied at time θ to a specimen which has no previous stress history, the strain in the specimen at any time t is related to the applied stress by the following relationship:

$$\epsilon(t) = \sigma J(t - \theta). \quad (8)$$

Next, consider a series of stress increments σ_i applied at times θ_i prior to the time t ; now the strain $\epsilon(t)$ at time t would be related to the stress increments σ_i by the following equation:

$$\epsilon(t) = \sum_{i=0}^t \sigma_i J(t - \theta_i) \quad (9)$$

Thus, the above finite relationship relates the strain $\epsilon(t)$ at time t to all the previous stress history by way of the creep compliance J . The above equations are finite forms of the Boltzmann superposition principle. These equations are useful in describing step-function experiments. For example, consider the creep experiment described by figure 2(a) where the stress has been introduced and removed in a stepwise manner and the stress σ was maintained over a sufficient time for a steady state condition to be reached. If the time of removal of the stress σ is considered $t=0$, then the stress σ was applied at a time $-t_L$. Since $t=0$ at load removal, the strain at the instant before load removal is designated $\epsilon(0)$ and is related to its elastic, retarded elastic and viscous compliances as follows:

$$\epsilon(0) = \sigma(J_0 + J_R + t_L/\eta) \quad (10)$$

At a time t after stress removal (stress increment of $-\sigma$) as shown in figure 2(a), the strain $\epsilon(t)$ is related to the two incremental stresses σ and $-\sigma$ as follows:

$$\epsilon(t) = \sigma \left[J_0 + J_R + \frac{(t_L + t)}{\eta} \right] - \sigma J(t). \quad (11)$$

Now, substituting $\epsilon(0)$ for $\sigma(J_0 + J_R + t_L/\eta)$

$$\epsilon(0) - \epsilon(t) = \sigma[J(t) - t/\eta] \quad (12)$$

which is the transformation mentioned earlier for the unloaded portion of the curve.

If the stress increments are not introduced in steps, but in a continuous manner with time, the strain function becomes a strain integral in accordance with the superposition principle taking the following form:

$$E(t) = \lim_{\Delta\sigma \rightarrow 0} \sum_0^t J(t - \theta_i) \Delta\sigma_i = \int_0^t J(t - \theta) d\sigma(\theta) \quad (13)$$

or by the use of the chain rule and where the entire stress history from $\theta \rightarrow -\infty$ is considered, the above equation takes the following form:

$$E(t) = \int_{-\infty}^t J(t - \theta) \frac{d\sigma(\theta)}{d\theta} d\theta \quad (14)$$

The Boltzmann superposition principle in the form of eqs (13) and (14) specifies the transformation relationship (for a linear viscoelastic material) between the creep experiment by way of the creep compliance, and the stress-strain experiment where the stress-time relation is prescribed, on the same material. Similarly, the Boltzmann principle can be applied to the determination of stress as a function of stepwise introduction of strain increments leading to the equation:

$$\sigma(t) = \sum_{i=0}^t G(t - \theta_i) \epsilon_i \quad (15)$$

where G is the relaxation modulus defined earlier, thus relating the stress to prior strain history. When the strain increments are introduced in a continuous manner, the above equation becomes a stress integral as follows:

$$\sigma(t) = \int_{-\infty}^t G(t - \theta) \frac{d\epsilon(\theta)}{d\theta} d\theta \quad (16)$$

relating the total stress to the strain history.

The superposition eq (14) is the transformation equation between the creep function obtained in a creep experiment on a linear viscoelastic material and the strain function (strain integral) in a stress-strain experiment on that same material, where the stress is known as a point by point function of experimental time. Also, the superposition eq (16) is the transformation equation between a stress relaxation experiment and a stress-strain experiment on a given material where the strain is known in a point by point relation to experimental time. For the case of a constant stress rate,

$\left(\frac{d\sigma(\theta)}{d\theta} = \dot{\sigma} = \text{a constant}\right)$, substitution of the con-

tinuous spectrum form of the creep function given by eq (2a),

$$J(t) = \int_{-\infty}^{+\infty} L(\tau) [1 - e^{-t/\tau}] d \ln \tau + t/\eta + J_0$$

in eq (14) followed by differentiation results in

$$\frac{dE(t)}{d\sigma} = \frac{1}{\dot{\sigma}} \frac{d\epsilon}{dt} = J(t). \quad (17)$$

Thus, the slope of the strain-stress curve in a constant stress rate experiment is the creep function $J(t)$ for a linear material where the time is given by $t = \sigma/\dot{\sigma}$ since $\dot{\sigma} = \text{a constant}$. Looking at the con-

stant strain rate case for a stress-strain experiment, by substituting eq (6) into the superposition eq

(16), and assuming $\frac{d\epsilon(\theta)}{d\theta} = \dot{\epsilon}$ (a constant), one obtains the result

$$\sigma(t) = \dot{\epsilon} \left[\int_{-\infty}^{+\infty} \tau H(\tau) (1 - e^{-t/\tau}) d \ln \tau + G_e t \right] \quad (18)$$

which relates the stress integral $\sigma(t)$ to the relaxation spectrum $H(\tau)$ and thus to the relaxation modulus function of the relaxation experiment in a simple manner since for the constant stress rate experiment, $t = \epsilon/\dot{\epsilon}$; thus stress versus strain is equivalent to a stress-time plot.

5. The Spherical Indentation Test

The problem of the contact of a smooth rigid sphere of radius R against an initially plane surface of a linear viscoelastic material was analyzed by Lee and Radok [6]. Their analysis has been the basis of further study and generalizations by other workers [7]. The solution developed by Lee and Radok is:

$$\int_0^t J(t-\theta) \frac{dP(\theta)}{d\theta} d\theta = \frac{16}{3R} [l(t)]^3 = \frac{16}{3} R^{1/2} [\alpha(t)]^{3/2}$$

where

$P(\theta)$ = the total force as a function of time or the loading history

$J(t)$ = the shear creep compliance for the linear material

R = the radius of the indenter

$l(t)$ = the radius of indentation contact

$\alpha(t)$ = the depth of penetration of the sphere into the plane surface.

If the total force is applied in the form of instantaneous constant force P_0 , then $P(t) = P_0 H(t)$ where $H(t)$ is the Heaviside step function [$H(t) = 0$ for $t < 0$, $H(t) = 1$ for $t > 0$] and the above solution takes the form in terms of the shear compliance as follows:

$$J(t) = \frac{16}{3R} \frac{[l(t)]^3}{P_0 H(t)} = \frac{16R^{1/2} [\alpha(t)]^{3/2}}{3P_0 H(t)}$$

Using this equation $J(t)$ in theory could be determined by measuring the central indentation depth $\alpha(t)$ as a function of time. Practically, however, this equation has application only when the period of load application is short compared with the experimental time scale needed to evaluate $J(t)$ completely.

The first group to recognize the application of the spherical indenter as a viscoelastic test for various dental materials was W. T. Sweeney and co-workers [8, 9].

6. Dynamic Test Methods

Often a type of test is used where the system in which the material is a component is excited into vibration. The stress and strain in the material vary sinusoidally with time as opposed to the creep or stress relaxation tests which are essentially step-function experiments. Such vibratory tests measure the dynamic response of a material. As in the earlier discussion on creep and relaxation, this discussion will be restricted to linear viscoelastic materials where the strain amplitude is proportional to the stress amplitude.

The vibrational character of a system composed of a linear viscoelastic material may be described by a linear time-invariant differential equation of the form

$$\sum_{i=0}^n a_i \frac{d^i y}{dt^i} = \sum_{i=0}^n b_i \frac{d^i x}{dt^i} \quad (19)$$

where y represents the output and x the input. Such systems described by the above differential equation may also be described by means of their weighting or impulse functions [10]. The impulse response function $g(t-\tau) = W(t-\tau)$ associated with the above differential equation has the form

$$g(t-\tau) = \sum_{i=1}^n c_i g_i(t-\tau) \quad (20)$$

where $g_i(t-\tau)$ is a set of basic solutions to the homogenous differential equation. The relation of the input x to the output y for the above system is expressed by the superposition principle as follows:

$$y(t) = \int_{-\infty}^t g(t-\tau) x(\tau) d\tau. \quad (21)$$

The ease of determining the weighting function depends on the form of the differential equation of the system. A third method of description of the linear viscoelastic systems is by means of a frequency function [4, 11]. This frequency function bears a close relation in properties to the system's weighting function and is related to the weighting function by the following integral pair:

$$H(i\omega) = \int_{-\infty}^{+\infty} W(t-\tau) e^{-i\omega(t-\tau)} d\tau \quad (22)$$

$$W(t-\tau) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} H(i\omega) e^{i\omega(t-\tau)} d\omega \quad (23)$$

The relation of the system's input x to the system's output y in terms of the frequency function is given by the following:

$$y(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} H(i\omega) X(i\omega) e^{i\omega t} d\omega \quad (24)$$

where $X(i\omega)$ is the Fourier transform of the input x .

The difficulty in determining $H(i\omega)$ from the differential equation of the system is similar to that of the weighting function determination.

The terms such as dynamic modulus and compliance, mechanical impedance, logarithmic decrement, and phase angle most often determined for a vibrating linear, viscoelastic system may be arrived at by examining the resulting differential equation of motion or a system with a single degree of freedom y , having an elastic element as well as viscous character such that the sum of the forces are zero in accordance with d'Alembert's principle as given:

$$A_I \ddot{y} + B_v \dot{y} + Ky = f(t) \quad (25)$$

(inertia) (viscous) (elastic) (exciting)
(force) (force) (force) (force)

In the above system, the viscous and elastic forces are usually exerted by the viscoelastic material while the inertia force may be due to the material sample or may be due to another part of the system, depending on the system design. The complete solution of the above differential equation is the sum of the complementary solution y_c and the particular solution y_p :

$$y = y_c + y_p \quad (26)$$

The complementary solution y_c is the solution to the above differential equation when the exciting force is zero or what is called the homogenous differential equation. The complementary solution y_c to the homogenous portion of the differential equation describes the displacement behavior of the system upon removal of the exciting force or what is called the free vibrational character of the system. An important term evaluated for a system containing a viscoelastic material in free vibration when the system is in the underdamped condition is the logarithmic decrement. This term will be discussed in more detail later. The second part of the solution to the above differential equation called the particular solution is a specific solution of the equation when $f(t)$ is not zero, that is when the exciting force $f(t)$ is acting on the system. It is a specific solution in that it describes the displacement behavior of the system under steady-state conditions after the transient behavior (which is described by y_c) has vanished as a component of the displacement y . The terms commonly evaluated for a system containing a viscoelastic material, under steady-state vibratory conditions, are the mechanical impedance and phase angle for the system and, or the material, as a function of exciting frequency. Also, the mechanical Q factor is determined from the frequency response curve of the mechanical impedance. All of these will be discussed later in more detail.

First considering the free vibration of the viscoelastic system after removal of the exciting

force, that is when $f(t)=0$, the resulting homogenous differential equation is

$$A_I \ddot{y} + B_v \dot{y} + Ky = 0 \quad (27)$$

The displacement y_c takes the following form when the system is underdamped

$$(B_v^2 - 4A_I K < 0):$$

$$y_c = y_0 e^{-\alpha t} e^{i\omega_d t} = y_0 e^{(i\omega_d - \alpha)t} \quad (28)$$

where α is the attenuation factor and ω_d the damped oscillation frequency. The attenuation factor α is related to the logarithmic decrement δ and the damping frequency ω_d and to the coefficients of the differential equation by:

$$\alpha = \frac{\omega_d \delta}{2\pi} = B_v / 2A_I \quad (29)$$

The logarithmic decrement is defined as the natural logarithm of the ratio of two successive maxima y_n and y_{n+1} which occur in the period $T_d = 2\pi/\omega_d$ and is given by:

$$\delta = \ln (y_{n-1}/y_n) = \alpha T_d \quad (30)$$

Since the antilog of eq (30) is

$$e^\delta = y_1/y_2 = y_2/y_3 = \dots = y_n/y_{n+1}$$

then

$$(e^\delta)^n = (y_1/y_{1+1})(y_{1+1}/y_{1+2}) \dots (y_{1+n-1}/y_{1+n}) = e^{n\delta}$$

or

$$\delta = \frac{1}{n} \ln (y_1/y_{1+n}) \quad (31)$$

Therefore the logarithmic decrement can be obtained from two displacement maxima separated by n periods by use of eq (31). The elastic energy stored by the system described by eq (27) when the displacement y is at a maximum during the free oscillation is represented as follows for each successive maximum:

$$V_1 = \frac{1}{2} Ky_1^2, V_2 = \frac{1}{2} Ky_2^2 \dots V_n = \frac{1}{2} Ky_n^2 \quad (32)$$

The energy loss between two successive maxima V_1 and V_2 divided by the original energy is

$$\begin{aligned} \frac{V_1 - V_2}{V_1} &= 1 - \frac{V_2}{V_1} = 1 - \left(\frac{y_2}{y_1}\right)^2 \\ &= 1 - e^{2\delta} = 2\delta - \frac{(2\delta)^2}{2!} + \frac{(2\delta)^3}{3!} - \dots \quad (33) \end{aligned}$$

When δ is small, the energy loss per cycle is approximately:

$$\frac{\Delta V}{V} \cong 2\delta \quad (33a)$$

Next, looking at the linear system under steady-state conditions when force vibrated, the motion of which is governed by eq (25), when the exciting force is harmonic, the steady-state displacement y_p is a harmonic function. Hence, let the exciting force be represented by the harmonic function.

$$f(t) = F_0 e^{i\omega t} \text{ (external excitation)}$$

Now the displacement would take the form $y = Y_0 e^{i\omega t}$. Substitution of these two functions into (25) leads to:

$$\frac{f}{y} = \frac{F_0}{Y_0} = G^* = (K - A_I \omega^2) + i\omega B_n \quad (34)$$

where G^* is defined as the complex modulus or stiffness. Therefore, a system like that described by eq (25) has a steady-state modulus G^* or compliance $J^* = 1/G^*$. From eq (34) we note that:

$$f = G^* y \quad (35a)$$

$$y = J^* f \quad (35b)$$

The complex quantity G^* can be written in rectangular form and polar form as follows:

$$G^* = G' + iG'' = |G^*|(\cos \theta + i \sin \theta) = |G^*|e^{i\theta} = \left| \frac{F_0}{Y_0} \right| e^{i\theta} \quad (36)$$

where $|G^*| = \left| \frac{F_0}{Y_0} \right|$ is the absolute value of the stiffness G^* and θ is the phase angle between the input f and the output y .

Also:

$$G' = |G^*| \cos \theta = \left| \frac{F_0}{Y_0} \right| \cos \theta \quad (37a)$$

and

$$G'' = |G^*| \sin \theta = \left| \frac{F_0}{Y_0} \right| \sin \theta \quad (37b)$$

The moduli G' and G'' are defined as the storage and loss moduli of the system. The complex quantity, G^* represents simultaneously the elastic and damping properties of the system. Since the complex modulus G^* and the complex compliance J^* are reciprocally related as defined by (35a) and (35b) then from eq (36):

$$J^* = 1/G^* = \left| \frac{Y_0}{F_0} \right| e^{-i\theta} = |J^*|(\cos \theta - i \sin \theta) = J' - iJ'' \quad (38)$$

where J' and J'' are the storage and loss compliances:

$$J' = |J^*| \cos \theta = \left| \frac{Y_0}{F_0} \right| \cos \theta \quad (39a)$$

$$J'' = |J^*| \sin \theta = \left| \frac{Y_0}{F_0} \right| \sin \theta \quad (39b)$$

It is noted that the absolute values and their respective storage and loss values of moduli and compliances are related as:

$$|G^*| = \sqrt{G'^2 + G''^2} \quad (40a)$$

$$|J^*| = \sqrt{J'^2 + J''^2} \quad (40b)$$

The ratio of either G''/G' from equations (37a and b) or J''/J' from (39a and b) is:

$$G''/G' = J''/J' = \tan \theta \quad (41)$$

where θ is the phase angle between input and output and $\tan \theta$ is called the loss tangent. If one uses eq (35a) for the harmonic input $f = F_0 e^{i\omega t}$, the output y of the system for steady-state motion is:

$$y = \frac{F_0}{|G^*|} e^{i(\omega t - \theta)} \quad (42)$$

The output y lags the input f by the phase angle θ

Now, returning to eq (34), it is seen that for a system in steady-state motion governed by eq (25), the expressions for $|G^*|$, $|J^*|$ and $\tan \theta$ are as follows:

$$|G^*| = \sqrt{(K - A_I \omega^2)^2 + \omega^2 B_n^2} = \left| \frac{F_0}{Y_0} \right| = \left| \frac{1}{J^*} \right| \quad (43a)$$

$$\tan \theta = \omega B_n / (K - A_I \omega^2) \quad (43b)$$

The two terms above are usually measured as a function of exciting frequency ω . The phase angle θ is measured between the exciting input function and the output function for a given exciting frequency. Usually, the reciprocal of $|G^*|$ is measured at each driving frequency and plotted as a function of frequency. This reciprocal $1/|G^*|$, the magnification factor of the system, is determined by measuring the amplitude of the output in respect to the input amplitude at a given exciting frequency. The magnification factor is:

$$1/|G^*| = \frac{1}{K \sqrt{[1 - (\omega/\omega_n)^2]^2 + \left(\frac{B_n \omega}{A_I \omega_n^2} \right)^2}} \quad (44)$$

where

$$\omega_n = \sqrt{K/A_I}$$

= resonance frequency of an undamped system

Resonance occurs when the phase angle θ is 90° and $\omega = \omega_n$. Substituting $\omega = \omega_n$ in eq (44) gives:

$$[1/|G^*|]_{res} = \frac{1}{B_n \omega_n} \quad (45)$$

or

$$K[1/|G^*|]_{res} = \frac{K}{B_n \omega_n} \quad (45a)$$

The quantity given by equation (45a) is called the mechanical Q factor of the system described by eq (25). The Q factor of the system is usually obtained by taking the frequency difference for two frequencies on each side of the resonance maximum [12] where

$$K/|G^*| = \frac{\sqrt{2}}{2} \frac{K}{B_\eta \omega_n}$$

called the half power points; thus Q is defined as

$$Q = \frac{\omega_n}{\omega_2 - \omega_1} = \frac{K}{B_\eta \omega_n} \quad (46)$$

If the system contains a viscoelastic material sample where the damping and elastic responses of the system are entirely due to the sample and the inertia of the sample is negligible compared with that of the system so that when the phase angle is measured between the input at the sample and the output displacement, the expression (43b) becomes—

$$\tan \theta_m = \frac{\omega B_\eta}{K} \quad (47)$$

which shows that the phase angle between the force on the sample and its displacement is directly proportional to the driving frequency ω and is equal to Q^{-1} given by eq (46) when the driving frequency is the resonance frequency ω_n of the total system. It is further noted that the definitions of G' and G'' in (37 a and b) take the following form using eq (34) for the steady-state response of the system described by eq (25).

$$G' = K - A_I \omega^2 \quad (48a)$$

$$G'' = \omega B_\eta \quad (48b)$$

It is seen that G'' is directly proportional to the damping constant B_η and the exciting frequency ω . Now again examining the case where the damping and elastic response is due entirely to a viscoelastic sample of negligible inertia compared to that of the system we see that the equations (48 a and b) take the following form for the viscoelastic material

$$G'_m = K/\mathcal{K} \quad (49a)$$

$$G''_m = \frac{\omega B_\eta}{\mathcal{K}} = G'' \quad (49b)$$

where G'_m and G''_m are the storage and loss moduli of the material when corrected with the appropriate shape factor \mathcal{K} . It is further noted that the loss modulus of the material G''_m is the same as that of the system since all the loss is in the material. Now if the system described by eq (25) has its damping and elastic forces completely

due to a viscoelastic sample as described above and the external excitation is of the form $F_0 e^{i\omega t}$ (a harmonic function) then the differential eq (25) can be expressed in terms of the viscoelastic material moduli G'_m and G''_m as follows—

$$A_I \ddot{y} + (G'_m + i G''_m) y = F_0 e^{i\omega t}$$

or

$$A_I \ddot{y} + G_m^* y = F_0 e^{i\omega t} \quad (50)$$

In the absence of external excitation, $f(t) = 0$, in the case of the system described by eq (50), some investigators [13] have attempted to solve the free vibration by trying to solve the homogeneous differential eq (50).

$$A_I \ddot{y} + (\bar{G}'_m + i \bar{G}''_m) y = 0 \quad (51)$$

But it must be pointed out that the form of G'_m and G''_m in (50) occurred only because the form of the external exciting function $f(t)$ was known and the solution under steady-state conditions is the same form as that of the excitation source. But there is no such analogous situation in the case of free vibrations. Assuming the solution is of the form expressed by eq (28), then

$$\bar{G}'_m = A_I (\omega_d^2 - \alpha^2) / \mathcal{K} \quad (52a)$$

$$\bar{G}''_m = 2\omega_d \alpha A_I / \mathcal{K} \quad (52b)$$

where

$$\omega_d = \omega_n \sqrt{1 - f_d^2} = \text{damping frequency}$$

$$\omega_n = \sqrt{\frac{K}{A_I}} = \text{resonance frequency of the un-}$$

damped system

$$f_d^2 = B_\eta^2 / 4A_I K$$

$$\alpha = B_\eta / 2A_I$$

\mathcal{K} = shape factor

If damping is small enough so that $B_\eta^2 \ll 4A_I K$ hence $f_d^2 \ll 1$ than equation (52a) and (52b) take the following form:

$$\bar{G}'_m \cong (K - B_\eta^2 / 4A_I) / \mathcal{K} \quad (53a)$$

$$\bar{G}''_m \cong \omega_n B_\eta / \mathcal{K} \quad (53b)$$

One sees that \bar{G}''_m in (53b) is of the same form as G''_m in (49b) and will be equal when the exciting frequency in (49b) is equal to ω_n . Further, it is noted that if

$$B_\eta^2 \ll 4A_I$$

then

$$\bar{G}'_m = K / \mathcal{K} \quad (54)$$

which is the same as the G'_m in the steady-state case of (49a)

Dynamic methods in which the inertia of the system is large compared with that of the specimen of viscoelastic material being characterized are sometimes called dynamic methods with added inertia. Two examples of this type of method are (1) the torsion pendulum which is usually used in free vibration and is very useful for measurement of energy loss in linear systems through the logarithmic decrement, and (2) the rocking-beam oscillator. Both of these methods are low-frequency methods but may be used in free or forced oscillation. The torsion pendulum essentially consists of a shaft composed of the viscoelastic material to which a disk of moment of inertia I is attached. The torsion pendulum as a dynamic test method and the theory of its free vibration is discussed in detail in an article by Nielsen [14]. The differential equation of motion for the torsion pendulum would be that given by eq (25) where $A_I = I$, the moment of inertia, $y = \theta$, the angular displacement for an external torque $f(t)$

$$I\ddot{\theta} + B\dot{\theta} + K\theta = f(t) \quad (55)$$

Equation (55) holds for small angular displacement. Since the inertia of the viscoelastic specimen shaft is negligible compared to I , the moment of inertia of the disk, the equation can be written in accordance with eq (50a).

$$I\ddot{\theta} + (G'_m + iG''_m)\theta = f_0 e^{i\omega t} \quad (56)$$

In free vibration $f_0 e^{i\omega t} = 0$ and eq (56) takes the form of eq (51).

$$I\ddot{\theta} + (\bar{G}'_m + i\bar{G}''_m)\theta = 0 \quad (57)$$

or

$$I\ddot{\theta} + \bar{G}^*_m \theta = 0$$

where the complex modulus \bar{G}^* in this case is the complex shear modulus of the viscoelastic material with \bar{G}' and \bar{G}'' being the storage and loss components. The solution to eq (57) would be of the form of eq (28).

$$\theta = \theta_0 e^{(i\omega_d - \alpha)t} \quad (58)$$

expressing the angular rotation θ , as a function of time for free vibration. Since the above solution is of the form expressed by eq (28) then G' and G'' are related to the attenuation factor according to eqs (52a) and (52b) as follows:

$$G'_m = I(\omega_d^2 - \alpha^2)/\mathcal{K} \quad (59a)$$

$$G = 2I''_m \omega \alpha / \mathcal{K} \quad (59b)$$

where \mathcal{K} is again the shape factor. Now assuming damping is small enough so that $\omega_d = \omega_n$ and recalling that the attenuation factor α is related to

the logarithmic decrement δ as expressed by eq (29), substitution into (59a) and (59b) leads to the result:

$$G'_m = \frac{I\omega_n^2}{4\pi^2} (4\pi^2 - \delta^2) / \mathcal{K} \quad (60a)$$

or

$$G'_m = I f_n^2 (4\pi^2 - \delta^2) / \mathcal{K}$$

$$G''_m = I \frac{\omega_n^2}{\pi} \delta / \mathcal{K} \quad (60b)$$

or

$$G''_m = 4\pi I f_n^2 \delta / \mathcal{K}$$

where f_n is the resonance frequency of the undamped vibration of the system recalling that $\omega_n = 2\pi f_n$. Now the ratio of \bar{G}''_m to \bar{G}'_m using eqs (60a) and (60b) would be the following for a viscoelastic material:

$$\frac{\bar{G}''_m}{\bar{G}'_m} = \frac{4\pi\delta}{4\pi^2 - \delta^2} \quad (61)$$

which for small damping takes the form

$$\bar{G}''_m / \bar{G}'_m = \delta / \pi \quad (62)$$

The shape factor \mathcal{K} takes the following forms [14] for (1) rectangular cross-section specimens and (2) circular cross-section specimens of the viscoelastic material:

$$(1) \quad \mathcal{K} = CD^3M/16L$$

$$(2) \quad \mathcal{K} = \pi R^4/2L$$

where

- C = width of the specimen
- D = thickness of the specimen
- R = radius of the specimen
- L = length of the specimen
- M = a shape factor obtained from tables

The rocking beam method [15], like the torsion pendulum, has the restoring force and damping force provided by the sample of viscoelastic material. The excited motion of the rocking beam like that of the torsion pendulum may also be described by eq (25), but the displacement of the sample in the case of the rocking beam is linear, not angular, the inertial term A_I is the effective mass (m_e) of the system, and the external exciting source is a force $f(t)$, not torque in the equation as shown:

$$m_e \ddot{y} + B\dot{y} + Ky = f(t) \quad (63)$$

The rocking beam consists of a beam of large mass compared to that of the sample, with the beam resting on a knife edge and having adjustable weights. The specimen is positioned in the vertical direction with one end clamped to the horizontal

beam out from the knife edge and the other end to a fixed position. The specimen undergoes motion only in the y coordinate upon excitation of the beam for small oscillation. Returning to the equation of motion of the rocking beam, it is noted that since the mass of the viscoelastic specimen is small compared to the effective mass of the beam, eq (63) can be written using eq (50 a and b) in the following form:

$$m_e \ddot{y} + (E'_m + iE''_m)y = f_0 e^{i\omega t} \quad (64)$$

or

$$m_e \ddot{y} + E_m^* y = f_0 e^{i\omega t}$$

where E_m^* is the complex Young's modulus with E' and E'' being the respective storage and loss components. Now in free vibration again $f_0 e^{i\omega t} = 0$ and eq (64) becomes:

$$m_e \ddot{y} + \bar{E}_m^* y = 0 \quad (65)$$

or

$$m_e \ddot{y} + (\bar{E}'_m + i\bar{E}''_m)y = 0$$

The solution to eq (65) is again of the form of eq (28):

$$y = y_0 e^{(t\omega_d - \alpha)t} \quad (66)$$

expressing the linear displacement y as a function of time for free vibration for an underdamped system; therefore, E'_m and E''_m are related to the attenuation factor α according to eqs (52a) and (52b) as shown:

$$\bar{E}'_m = m_e(\omega_d^2 - \alpha^2)/\mathcal{K} \quad (67a)$$

$$\bar{E}''_m = 2m_e\omega_d\alpha/\mathcal{K} \quad (67b)$$

If damping is small enough so that $\omega_d \cong \omega_n$ and using eq (29) which relates the attenuation factor α to the logarithmic decrement, upon substitution in eq (67a) and (67b) the moduli are related to the logarithmic decrement δ as follows:

$$\bar{E}'_m = m_e \frac{\omega_n^2}{4\pi^2} (4\pi^2 - \delta^2)/\mathcal{K}$$

or

$$\bar{E}'_m = m_e f_n^2 (4\pi^2 - \delta^2)/\mathcal{K} \quad (68a)$$

$$\bar{E}''_m = m_e \frac{\omega_n^2}{\pi} \delta/\mathcal{K}$$

o

$$\bar{E}''_m = 4\pi m_e f_n^2 \delta/\mathcal{K} \quad (68b)$$

where $\omega_n = 2\pi f_n$ with f_n being the undamped vibrational frequency of the system. Now the ratio of \bar{E}''_m to \bar{E}'_m is the following:

$$\bar{E}''_m/\bar{E}'_m = 4\pi\delta/(4\pi^2 - \delta^2) \quad (69)$$

which if damping is small reduces to

$$\bar{E}''_m/\bar{E}'_m = \delta/\pi$$

The effective mass of the system m_e is determined by substituting a spring of negligible mass and determining free vibrational frequency $\omega_1 = 2\pi f_1$ of the system with the spring in place of the viscoelastic specimen. Now if the natural frequency $\omega_0 = 2\pi f_s$ of the spring is determined using a known mass m_0 in free vibration or if the spring constant K_s is determined by adding weights to the spring and using Hooke's law, $\bar{F} = -K_s x$ the effective mass m_e is given as follows:

$$m_e = \frac{K_s}{\omega_1^2} = m_0 \frac{\omega_s^2}{\omega_1^2} = m_0 \frac{f_s^2}{f_1^2} \quad (70)$$

The shape factor \mathcal{K} for the rocking beam is as follows:

$$\mathcal{K} = A/l$$

where l is the stretched length of the viscoelastic specimen and A is the corresponding cross-sectional area at such length l . The cross-sectional area A_0 of the undistorted specimen is related to A as follows, assuming constant volume of sample:

$$l_0 A_0 = l A$$

or

$$A_0 = A l / l_0 = A \left(1 + \frac{\Delta l}{l_0}\right)$$

where l_0 is the undistorted length and Δl the change in length upon stretching.

7. Theory of the Time-Temperature Superposition Principle

Earlier in this discussion it was stated that the time-temperature superposition principle is applicable to various mechanical test data, creep, stress relaxation, and various dynamic mechanical tests, and that Leaderman [1] and others [16-20] have demonstrated that a composite curve of the mechanical response can be constructed by shifting of data obtained at different temperatures along a logarithmic time or reciprocal frequency axis. This has also been shown to be applicable to dielectric or magnetic relaxation phenomena. If this principle is applicable to the data obtained on a material under different test methods, a micromechanism occurring in the material may be confirmed and examined by each of these methods; for example, transitions in an amorphous polymer may be explored by examining the distinct dispersion regions by mechanical means. For certain materials, in order to obtain the composite curve for the reference temperature T_0 by reduction of measurements at various temperatures, the modulus function must be multiplied by a factor $T_0 \rho_0 / T \rho$ where T_0 is the reference temperature and ρ_0 is the density of the material at that temperature, while ρ is the density at T , the temperature of data meas-

urement. This factor times the modulus function is plotted against $\ln \frac{t}{A_T}$ or $\ln (\omega A_T)$ to give the composite curve; recalling that $\ln A_T = (\ln t - \ln t_0)$ expresses the amount the curves at temperature T are shifted along the \ln time axis to form the composite curve at the reference temperature T_0 . This application of the factor $T_0 \rho_0 / T \rho$ to the mechanical response of a material is in accordance with the method of reduced variables which involves two assumptions. The first is that the modulus function for the material is proportional to the absolute temperature T and density. Therefore,

$$\frac{M_0}{T_0 \rho_0} = \frac{M}{T \rho} \quad (71)$$

where M_0 and M are the modulus function at temperatures T_0 and T . The second assumption is that the molecular mobilities of the material at any temperature T all have the same frequency-temperature dependence which can be described as a single activation energy of flow ΔH_a which is related to the shift factor A_T and temperature by the Arrhenius equation.

$$\Delta H_a = \frac{R \ln A_T}{(1/T - 1/T_0)} \quad (72)$$

where R = the gas constant.

The temperature dependence of the activation energy of flow ΔH_a for the viscoelastic response of amorphous polymers at and above the glass transition temperature T_g of the polymer has been described by the WLF equation, a semi-empirical relation developed by Williams, Landel, and Ferry [21] and given as:

$$\Delta H_a \left(\frac{\text{kcal}}{\text{mole}} \right) = \frac{4.12 T^2}{(51.6 + T - T_g)^2} \quad (73)$$

This equation shows ΔH_a to increase with T_g and to fall off above T_g . Since ΔH_a measures the change in molecular motion with temperature, ΔH_a is a maximum at the glass-transition temperature of an amorphous polymer and is low at temperatures far above and below the transition.

Using tensile creep data, Bueche [22] calculated the experimental ΔH_a versus T for polymethylacrylate in the vicinity and above the glass transition temperature T_g . Bueche gives an extensive discussion of the molecular theory of such transitions and their relation to ΔH_a .

McCrum and Morris [23] examined the experimental values of ΔH_a for various polymers including poly(methyl methacrylate) and polytetrafluoroethylene as obtained by creep or stress relaxation experiments and compared them to those obtained by internal friction measurements. They observed that the ΔH_a values from creep and stress relaxation measurements were larger than those obtained by internal friction measure-

ments. Upon analysis, they concluded that the true value of ΔH_a was obtained from the tangent loss (internal friction measurements). They explained the discrepancy in the ΔH_a values from creep or stress relaxation measurements on the basis of the temperature dependence of the relaxed and unrelaxed compliances or moduli which are the limiting values. As pointed out in the earlier discussion on creep and stress relations, the unrelaxed creep compliances and moduli are the instantaneous values, while the relaxed compliance is the instantaneous compliance plus the limiting or asymptotic value of the retarded elastic compliance, and the relaxed modulus is just the equilibrium modulus G_e . The inclusion of the temperature dependence of the limiting moduli and compliances into the time-temperature superposition principle led McCrum and Morris [23] to the following relations which define the McCrum-Morris superposition principle:

$$A_T = e^{\frac{\Delta H_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right)} \quad (74a)$$

$$b_T = \frac{J_{RT} - J_{uT}}{J_{RT_0} - J_{uT_0}} = c_T d_T \frac{G_{uT} - G_{RT}}{G_{uT_0} - G_{RT_0}} \quad (74b)$$

$$c_T = \frac{J_{uT}}{J_{uT_0}} = \frac{G_{uT_0}}{G_{uT}} \quad (74c)$$

$$d_T = \frac{J_{RT}}{J_{RT_0}} = \frac{G_{RT_0}}{G_{RT}} \quad (74d)$$

where J_{uT} and J_{RT} are the unrelaxed and relaxed compliances for any temperature T while J_{uT_0} and J_{RT_0} are values at some reference temperature T_0 . In the above equation G_{uT} , G_{RT} , and G_{uT_0} and G_{RT_0} are the respective unrelaxed and relaxed moduli at any temperature T and reference temperature T_0 .

From eqs (74 a, b, and c) it can be shown that the retardation spectrum $L_T (\ln \tau)$ and the relaxation spectrum $H_T (\ln \tau)$ at temperature T , for a solid, obeying the Boltzmann superposition principle, can be related to their respective spectra at a reference temperature T_0 by the following relation:

$$L_T (\ln \tau) = b_T L_{T_0} (\ln \tau / A_T) \quad (75a)$$

$$H_T (\ln \tau) = \frac{b_T}{c_T d_T} H_{T_0} (\ln \tau / A_T) \quad (75b)$$

From these results, McCrum and Morris developed the following general relations for the creep compliance and the relaxation modulus at temperatures T and T_0 :

$$J_{T_0}(t/A_T) = \frac{1}{b_T} J_T(t) + J_{uT_0} \left(1 - \frac{c_T}{b_T} \right) \quad (76a)$$

$$G_{T_0}(t/A_T) = \frac{c_T d_T}{b_T} G_T(t) + G_{RT_0} \left(\frac{b_T - c_T}{b_T} \right) \quad (76b)$$

The above equations are very general and it can be shown that with appropriate assumptions, such as $b_T = d_T$ and $c_T = 1$ that WLF relations are special cases. Glass state transitions may be evaluated by means of the above equation. For example, such transitions have been usually described by the following:

$$J_{T_0}(t/A_T) = J_T(t) \quad (77a)$$

$$G_{T_0}(t/A_T) = G_T(t) \quad (77b)$$

which can be obtained from (76a and b) by assuming $b_T = c_T = d_T = 1.0$. But McCrum and Morris assumed for such transitions that $b_T = c_T = d_T \neq 1$ which leads to the following:

$$J_{T_0}(t/A_T) = \frac{1}{c_T} J_T(t) \quad (78a)$$

$$G_{T_0}(t/A_T) = c_T G_T(t) \quad (78b)$$

The above equations, when applied to creep data and stress relaxation data in the vicinity of a glass transition [23] gave values of ΔH_a which agreed with the values obtained by internal friction measurements when applied to data for various transitions.

8. Approximate Methods for Calculation of the Relaxation and Retardation Spectra of a Material and the Interrelation of Viscoelastic Response Functions

Alfrey [24] developed first order approximations for the calculation of the relaxation spectrum and the retardation spectrum of a material. The retardation spectrum using Alfrey's method is simply found by taking the slope of the creep compliance ($J(t) - t/\eta$) versus the logarithm of time (t), or, in the case of a dynamic experiment the slope of the storage compliance versus the logarithm of frequency (ω) as expressed by the following equations [5, 25]

$$L_1(t) = \frac{d[J(t) - t/\eta]}{d \ln t} \quad \text{for creep experiment} \quad (79a)$$

$$L'_1(1/\omega) = -\frac{d[J'(\omega)]}{d \ln \omega} \quad \text{for dynamic experiment} \quad (79b)$$

To calculate the relaxation spectrum using this method one takes the slope of the relaxation modulus $G(t)$ versus the logarithm of time (t), or, for the dynamic experiment, the slope of the storage modulus $G'(\omega)$ versus the logarithm of frequency (ω) given by the following equations

$$H_1(t) = -\frac{dG(t)}{d \ln t} \quad \text{for relaxation experiment} \quad (80a)$$

$$H'_1(1/\omega) = \frac{dG'(\omega)}{d \ln \omega} \quad \text{for dynamic experiment} \quad (80b)$$

Schwarzl and co-workers [5, 26] developed approximations of the spectra using higher derivatives of the experimental response function $J(t)$, $J'(\omega)$, $J''(\omega)$, $G(t)$, $G'(\omega)$, and $G''(\omega)$, but, while these relations are better approximations to the spectra, the observed response functions are not accurate enough to get second derivatives from the experimental data in most cases. The approximation relations are expressed as follows:

Retardation spectrum

$$L_2(t/2) = \frac{df_1(t)}{d \ln t} - \frac{d^2 f_1(t)}{d(\ln t)^2} \quad \text{for creep data} \quad (81a)$$

$$L''_2(1/\omega) = \frac{2}{\pi} \left[f_2(\omega) - \frac{df_2(\omega)}{d(\ln \omega)^2} \right] \quad \text{for dynamic compliance data} \quad (81b)$$

where

$$f_1(t) = J(t) \text{ or } J(t) - t/\eta$$

$$f_2(t) = J''(\omega) - 1/\omega\eta$$

Relaxation spectrum

$$H_2(t/2) = \frac{dG(t)}{d \ln t} + \frac{d^2 G(t)}{d(\ln t)^2} \quad \text{for relaxation data} \quad (82a)$$

$$H''_2(1/\omega) = \frac{2}{\pi} \left[G''(\omega) - \frac{d^2 G''(\omega)}{d(\ln \omega)^2} \right] \quad \text{for dynamic data} \quad (82b)$$

An interrelation between two different viscoelastic responses was given earlier in the case of creep and stress relaxation function by eq (7). The relation between the dynamic compliance and the retardation spectrum of a linear viscoelastic material can be shown to be represented [5] by the following:

$$J'(\omega) = J_e + \int_{-\infty}^{+\infty} \frac{L(\tau)}{1 + \omega^2 \tau^2} d \ln \tau \quad (83a)$$

$$J''(\omega) = \int_{-\infty}^{+\infty} \frac{L(\tau) \omega \tau}{1 + \omega^2 \tau^2} d \ln \tau + \frac{1}{\omega \eta} \quad (83b)$$

The relations between the dynamic moduli (storage and loss) and the relaxation spectra are as follows

$$G'(\omega) = \int_{-\infty}^{+\infty} \frac{H(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln \tau + G_e \quad (84a)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} \frac{H(\tau) \omega \tau}{1 + \omega^2 \tau^2} d \ln \tau \quad (84b)$$

Since the dynamic and static responses are interrelated through the spectra for the material, one can be calculated from the other using the above equations and eqs (2a and b) and (6).

9. Nonlinear Viscoelastic Behavior

Leaderman [1] found in his earlier investigations of the creep of fibers that the creep and recovery behavior were nonlinearly related to the stress, and he proposed a modification of the Boltzmann superposition principle containing an empirical function $f[\sigma(\tau)]$. However, Leaderman's modification did not explain nonlinearities later observed in the mechanical behavior of polymers. In 1960, Nakada [27, 28] (see also Greene and Rivlin [29]) proposed a theory of nonlinear responses where the excitation $\sigma(t)$ and the resulting response are related through a series of normalized orthogonal functions

$$\sigma(t) = \sum_{i=1}^{\infty} a_i \phi_i(t) \quad (85)$$

$$\epsilon(t) = \sum_{i=1}^{\infty} b_i \phi_i(t) \quad (86)$$

where the coefficients a_i and b_i are given by

$$a_i = \int_{-\infty}^{+\infty} \sigma(t) \bar{\phi}_i(t) dt \quad (87)$$

$$b_i = \int_{-\infty}^{+\infty} \epsilon(t) \bar{\phi}_i(t) dt \quad (88)$$

$\bar{\phi}_i(t)$ being the complex conjugate of $\phi_i(t)$.

If the excitation always precedes the response and if each of the coefficients, b_i 's, of the response function can be expanded by means of Taylor series in the coefficients, a_i 's, of the excitation function $\sigma(t)$, then the response function $\epsilon(t)$ can be represented by:

$$\begin{aligned} \epsilon(t) = & \int_{-\infty}^{+\infty} \sigma(t_1) J_1(t, t_1) dt_1 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t_1) \sigma(t_2) J_2(t, t_1, t_2) dt_1 dt_2 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t_1) \sigma(t_2) \sigma(t_3) \\ & J_3(t, t_1, t_2, t_3) dt_1 dt_2 dt_3 + \dots \quad (89) \end{aligned}$$

or

$$\begin{aligned} \epsilon(t) = & \int_{-\infty}^{+\infty} \sigma(t-\tau_1) J_1(t, \tau_1) d\tau_1 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t-\tau_1) \sigma(t-\tau_2) J_2(t, \tau_1, \tau_2) d\tau_1 d\tau_2 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t-\tau_1) \sigma(t-\tau_2) \sigma(t-\tau_3) \\ & J_3(t, \tau_1, \tau_2, \tau_3) d\tau_1 d\tau_2 d\tau_3 + \dots \end{aligned}$$

where $J_n(t, t_1, t_2, \dots, t_n)$ or $J_n(t, \tau_1, \tau_2, \dots, \tau_n)$ are characteristic weighting functions of the excitation-response system; where

$$J_n(t, t_1, t_2, \dots, t_n) = 0 \quad t_i > t$$

$$J_n(t, \tau_1, \tau_2, \dots, \tau_n) = 0 \quad \tau_i < 0$$

This general relationship can be applied to static as well as the dynamic response of a nonlinear viscoelastic material. It will be discussed later in this paper in respect to the nonlinear behavior of dental amalgam on which creep data were obtained. If the response of the system is stationary, the above equation takes the following form

$$\begin{aligned} \epsilon(t) = & \int_{-\infty}^{+\infty} \sigma(t-\tau_1) J_1(\tau_1) d\tau_1 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t-\tau_1) \sigma(t-\tau_2) J_2(\tau_1, \tau_2) d\tau_1 d\tau_2 \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(t-\tau_1) \sigma(t-\tau_2) \sigma(t-\tau_3) \\ & J_3(\tau_1, \tau_2, \tau_3) d\tau_1 d\tau_2 d\tau_3 + \dots \quad (90) \end{aligned}$$

where $J_n(\tau_1, \tau_2, \dots, \tau_n) = 0 \quad \tau_i < 0$

For example, if we assume a dynamic excitation of the form $\sigma(t) = \sigma_0 \cos \omega t$, then the resulting response, $\epsilon(t)$, from the above equation is

$$\begin{aligned} \epsilon(t) = & \sigma_0 [A_1 \cos \omega t + A_2 \sin \omega t] \\ & + \sigma_0^2 [B_1 \cos 2\omega t + B_2 \sin 2\omega t + B_3] \\ & + \sigma_0^3 [C_1 \cos 3\omega t + C_2 \sin 3\omega t \\ & + C_3 \cos \omega t + C_4 \sin \omega t] + \dots \quad (91) \end{aligned}$$

where

$$\begin{aligned} A_1 &= \bar{J}_1'(\omega), & A_2 &= \bar{J}_1''(\omega), \\ B_1 &= \left(\frac{\pi}{2}\right)^{1/2} \bar{J}_2'(\omega, \omega), & B_2 &= \left(\frac{\pi}{2}\right)^{1/2} \bar{J}_2''(\omega, \omega), \\ B_3 &= \left(\frac{\pi}{2}\right)^{1/2} \bar{J}_2'(\omega, -\omega), \\ C_1 &= \frac{\pi}{2} \bar{J}_3'(\omega, \omega, \omega), & C_2 &= \frac{\pi}{2} \bar{J}_3''(\omega, \omega, \omega), \\ C_3 &= \frac{3\pi}{2} \bar{J}_3'(\omega, \omega, -\omega), & C_4 &= \frac{3\pi}{2} \bar{J}_3''(\omega, \omega, -\omega). \end{aligned}$$

For step function excitation or creep where $\sigma = 0, t < 0$ or $\sigma = \sigma_0, t \geq 0$,

the above integral takes the form

$$\epsilon(t) = \sigma_0 \kappa_1(t) + \sigma_0^2 \kappa_2(t, t) + \sigma_0^3 \kappa_3(t, t, t) + \dots \quad (92)$$

This creep function was used to describe the creep response of dental amalgam [30].

10. Viscoelastic Methods Applied To Dental Materials

There are numerous reports in the literature containing data showing viscoelastic characteristics of dental materials. However, in only a few of these has there been an attempt to analyze the data in terms of rheological theory. A few examples are cited below.

The primary polymeric component of denture base resins is usually poly (methyl methacrylate), one of the dental material components to which viscoelastic methods have been applied. Both static and dynamic methods have been used to study its mechanical behavior and the relation to its chemical structure. Creep studies [31-36] and stress relaxation studies [37], as well as dynamic testing [38-42], have been reported. Denture base resins were studied mechanically by the use of stress-strain tests conducted by Barber [43] in 1934 and by Sweeney and Schoonover [44] in 1936. Their time dependent characteristics were pointed out by Sweeney, Passenbarger and Beall [45] in 1942. Later Myerson [46, 47] using the dynamic torsion pendulum method, studied the change in stiffness and damping capacity as a function of temperature and cross-linking of various methacrylates used in denture base resins and examined the transitions occurring in various methacrylates at different temperatures. Application of the dynamic torsion pendulum was later extended to the study of denture base viscoelasticity by Braden and Stafford [48] who compared the denture base polymers of vinyl acrylate with polycarbonate. They examined the shear modulus and loss tangent (damping capacity) of these polymers as a function of temperature. Static viscoelastic testing of methyl methacrylate direct filling resin and artificial teeth was carried out by W. T. Sweeney and co-workers [8, 9] using the indentation testing procedure mentioned previously.

Viscoelastic investigations of impression materials were conducted by Braden using a cylinder viscometer [49] on alginates and both a cone and plate, and a parallel plate viscometer [50] on rubber base impression materials.

Much information has been published on the flow of dental waxes [51-53], but the emphasis has been on determining temperatures at which large changes in flow rates take place, rather than in making comprehensive analyses of the viscoelastic properties of the materials.

The viscoelastic nature of dental amalgam has been recognized for many years. Data on the creep of dental amalgams for a period of up to 8 days were shown by Souder and Peters in 1919 [54], and, in fact, a flow or creep test was included in the Federal Specification for amalgam in 1926 [55]. This test would be difficult to analyze precisely since it is used as a measure of the setting time or setting rate of dental amalgam. Thus, it provides a summation of the creep of a specimen over a 21-

hour period during which the mechanical characteristics of the specimen are changing to a considerable extent.

Stress-strain measurements on dental amalgam in compression were carried out by Smith, Caul, and Sweeney [56] prior to 1956, while tensile stress-strain measurements on amalgam were conducted by Rodriquez and Dickson [57] 1960-61. Because these stress-strain measurements resulted in a nonlinear relation which depended on the strain rate, a study of tensile viscoelastic behavior of dental amalgam was undertaken using static creep tests on tensile specimens. These creep studies by Oglesby, Dickson, Rodriquez, Davenport, and Sweeney [30] showed that dental amalgam is nonlinear in its viscoelastic behavior. Strain hardened amalgam in tension was found to exhibit three types of mechanical behavior: (1) instantaneous elastic strain, (2) retarded elastic strain (transient creep), and (3) viscous strain (steady state creep). Viscoelastic theory was applied to the creep data obtained for dental amalgam to calculate the tensile stress-strain behavior. Since the amalgam creep strain was a nonlinear function of stress, the usual Boltzmann superposition principle could not be used so the nonlinear generalization of the superposition principle developed by Nakada [27] was applied. The experimental tensile stress-strain data were found to be in good agreement with that obtained by transformation of the creep data. Since the creep data indicated that the retarded elastic behavior could not be clearly separated from instantaneous elastic behavior due to short retardation times, it was necessary to employ dynamic tests to obtain the instantaneous elastic modulus.

The first method used for this purpose was the ultrasonic pulse-echo technique. Young's modulus as well as shear and bulk modulus for amalgam were determined by this technique by Dickson and Oglesby [58]. Later testing on amalgam has been carried out by Larson [59] using a forced resonance technique (50 kHz range), advantageous in measuring internal friction. Larson also measured Young's modulus obtaining values in the range of those reported by Dickson and Oglesby by the ultrasonic pulse-echo technique. Recently using the torsion pendulum in free vibration Barton and Dickson [60] measured the shear modulus as well as the damping capacity of amalgam over the temperature range 23-51 °C. They found the shear modulus to be about 3×10^6 psi, and the internal friction was found to increase with temperature in the range covered. Mahler investigated the secondary or nonrecoverable creep of amalgam [61] and found it to be related to clinical performance in the mechanical function of amalgam in the mouth. This secondary creep behavior of amalgam was studied as a function of temperature by Dickson, Oglesby, and Davenport [62]. The creep and stress-relaxation responses have been used to study the setting time of amalgam by Fuse [63].

Compressive stress-strain tests were carried out on dentin, by Peyton, Mahler, and Hershenov [64] and again later by Craig and Peyton [65]. In this work Craig and Peyton also conducted compressive creep tests on human dentin. Dentin was shown to be a viscoelastic material with a yield point above which it appears to exhibit (1) instantaneous elastic strain, (2) retarded elastic strain, and (3) viscous strain, but below the yield point only the first two phenomena are observed. Work on the creep behavior of dentin should be extended in order to analytically describe the viscoelastic behavior in compression and then using the appropriate transformations, the correspondence between the compressive stress-strain and creep behavior should be demonstrated. These data could then be compared with that obtained by stress relaxation experiments and dynamic experiments accounting for anisotropy effects. In 1968, Lugassy and Korostoff [66, 67] reported an experiment using stress relaxation techniques in dentin in which they studied the viscoelastic properties in relation to structural anisotropy and compared the results to polymer viscoelasticity. Recently Barton and Dickson [60] have used the torsion pendulum to determine the moduli and the damping capacity of dentin at mouth temperature as well as at room temperature.

Little work has been done in the relation of the viscoelastic behavior of dental materials and tissues in relation to their atomic, molecular, and microstructural properties and processes; yet there is a large amount of theory and experimental technology that could be brought to bear. Two works in the dental field in relation to microproperties are Myerson's work [46, 47] on methacrylate cross-linking in respect to mechanical properties and the work of Dickson and Oglesby [62] on the steady-state creep of amalgam and the determination of the activation energy of the process.

11. References

- [1] Leaderman, H., *Elastic and Creep Properties of Filamentous Materials and Other High Polymers*, (The Textile Foundation, Washington, D.C., 1943).
- [2] Catsiff, E., and Tobolsky, A. V., Stress-relaxation of polyisobutylene in the transition region (1, 2), *J. Colloid Sci.* **10**:375 (1955).
- [3] Ferry, J. D., *Viscoelastic Properties of Polymers* (John Wiley and Sons, Inc., New York, 1961).
- [4] Gross, B., *Mathematical Structure of the Theories of Viscoelasticity* (Hermann, Paris, 1953).
- [5] Leaderman, H., Viscoelasticity phenomena in amorphous high polymeric systems. Chapter 1 in *Rheology*, Vol. 2, Eirich, F. R., Ed. (Academic Press, Inc., New York, 1958).
- [6] Lee, E. H., and Radok, J. R. M., The contact problem for viscoelastic bodies, *J. Appl. Mech.* **27**:438 (Sept. 1960).
- [7] Nolt, I. G., and Meier, J. A., On the spherical indenter as a means for determining viscoelastic material functions, *Proceedings of the Fourth International Congress on Rheology*, Part 2, Lee E. H., Ed., pages 167-181 (Interscience Publishers, New York, 1965).
- [8] Sweeney, W. T., Sheehan, W. D., and Yost, E. L., Mechanical properties of direct filling resins, *J. Am. Dent. Assoc.* **49**:513 (Nov. 1954).
- [9] Sweeney, W. T., Yost, E. L., and Fee, J. G., Physical properties of plastic teeth, *J. Am. Dent. Assoc.* **56**:833 (June 1958).
- [10] Merriam, C. W. III, Mathematics for linear systems, Chapter 4, in *Control Systems Engineering*, Seifert, W. W., and Steeg, C. W., Ed. (McGraw-Hill, New York, 1960).
- [11] Roesler, F. C., Some applications of Fourier series in the numerical treatment of linear behavior, *Proc. Phys. Soc.* **B68**:89 (1955).
- [12] Kolsky, H., *Stress Waves in Solids*, Chapter 5 (Oxford University Press, London, 1953).
- [13] Buchdahl, R., The rheology of organic glasses, Chapter 4, *Rheology*, Vol. 2, Eirich, F. R., Ed. (Academic Press, Inc., New York, 1958).
- [14] Nielsen, L. E., A recording torsion pendulum for the measurement of the dynamic mechanical properties of plastics and rubbers, *Rev. Sci. Instr.* **22**:690 (Sept. 1951).
- [15] Nolle, A. W., Methods for measuring dynamic mechanical properties of rubber-like materials, *J. Appl. Phys.* **19**:753 (1948).
- [16] Tobolsky, A. V., and McLaughlin, J. R., Elastoviscous properties of polyisobutylene, V. The transition region, *J. Polymer Sci.* **8**:543 (1952).
- [17] Ferry, J. D., Mechanical properties of substances of high molecular weight, VI. Dispersion in concentrated polymer solutions and its dependence on temperature and concentration, *J. Am. Chem. Soc.* **72**:3746 (1950).
- [18] Fox, T. G., and Flory, P. J., Viscosity-molecular weight and viscosity-temperature relationships for polystyrene and polyisobutylene, *J. Am. Chem. Soc.* **70**:2384 (1948).
- [19] Tobolsky, A. V., and Andrews, R. D., Systems manifesting superposed elastic and viscous behavior, *J. Chem. Phys.* **13**:3 (1945).
- [20] Andrews, R. D., Hofman-Bang, N., and Tobolsky, A. V., Elastoviscous properties of polyisobutylene, I. Relaxation stress in whole polymer at different molecular weights at elevated temperature, *J. Polymer Sci.* **3**:669 (1948).
- [21] Williams, M. L., Landel, R. F., and Ferry, J. D., The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids, *J. Am. Chem. Soc.* **77**:3701 (1955).
- [22] Bueche, F., *Physical Properties of Polymers*, (Wiley Interscience, New York, 1962).
- [23] McCrum, N. G., and Morris, E. L., On the measurement of the activation energies for creep and stress relaxation, *Proc. Roy. Soc.* **A281**:258 (1964).
- [24] Alfrey, T., *Mechanical Behavior of High Polymers*, p. 551 (Interscience, New York, 1948).
- [25] Nielsen, L. E., *Mechanical Properties of Polymers* (Reinhold, New York, 1962).
- [26] Schwarzl, F., and Staverman, A. J., Higher approximation methods for the relaxation spectrum from static and dynamic measurements of viscoelastic materials, *Appl. Sci. Res.* **A4**:127 (1953).
- [27] Nakada, O., Theory of non-linear responses, *J. Phys. Soc. Japan* **15**:2280 (1960).
- [28] Leaderman, H., McCrackin, F., and Nakada, O., Large longitudinal elastic deformation of rubberlike network polymers. II. Application of a general formulation of non-linear response, *Trans. Soc. Rheo.* **7**:111 (1963).
- [29] Greene, A. E., and Rivlin, R. S., The mechanics of nonlinear materials with memory, *Arch. Rational Mech. Anal.* **1**:1 (1957).

- [30] Oglesby, P. L., Dickson, G., Rodriguez, M. L., Davenport, R. M., and Sweeney, W. T., Viscoelastic behavior of dental amalgam. *J. Res. Nat. Bur. Stand. (U.S.)*, 72C (Eng. and Instr.) No. 3, 203-213 (July-Sept. 1968).
- [31] MacLeod, A. A., Design of plastic structures for complex static stress systems, *Ind. Eng. Chem.* 47:1319 (1955).
- [32] Weber, C. H., Robertson, E. N., and Bartoe, W. F., Time- and temperature-dependent modulus concept for plastics, *Ind. Eng. Chem.* 47:1311 (1955).
- [33] Fukada, E., On the relation between creep and vibrational loss of polymethylmethacrylate, *J. Phys. Soc. Japan* 6:254 (1951).
- [34] McCrackin, F. T., and Bersch, C. F., Creep behavior of transparent plastics at elevated temperatures, *Soc. Plastics Eng. J.* 15:791 (1959).
- [35] Thompson, E. V., Secondary processes of poly-(methyl methacrylate) and their activation energies as determined by shear and tensile creep compliance measurements, *J. Polymer Sci. Part A-2* 6:433 (1968).
- [36] Bueche, F., Viscoelasticity of polymethacrylates. *J. Appl. Phys.* 26:738 (1955).
- [37] McLaughlin, J. R., and Tobolsky, A. V., The viscoelastic behavior of polymethyl methacrylate, *J. Colloid Sci.* 7:555 (1952).
- [38] Deutsch, K., Hoff, E. A., and Reddish, W., Relation between the structure of polymers and their dynamic mechanical and electrical properties, Part I. Some alpha-substituted acrylic ester polymers, *J. Polymer Sci.* 13:565 (1954).
- [39] Heyboer, J., Dekking, P., and Staverman, A. J., The secondary maximum in the mechanical damping of polymethyl methacrylate: Influence of temperature and chemical modifications, Chapter 14. *Proceedings of the Second International Congress on Rheology*. Harrison, V. G. W., Ed. (Butterworths Scientific Pub., London 1954).
- [40] Koppelman, J., Über den dynamischen Elastizitätsmodul von Polymethacrylsäuremethylester bei sehr tiefen Frequenzen. *Kolloid Z.* 164:31 (1959).
- [41] Nielsen, L. W., Dynamic mechanical properties of high polymers, *Soc. Plastics Eng. J.* 16:525 (1960).
- [42] Schmieder, K., and Wolf, K., Über die Temperatur- und Frequenzabhängigkeit des mechanischen Verhaltens einiger hochpolymerer Stoffe. *Kolloid Z.* 127:65 (1952).
- [43] Barber, Ronald, Preliminary tests of some of the newer denture materials, *J. Am. Dent. Assoc.* 21:1969 (1934).
- [44] Sweeney, W. T., and Schoonover, I. C., A progress report on denture base material, *J. Am. Dent. Assoc.* 23:1498 (1936).
- [45] Sweeney, W. T., Paffenbarger, G. C., and Beall, J. R., Acrylic resins for dentures, *J. Am. Dent. Assoc.* 29:7 (1942).
- [46] Myerson, R. L., The Internal Friction of Linear and Crosslinked Phosphate Glasses and Methacrylate Polymers. M.I.T. Master's Thesis. May 1961.
- [47] Myerson, R. L., Effect of crosslinking on mechanical damping and stiffness of methacrylates, *IADR Abstracts, Fortieth General Meeting*, p. 89, (1962).
- [48] Braden, M., and Stafford, G. D., Viscoelastic properties of some denture base materials, *J. Dent. Res.* 47:519 (1968).
- [49] Fish, S. F., and Braden, M., Characterization of the setting process in alginate impression materials, *J. Dent. Res.* 43:107 (1964).
- [50] Braden, M., Viscosity and consistency of impression rubbers, *J. Dent. Res.* 46:429 (1967).
- [51] Craig, R. G., Eick, J. D., and Peyton, F. A., Properties of natural waxes used in dentistry, *J. Dent. Res.* 44:1308 (1965).
- [52] Ohashi, M., and Paffenbarger, G. C., Melting, flow and thermal expansion characteristics of some dental and commercial waxes, *J. Am. Dent. Assoc.* 72:1141 (1966).
- [53] Ohashi, M., and Paffenbarger, G. C., Some flow characteristics at 37 °C of ternary wax mixtures that may have possible dental uses, *J. Nihon Univ. Sch. Dent.* 11:109 (1969).
- [54] Souder, W., and Peters, G. C., Investigation of the physical properties of dental materials, *Dental Cosmos* 62:305 (1920).
- [55] Souder, W., Measurement and application of certain physical properties of dental materials, *J. Dent. Res.* 7:173 (1927).
- [56] Smith, D. L., Caul, H. J., and Sweeney, W. T., Some physical properties of gallium-copper-tin alloys, *J. Am. Dent. Assoc.* 53:677 (1956).
- [57] Rodriguez, M. S., and Dickson, G., Some tensile properties of amalgam, *J. Dent. Res.* 41:840 (1962).
- [58] Dickson, G., and Oglesby, P. L., Elastic constants of dental amalgam, *J. Dent. Res.* 46:1475 (1967).
- [59] Larson, R. V., Internal Friction Damping in Dental Amalgam. Thesis, Dept. of Mechanical Engineering, University of Utah, August 1967.
- [60] Barton, J. A. Jr., Dickson, G., and Oglesby, P. L., Determination of properties of dental materials by means of a torsion pendulum, *IADR Program and Abstracts of Papers*, p. 172 (March 1968).
- [61] Mahler, D. B., and Von Eysden, J., Dynamic creep of dental amalgam, *J. Dent. Res.* 48:50 (1969).
- [62] Dickson, G., Oglesby, P. L., and Davenport, R. M., The steady state creep behavior of dental amalgam, *J. Res. Nat. Bur. Stand. (U.S.)*, 72C (Eng. and Instr.), No. 3, 215-229 (July-Sept. 1968).
- [63] Fuse, N., Flow, stress relaxation and compressive strength of dental amalgam, *Bull. Tokyo Med. and Dent. Univ.* 16:17 (1969).
- [64] Peyton, F. A., Mahler, D. B., and Hershenov, B., Physical properties of dentin, *J. Dent. Res.* 31:366 (1952).
- [65] Craig, R. G., and Peyton, F. A., Elastic and mechanical properties of human dentin, *J. Dent. Res.* 37:710 (1958).
- [66] Lugassy, A. A., and Korostoff, E., Comparative viscoelastic properties of dentin and bone, *IADR Program and Abstracts*, 46th General Meeting, p. 99 (March 1968).
- [67] Lugassy, A. A., Mechanical and Viscoelastic Properties of Cow Bone and Sperm Whale Dentin Studied under Compression. Thesis, Graduate School of Arts and Sciences, University of Pennsylvania (1968).

Low Frequency Determination of Mechanical Properties

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The torsion pendulum is a valuable tool for use in determining the mechanical properties and molecular structure of dental materials. With the torsion pendulum the modulus of a material may be determined from the frequency of oscillation; the internal friction can be obtained from the rate of damping. Change in internal friction with change in frequency provides insight into type of structure and relaxation mechanisms. Activation energy of processes can be determined from shift in peak energy absorption temperature with change in frequency. A principal advantage of low frequency testing is in the resolution of dispersions or of internal friction peaks. The torsion pendulum method has been applied to various polymer materials in studies of the relationship of composition and transitions, effects of cross-linking, comparison of cast poly (methyl methacrylate) and powder-liquid molded poly (methyl methacrylate) and the relationship of impact resistance to peak energy absorption temperatures. Studies have been made of the relationships between peak temperatures and composition and cross-linking in sodium phosphate glasses. A review of equipment is presented.

Key words: Activation energy; dental materials; glass, sodium phosphate; internal friction; mechanical properties; polymers, dental; torsion pendulum.

1. Introduction

The focus of this report is to be on the use of the low frequency mechanical properties as a tool for analyzing the molecular structure of the materials being considered. The emphasis will be on the torsion pendulum. With the torsion pendulum one can determine the modulus of a material by observing the frequency of oscillation. The internal friction of a material is obtained from the rate of damping. By noting the change in values of internal friction with changes in frequencies, one can gain insight into the type of structure and the relaxation mechanisms. The activation energy of the processes involved can be determined from the shift in peak temperature with change in frequency.

If the internal friction of a material is plotted versus temperature for a fixed frequency of oscillation, there is usually a general rise in the value with a rapid increase in the area of softening. There will often be maxima at various lower temperature points. For silicate ceramics the lowest temperature peak has been usually ascribed to an alkali ion diffusion under stress, an intermediate peak to oxygen ion diffusion, and finally the high temperature peak to visco-elastic motion. In polymers these peaks at the lowest temperature have been ascribed to side chain motion and/or very local motion on the main backbone chain [1].¹ The higher temperature peaks are usually caused by softening of the material or by the melting of

crystallites in the case of a crystalline or semi-crystalline material.

Braden and Stafford [2] reviewed the viscoelastic properties of some denture base materials using a torsion pendulum at less than one cycle per second. They determined glass transition temperatures which are important in setting a limit of temperature to which a material can be safely exposed in cleaning, repair, etc. They determined the shear modulus with good agreement to calculations made from the tensile modulus. Finally they determined the internal friction spectrum from +20 °C to +105 °C. They concluded that some of the materials of high impact resistance gained their impact resistance by sacrifice of the glass transition temperature, which limited their higher temperature usefulness. One impact resistant material also had a higher internal friction. The authors stated that this might mean less elastic behavior.

I suggest that the value of $\tan \delta$ (internal friction) as an indication of specific end use properties might be misleading. First of all, the experimentation is done with very small strains operating in the linear viscoelastic range. Most stresses that are damaging will, of course, involve larger strains and will be nonlinear. Secondly, the loss component in plastics may be due to side chain motion rather than main chain motion, and this would probably reflect itself in retarded elasticity rather than in creep. A significant use of the internal friction spectrum is as a means of characterizing a material. It will provide some indication of the

¹ Figures in brackets indicate the literature references at the end of this paper.

likelihood of a build-up of heat during a cyclic loading. It provides a signal that there may or may not be creep under long term steady state loading by identification of relaxation processes and the time-temperature effects.

The energy absorption patterns versus frequency and temperature will yield information that, in part at least, is attributable to molecular structure specifics. By controlled experiments—as examples, varying the composition of a copolymer or the alkali ion ratio in ceramics—and by use of other information such as diffusion data, dielectric losses, etc., the peaks of energy absorption can be identified. Then the effect of the degree of polymerization or degradation or devitrification, etc., can be better understood by observing the internal friction spectrum changes.

An important consideration is the background level of internal friction apart from the peaks. The background gives an indication of the general molecular mobility. In the case of a completely cross-linked glass—i.e., fused quartz—there is virtually zero damping.

2. A Contrast of High and Low Frequency Testing

It is of interest to contrast the use of high and low frequency testing. Each has advantages, and the use of both high and low frequency measurements will give very valuable data relative to the activation energy of phenomena because of the large spread in rate of loading. There are also, of course, some very specific properties of importance in the end use for which damping properties measured at one end of the spectrum would be more important. The principal advantage of low frequency testing is in the resolution of dispersions or of internal friction peaks. The lower temperature peaks are usually of lower activation energy, and as the frequency is increased, they shift to higher temperatures at a more rapid rate than the higher frequency peaks. At sufficiently high frequencies this will lead to a blending of peaks.

Nielsen [1] points out that the torsion pendulum is useful over a very wide range of moduli, and from very low frequencies to moderately high. He felt the best frequency range was from a 100th of a cycle per second to 10 cycles per second.

For determining low frequency damping data there are three general types of equipment. The first, and the one which will be emphasized in this paper, is the freely oscillating pendulum operating at the system resonance. A second type is a driven system involving its natural resonance, such as a vibrating reed. Here the internal friction is determined by the shape of the amplitude versus frequency curve in the resonance area. The third type, a driven nonresonant rotating beam, developed by Maxwell, will be discussed briefly below.

3. Theoretical Aspects and Interpretation of Torsion Pendulum Data

The theoretical aspect of an oscillating stress as applied for a torsion pendulum has been well covered in the literature, and suitable references are included with this paper. Because of limitations of space, only the conclusions, with a minimum of the background, will be presented here.

In the Voigt solid (fig. 1), a model of a viscoelastic solid is presented. The relationship of stress and strain for such a solid is as shown in eq 1.

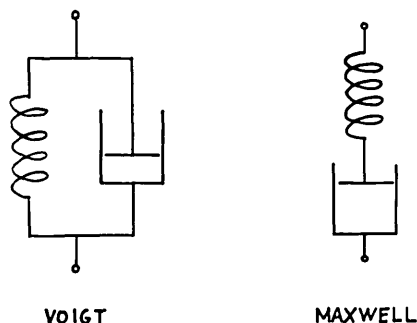


FIGURE 1. Voigt and Maxwell models for mechanical behavior.

$$\sigma = E\epsilon + \eta \frac{d\epsilon}{dt} \quad (1)$$

where:

$$\begin{aligned} \sigma &= \text{stress} \\ E &= \text{elastic modulus} \\ \epsilon &= \text{strain} \\ \eta &= \text{viscosity} \end{aligned}$$

It can be seen that if a force is cyclic (sinusoidal) the term for the elastic component will be in phase, whereas the viscous flow term will be 90° out of phase.

In a real solid, the resultant complex shear modulus of G^* will be the resultant of the real part of the solution, G' (representing the elastic portion) and the 90° out-of-phase, imaginary portion, G'' as is shown in figure 2.

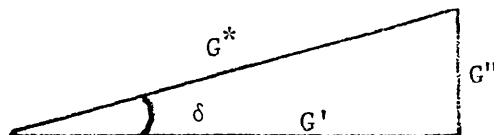


FIGURE 2. Relation of $\tan \delta$ to G' and G'' .

The angle δ represents the lag of the strain to stress. $\tan \delta$ is equal to G''/G' .

Zener [3] showed that for a given temperature, $\tan \delta$ is a maximum when the mean relaxation time (the mean of constant stress relaxation time and constant strain relaxation time) is equal

to $\frac{1}{2\pi F}$, where F is frequency. Thus, if the temperature is held constant and the frequency of loading varied, at one frequency there will occur a maximum in the damping. This will yield the relaxation time of the material at this temperature.

Zener also developed the equation for $\tan \delta$ as a function of the log decrement of the amplitude. The equation was arrived at by considering the rate of energy dissipation per unit volume (in the range where $\tan \delta$ is approximately equal to $\sin \delta$). He arrived at eq 2:

$$\tan \delta = \frac{\ln A_0/A_n}{n\pi} \quad (2)$$

A_0 is the initial amplitude; A_n is the amplitude after n cycles.

3.1. Activation Energies

Since the relaxation phenomena express rate processes that are temperature dependent, the activation energy can be determined by testing at several frequencies. If a viscoelastic solid is tested at a constant frequency, there will be a temperature showing a maximum in damping. By testing at several frequencies and determining the peak temperatures, the activation energy can be determined for a specific relaxation process by eq 3.

$$\frac{1}{2\pi F} = \tau = \tau_0 e^{E/RT} \quad (3)$$

Where: F =frequency
 τ =relaxation time
 E =activation energy
 R =gas constant
 T =absolute temperature

The in-phase component or the elastic component of the complex modulus stores energy as potential recoverable energy. The out-of-phase imaginary component results in an energy loss, principally in internal heat.

For real materials there is no single relaxation time as would be calculated for a simple Voigt solid. There will exist a distribution of relaxation times, hence a range of temperatures showing high damping for a single frequency. Ryder [4] pointed out that the area under a peak of $\tan \delta$ versus temperature curve will be related to a number of diffusing species. For the same number of diffusing elements a narrow distribution of relaxation times will result in a high narrow peak compared to a low broad peak for a broad distribution of relaxation times. The effect of changing compositions can, therefore, be reviewed for this factor as well as the locations of the peaks.

Fitzgerald [5, 6] listed some of the sources of energy loss in ceramic materials. He included:

1. Flow of heat
2. Diffusion of ionic species

3. Elasticoviscous effects
4. Viscous flow
5. Precipitated crystallites

For the typical alkali silicate ceramic there is a distinct $\tan \delta$ peak around room temperature that has been associated with the diffusion under stress of the sodium ion. A higher peak has been associated with the nonbridging oxygen ion. The elasticoviscous effects he relates to movements of large segments of the glassy network as the transformation region is approached. He explained the diffusion of the sodium ion by considering that under a stress there will be a redistribution of electrical charges, and in this way the equilibrium position of the sodium ion will shift. In some cases the ion must get past an obstacle in order to reach its new equilibrium position. The particles with sufficient energy will be able to get past an obstacle. The distribution of particle energy is related to temperature. Thus the diffusion rate will be temperature dependent and the typical activated process equations will result.

Kirby [7] showed that soda lime glasses and borosilicates have distinct peaks and different background values. Of interest was that fused silica, which has nonbridging oxygen ions and, of course, no alkali or alkaline earth ions, has extremely low damping coefficient until the elasticoviscous effects are reached. Blum [8] in a very carefully controlled experiment showed a value of 0.000012 for $\tan \delta$.

Forry [9] worked with three compositions of soda in sodium silicate glasses. As the soda percentage is increased, the low temperature peaks occurred at lower temperature, were higher, and were sharper. He found the height above background was almost linear with soda content, extrapolating to zero at about 10 percent soda content.

Hoffman and Weyl [10] reviewed the effect of alkali and alkaline earth oxide on silicate glasses. They found that lithium had the highest activation energy (the smallest ion and thus the most tightly bound), sodium the next, and potassium the lowest. The alkaline earth oxide additives, because they have network bridging properties, tighten the structure and suppress the alkali diffusion peak.

Shelby and Day [11] studied the effect of mixed alkalis and silicate glasses. Figure 3 shows some of their findings. As the second alkali is added, the alkali peak shifts to a higher temperature and becomes smaller. The nonbridging oxygen peak became slightly higher. A new damping peak, large and close to the nonbridging ion peak, was developed and, in fact, can mask it. From their work they found that it is easy to detect a small amount of a second alkali.

Fitzgerald [12] showed the effect of annealing versus chilling of sodium silicate glasses. In the annealed state—that is, the tighter structure state—the activation energy for the sodium ion

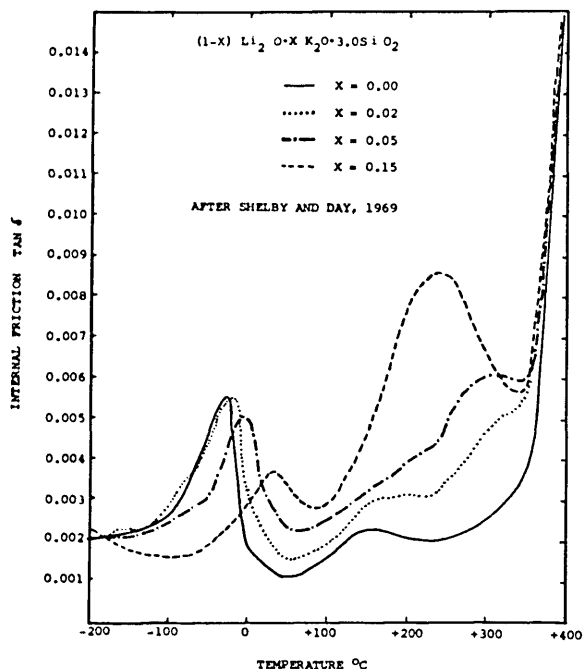


FIGURE 3. Internal friction of mixed alkali-silicate glasses.

diffusion was 20 kilocalories per mole versus 16 kilocalories per mole for the chilled glass, thus giving some indication of the effect of annealing on the network.

3.2. Viscoelastic Behavior

Fichter [13] listed a number of possible causes of viscoelastic relaxation damping for metals. These include:

1. Interfaces and grain boundaries.
2. Changes in lattice order due to stress.
3. Magnetoelasticity, particularly in ferromagnetic materials.
4. Phase changes (a function of local temperature).
5. Precipitation and recrystallization.

Nowick [14] also reviewed anelastic phenomena with emphasis on metals. He cited the example of aluminum where there is a substantial peak in $\tan \delta$ at low frequency at about 300 °F (150 °C) in a polycrystalline material. This peak is absent in a single crystal. He attributes this to viscoelastic behavior in the grain boundaries.

Kaelble [15] presented the diagram in figure 4 giving an overview of the phenomena in polymers. The plot is of modulus versus temperature at constant frequency. The relaxations accompanied by changes in modulus level will also be accompanied by peaks in the internal friction curve. At the very low temperature, polymer strain in response to stress is due to primary bond angle bending and stretching. Hence there is no diffusion and this

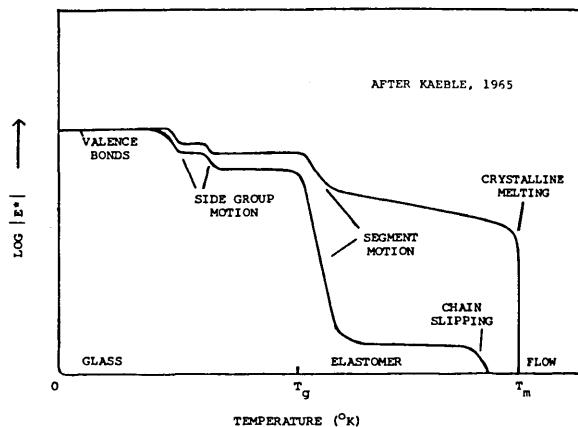


FIGURE 4. Modulus of polymers as a function of temperature at constant frequency.

results in very low internal friction and high modulus. As the temperature is increased, side chain motion or very local chain motion can take place and the modulus will go down. At the glass transition temperature, segments of the chain will start in motion and there will be a large drop in modulus. There will be a rubbery plateau above the glass transition temperature, depending on the degree of cross-linking and the molecular weight. The last reduction in modulus above the glass transition temperature for amorphous materials comes when the chains themselves actually slip as in molding. This region is very dependent on cross-linking, and if the material is cross-linked the slippage does not occur until decomposition starts. For linear materials, if there is high molecular weight, entanglements will act as temporary cross-linking sites and will raise the temperature of the slip point. In the case of crystalline materials, the glass transition temperature is not accompanied by a great change in modulus until the crystallites melt.

Boyer [16], in discussing the plastic transitions below the glass transition temperature, lists the following:

- (a) Side chain group motion such as the ester groups in polyalkyl methacrylates.
- (b) In-chain motions of subgroups as in the polycarbonates.
- (c) "Crank shaft" motion as in polyethylene when there are about four consecutive methylene groups.

He describes the glass transition temperature phenomenon as large "crank shaft" motions involving 30 to 40 carbons in the chain. Above the glass transition temperature the transitions occur with coordinated motions of entire chains.

McCrum et al. [17] point out that the assignment of mechanisms of relaxation to polymers has been done qualitatively by experiments rather than quantitatively. The convention used for polymeric materials is that the alpha peak is the highest

temperature, and beta the next lowest, etc. With the amorphous materials the alpha peak is usually the glass transition temperature when there is a modulus change of three orders of magnitude or more. The lower temperature transitions are due to the local motions in the polymers while they are still in the glass-like condition; that is, the larger segments of the chains are frozen in the glassy state, but the small groupings, are able to move above their own transition temperatures. In partially crystalline materials, such as polyethylene, the alpha peak is usually the melting of the crystallites and the beta the glass transition temperature of the amorphous phase. Thus the magnitude of this peak will be affected by the degree of crystallinity, and indeed this can be used as a measure of the degree of crystallinity in a study of a particular polymer. McCrum mentions that there is a low temperature absorption peak in nylons and methacrylates due to absorbed impurities (e.g., water). He also suggests that the "crank shaft" motion can be applied to other groupings in a chain other than four methylenes, provided they allow simultaneous rotation of two colinear bonds to give the "crank shaft" effect.

Nielsen [1] gives a qualitative picture for the energy absorption at the transition of a polymer, wherein as the temperature increases, frozen segments start to move. Below that temperature the damping is low because deformation is bond angle bending, and hence highly elastic with little heat dissipation. At temperatures well above the transition, damping is low because the chain segments are free to move, but the resistance is low and hence the modulus is low. Thus if the segments involved are either frozen or very free to move, damping would be low. The damping peak will occur at the intermediate condition.

Nielsen [18] points out that in polymeric materials, damping losses will be affected by the following:

- Crystallinity
- Cross-linking
- Number of phases
- State of aggregation
- Various chain motions

Deutsch et al. [19] noted that plasticizers, residual monomer, absorbed water, etc., complicated the systems.

3.3. Internal Friction and Copolymerization

Internal friction measurements are useful for the interpretation of copolymerization. If the starting materials are comonomers of close reaction rates, the end product will be homogenous with a distribution of effects such as glass transition temperature intermediate between the end members. The sharpness of the $\tan \delta$ versus temperature peaks will tend to be intermediate between the end members. McCrum, et al. [17] show in figure 5 the additive nature of a series of

copolymers of methyl and cyclohexyl methacrylate. The change in the nature of the curves is nearly quantitatively additive. Poly(methyl methacrylate) has no low temperature peak but a broad beta peak in the 40 °C region, whereas polycyclohexylmethacrylate has a similar glass transition temperature to poly(methyl methacrylate) and a low temperature beta peak below 0 °C. The intermediate copolymers are intermediate in both these respects. The glass transition temperature is relatively unchanged since the end members were similar.

Nielsen [1, 20] pointed out that if the rates of reaction are unequal, the initial polymer formed will be rich in the faster reacting material, and the final polymer formed rich in the slower material. This will result in broader and lower peaks than in homogenous copolymers.

With graft or block polymers, where there are two separate phases insoluble in each other present, the resultant $\tan \delta$ versus temperature curve will show the separate features of each phase in proportion to their concentration. Similarly, polyblends made by mechanical mixing will show the character of both phases.

Deutsch et al. [19] in comparing methyl methacrylate and methyl α -chloro-acrylate, showed that in replacing the methyl group with the more polar substituent, the glass transition temperature increased from 110° C to 140° C in the case of the methyl α -chloro-acrylate. Also, the beta peak temperature was increased and the activation energy of this peak significantly increased due to the stronger interchain bonding caused by the polar group.

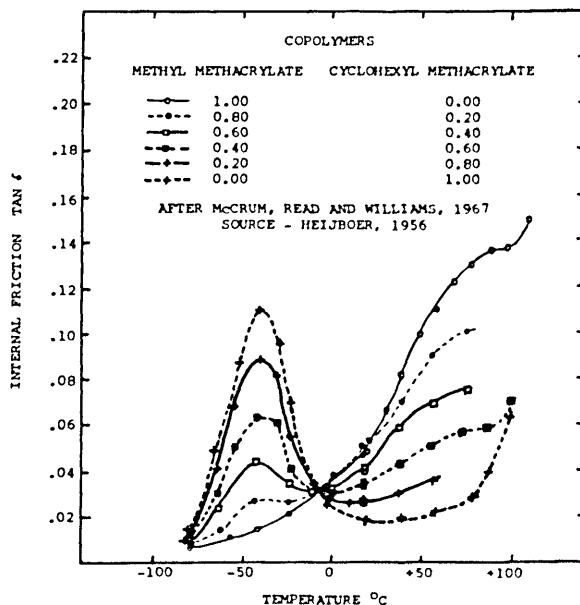


FIGURE 5. Relation of $\tan \delta$ to temperature for varying methacrylate copolymer ratios.

3.4. Impact Resistance and Low Temperature Peaks

Many authors [1, 21-26] have considered the relationship between the presence of a low temperature peak in a rigid material and impact strength. In early observations there seemed to be a correlation between the presence of such a peak and impact resistance. Later data show that the low temperature peak is neither a necessary nor sufficient condition for impact resistance. However, it is of significance in many cases and can lead to an interpretation of the mechanisms involved.

Matsuoka [25] in his review of the dynamic properties of glassy and partly crystalline materials versus impact resistance, points out that in polymers, ahead of a propagating crack tip, there is plastic deformation. The greater this deformation the more energy is required to propagate a crack and the tougher the material will be. The low temperature transition signifies molecular motion and should relate to impact resistance. However, low temperature peaks due to side chain motion do not relate to the ability of the chains to draw under stress and, hence, are not related to impact resistance. Peaks due to local motion in the main chains are related to impact resistance.

In partially crystalline materials the beta peak usually signifies the glass transition temperature of the amorphous phase, and thereby molecular motion. These materials have good impact resistance between the glass transition temperature and the temperature corresponding to the alpha peak indicative of the melting of the crystallites.

The relationship between the secondary low temperature peak and impact resistance is indirect. When it signifies side chain motion, as in a cyclohexyl methacrylate, it is of no significance. In mixtures of two materials (or in some block and graft copolymers) wherein there are two phases, if one phase is a rubber there will be a low temperature peak. This does not necessarily mean impact resistance. If the rubbery particles are of the proper size and distribution and well bonded to the matrix, they will nucleate drawing of the glassy phase under stress and impart impact resistance.

Heijboer [23] and Turley [22] point out that the relation between the temperature of the peak and the tough brittle transition is not clear. Also, as in the case of poly(2-6 dimethyl-p-phenylene oxide), one can have impact resistance with no low temperature peak. It should be borne in mind in the correlation of $\tan \delta$ and impact resistance, that the torsion pendulum data is in the linear viscoelastic range, whereas impact failures involve large scale molecular movement.

3.5. Composites, Crosslinking, and Orientation

Maeda [27] and Galperin [28] show that in the case of composites there is a tendency towards a decrease in the height of the $\tan \delta$ peak and an

increase in the temperature of the $\tan \delta$ peak relative to the matrix resin.

Reinhardt [29] was concerned with the means of measuring the progress of the final stages of cross-linking that would be more meaningful than some of the indirect physical property tests. The validity of the chemical tests for unsaturation is doubtful because of the insolubility of the cross-linked polymers. His study was based on dynamic mechanical tests with specimens of varying cure. During the termination of cure, as the network lightens there is an asymptotic increase in modulus and a decrease in $\tan \delta$. He showed that curing for 2 hr at 100° C produces a higher modulus and lower $\tan \delta$ (presumably more cross linking) than in the self-curing system cured 500 hours at 35 °C.

Malpass [30] showed that high strains (orientation in the polymer) produced a definite peak that correlated with physical properties (they helped when in the direction of the stress, but were detrimental when at 90° to the stress). Annealing eliminated these peaks and brought the properties in line with the normal material.

4. Experimental Results

4.1. Glasses

A series of tests on sodium phosphate glasses were conducted by this author [31]. The glasses were drawn into fibers and internal friction versus temperature curves made at frequencies around one cycle per second. Sodium phosphate glasses will vary in structure depending on the ratio of sodium oxide to phosphorous pentoxide. When the molar ratio is 1, the theoretical structure will be a long chain. As the ratio becomes greater than 1, chains become shorter and shorter. If the ratio is less than 1—that is, the molar proportion of phosphorous pentoxide is greater than the molar proportion of sodium oxide—the structure is cross-linked. The greater the percentage of phosphorous pentoxide, the greater the degree of cross-linking.

In the sodium phosphate glasses the backbone structure is an alternating series of oxygen phosphorous atoms. Each phosphorous atom is surrounded by four oxygen atoms, three of which are capable of bonding with another phosphorous or sodium atom, and the fourth is a nonbridging oxygen atom with a double bond to the phosphorous. Thus there is present in this structure the sodium ion and the nonbridging oxygen ion as in the sodium silicate glasses. In figure 6 it can be seen that there are indeed two peaks below the glass transition temperature; the lowest temperature peak is probably the sodium ion diffusion peak, the intermediate the nonbridging oxygen ion. As the sodium to phosphorous ratio is dropped, the low temperature peak drops. Conversely, as the sodium to phosphorous ratio drops, the medium temperature peak increases in height. Both of these phenomena are in line with the fact that as the

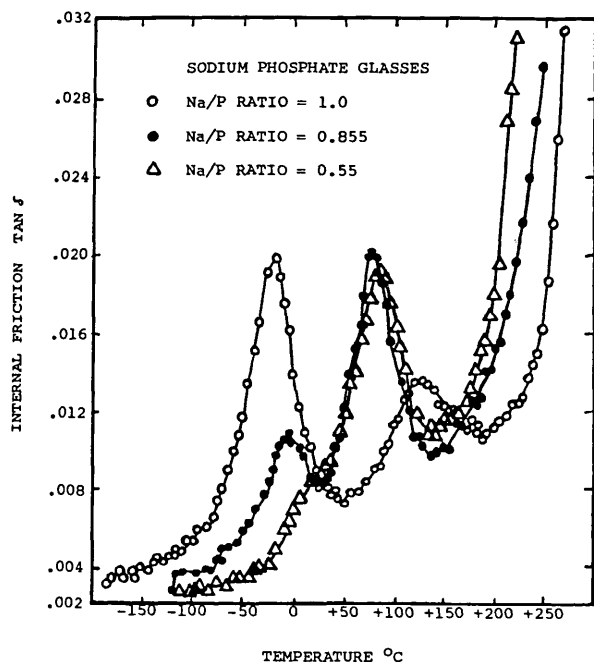


FIGURE 6. Internal friction of glasses with varying Na/P ratios.

sodium to phosphorous ratio decreases, the sodium ion concentration decreases, but the nonbridging oxygen ion concentration increases.

It is of interest to note that the glass transition temperature goes down as the phosphorous pentoxide content goes up and as the cross-linking goes up, contrary to what is seen in organic glasses. This suggests that the sodium ion, in coordination with oxygen ions of other chains, bonds the chains more strongly than does the actual chain cross-linking. This is supported by the data of van Wazer and Holst [32] who found that when three oxygens were shared with other PO_4 tetrahedra the compound was less stable than when only two or one oxygens were shared with other PO_4 tetrahedra.

4.2. Polymers

Work done by this author on the effect of cross-linking with a hexyl methacrylate-ethylene dimethacrylate system was presented to the Dental Materials Group of the International Association for Dental Research in 1962 [31-33]. Figure 7 shows the salient features of that series of tests. There is a reduction in background as cross-linking increases. For the hexyl methacrylate formulations there is a low temperature dispersion off scale—that is, around -200°C —probably related to the hexyl group. There appears to be, in the hexyl methacrylate, a beta peak at about -100°C . The glass transition temperature was raised considerably by addition of 25 percent ethylene dimethacrylate. It should be noted in this case that there is a very broad peak, possibly similar to the

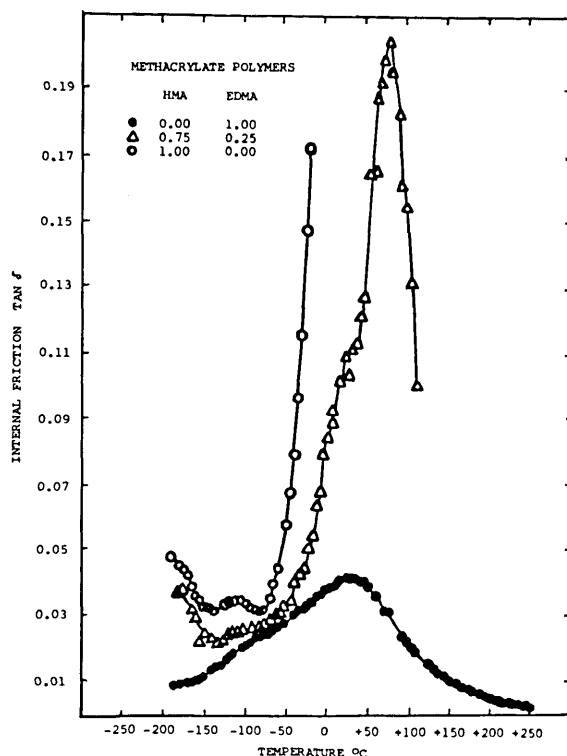


FIGURE 7. Internal friction as effected by crosslinking in a hexyl methacrylate-ethylene dimethacrylate system.

beta peak of methyl methacrylate at about 40°C . The internal friction in the rubbery region falls off to a low value, lower than that in the glassy region.

Ethylene dimethacrylate showed a very broad peak at 45°C . The rate of fall of the modulus through this transition was small, indicating that it is not the normal glass transition phenomenon. Again this may be similar to the methyl methacrylate beta peak. Decomposition of the materials started above 200°C . The modulus of the ethylene dimethacrylate polymer at $+200^\circ\text{C}$ was approximately half that at nearly -200°C , thus showing a remarkably small rate of fall with temperature.

A recent series of experiments were conducted with a number of dental materials. They were fabricated and machined to specimens approximately 2 in (50 mm) in length between grips, 0.200 in (5 mm) wide and 0.062 in (1.5 mm) thick. The specimens were maintained free from water by storage in a desiccator until testing was done.

The tests were conducted on the Plas-Tech Direct Recording Torsion Pendulum. The frequency was in the range of 2 to 10 cycles per second, and the temperature ranged from -120°C to $+120^\circ\text{C}$. The tests were of a scanning nature. The chamber was cooled to about -120°C with liquid nitrogen, and then the temperature raised about 1°C per minute. Readings were taken every 10°C . Equilibrium was not reached for each temperature

and the results, therefore, are to a certain extent relative. Only one specimen for most experiments was tested; for more precise data of certain key-points the temperature should be controlled and a number of runs made.

Samples of methyl methacrylate polymer, ethyl methacrylate polymer, and an equal-by-weight copolymer of the two were cast in test tubes and machined to the specimen geometry. Figure 8 shows $\tan \delta$ versus temperature curves for the three materials. It can be seen that the ethyl methacrylate and methyl methacrylate produce similar polymers, with, as expected, the ethyl methacrylate having a lower softening temperature. The copolymer is intermediate although much closer to the ethyl methacrylate than might be expected. Figure 9 shows the modulus versus temperature data. The copolymer is intermediate between the two end members in this property.

To test the effect of a mixture rather than a copolymer of ethyl methacrylate and methyl methacrylate, 50 parts by weight of ethyl methacrylate monomer and 50 parts of methyl methacrylate polymer were mixed together in a dough and molded in the usual dental fashion, machined and tested. Figure 10 shows data for the copolymer and the mixture plotted together. It can be seen that the mixture has a broader softening transition point, as is shown by the lower rate of increase of $\tan \delta$ with temperature. Of great interest in this figure is the prominent peak at ap-

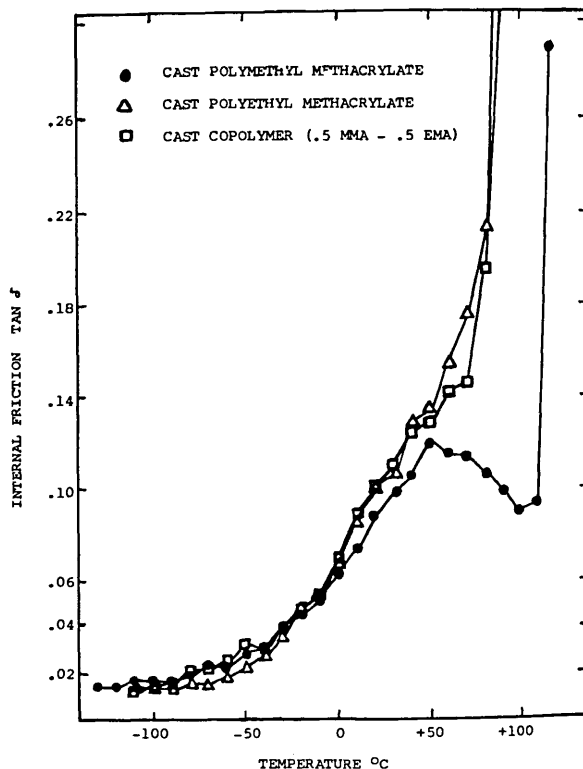


FIGURE 8. Internal friction of methyl methacrylate, ethyl methacrylate and an equal weight copolymer of the two methacrylates.

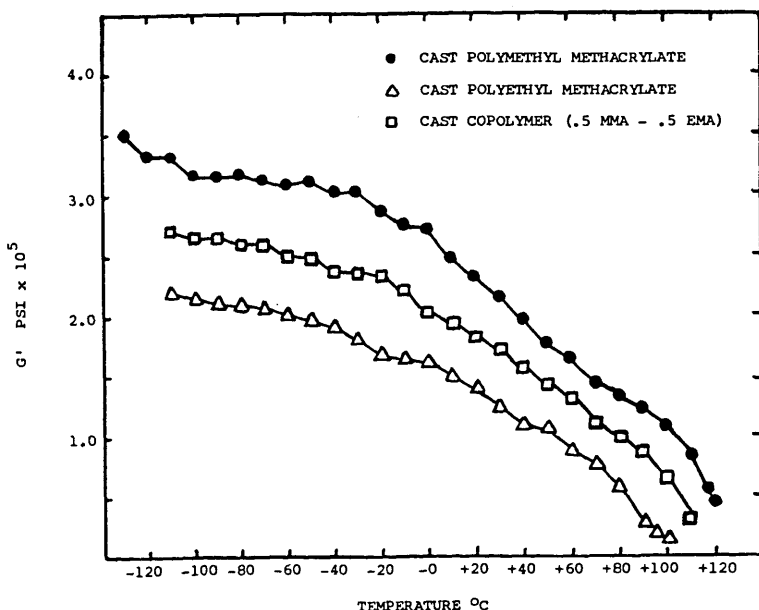


FIGURE 9. Effect of temperature on modulus of methyl methacrylate, ethyl methacrylate and equal weight copolymer of the two methacrylates.

To convert from psi (pounds per square inch) to N/m^2 (newtons per square meter), multiply by 6895.

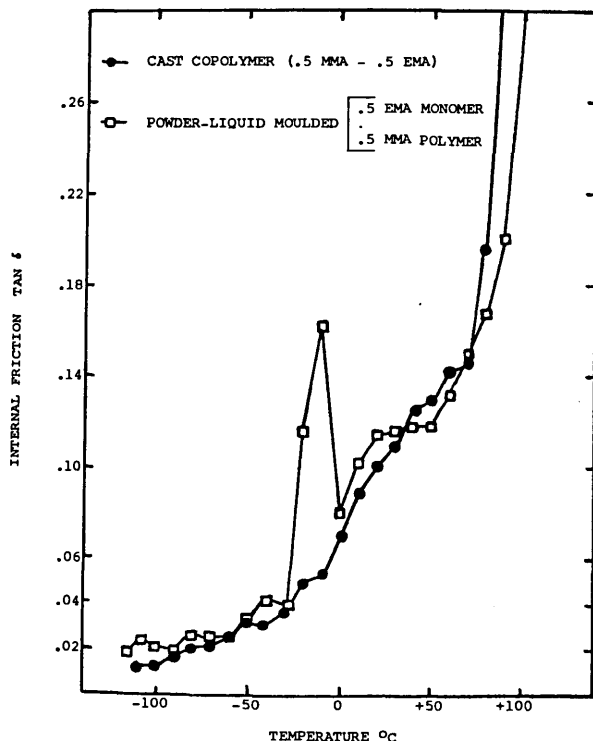


FIGURE 10. Internal friction versus temperature for ethyl methacrylate-methyl methacrylate copolymer and mixture.

proximately -10°C . This was unexpected and, as will be shown below, is in some way associated with the polymer phase. Figure 11 shows the modulus versus temperature data for the copolymer and the mixture. Over most of the range the modulus of the mixture is greater than the copolymer. There appears to be a change in modulus level at about the same temperature as the low temperature maximum.

To determine the effect of the polymer-monomer fabrication versus casting, a mixture of the above poly (methyl methacrylate) powder and methyl methacrylate monomer was made of equal parts by weight and molded. In addition a compression molded sample of the polymer was also made. In figure 12, the internal friction versus temperature curves are plotted. The data from the compression molded sample are remarkably similar to the data of the cast sample with the exception of the pronounced low temperature peak. It is clear that this phenomenon is related to this polymer, possibly to the complex surface of the material. The polymer-monomer mix material showed a similar low temperature peak and a lower glass transition temperature. It can be seen in figure 13 that the cast specimen produced the highest modulus of rigidity presumably because of a higher molecular weight produced by the slow cure.

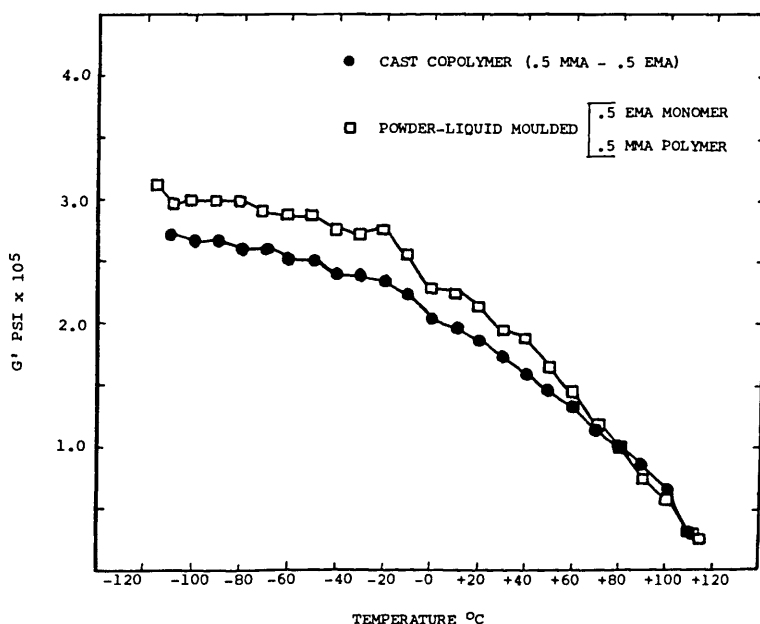


FIGURE 11. Modulus versus temperature for ethyl methacrylate-methyl methacrylate copolymer and mixture.

To convert from psi (pounds per square inch) to N/m^2 (newtons per square meter), multiply by 6895.

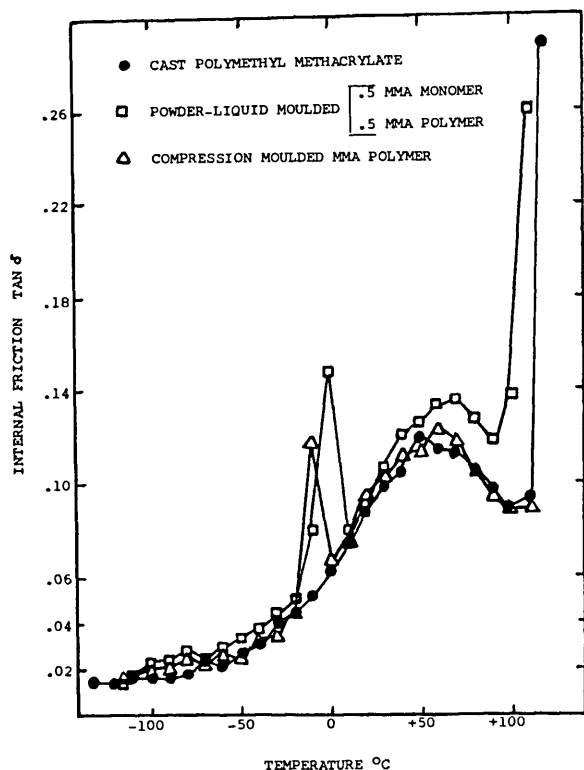


FIGURE 12. Internal friction versus temperature for methyl methacrylate polymer prepared by casting from liquid, by molding powder-liquid mixture and by compression molding powder only.

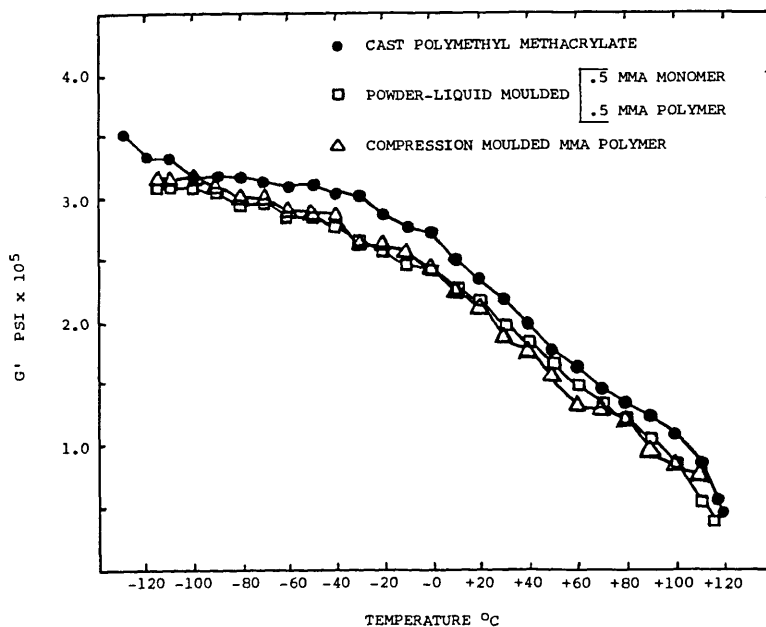


FIGURE 13. Modulus versus temperature for methyl methacrylate polymer prepared by casting from liquid, by molding powder-liquid mixture and by compression molding powder only.

To convert from psi (pounds per square inch) to N/m^2 (newtons per square meter), multiply by 6895.

A comparison of the internal friction curve of "powder-liquid" denture base material of conventional impact resistance with cast poly (methyl methacrylate) is shown in figure 14. The low temperature properties are similar with the exception of the polymer associated peak described above. Since the impact resistance is not enhanced, this peak is not likely to be an "in the chain" molecular phenomenon. The slightly subdued beta peak would indicate the presence of a nonmethacrylate component.

The internal friction curves for two impact resistant denture materials compared to cast poly (methyl methacrylate) are shown in figure 15. Impact resistant material II shows a glass transition temperature similar to poly (vinyl chloride). Poly (vinyl chloride) has a broad low temperature peak at about $-25^{\circ}C$ and a minimum at about $+20^{\circ}C$. There is no evidence of this in this curve; however, a blend with poly (methyl methacrylate) would mask the peak because of the poly (methyl methacrylate) beta peak.

Impact resistant denture base I is obviously closely related to poly (methyl methacrylate). There is a slight indication of a low temperature peak superimposed on a poly (methyl methacrylate) curve between $-50^{\circ}C$ and $-20^{\circ}C$. Also, there appears to be a slight low temperature "polymer" peak near $0^{\circ}C$. The modulus versus temperature plot of the same three materials shown in figure 16 shows a dispersion starting about $-60^{\circ}C$ with impact resistant material I

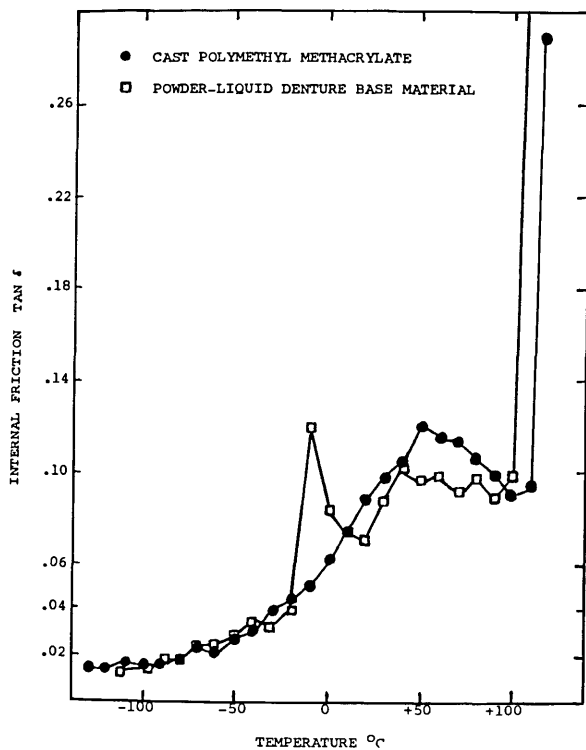


FIGURE 14. Internal friction versus temperature for cast poly (methyl methacrylate) and powder-liquid denture base material.

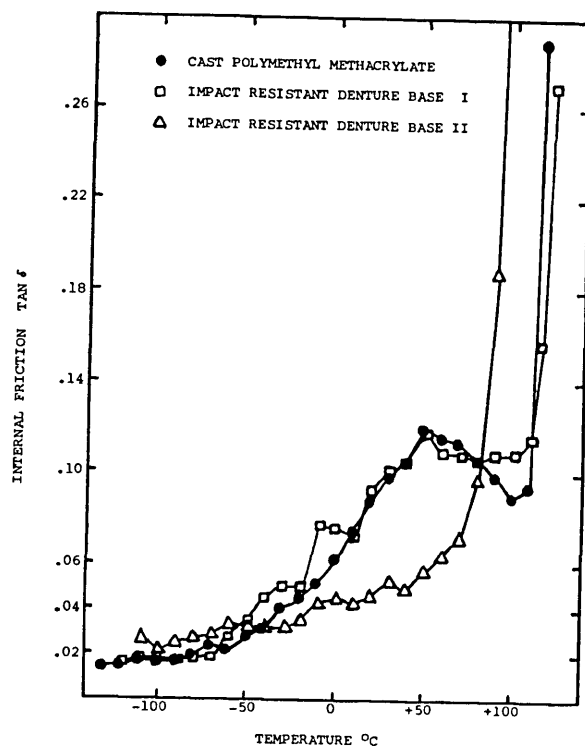


FIGURE 15. Internal friction versus temperature for cast poly (methyl methacrylate) and impact resistant denture base materials.

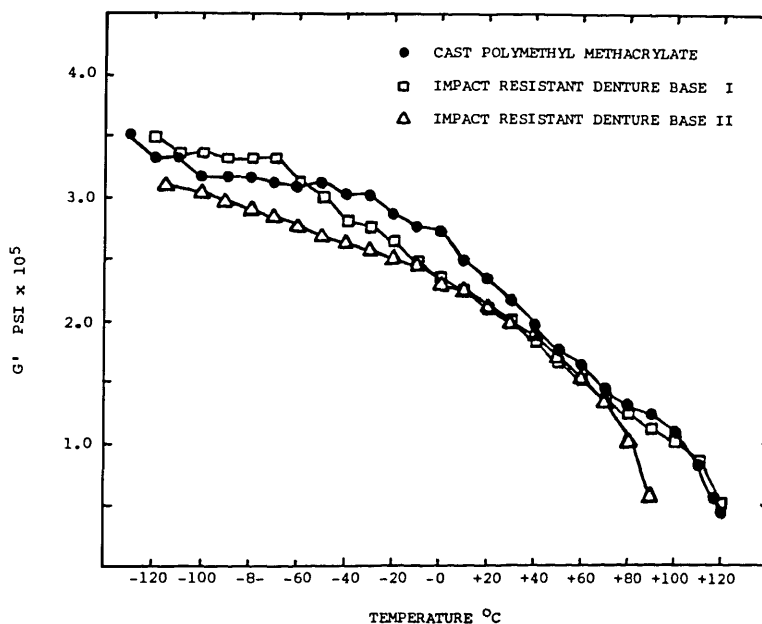


FIGURE 16. Modulus versus temperature for cast poly (methyl methacrylate) and impact resistant denture base materials.

To convert from psi (pounds per square inch) to N/m^2 (newtons per square meter), multiply by 6895.

that would support theory that there is some low temperature transition taking place that might relate to the toughness of the material.

From the stress strain curves shown in figure 17 of the two impact resistant materials, it can be seen that there is very little drawing during the tensile failure, hence one would not expect evidence of pronounced low temperature phenomena.

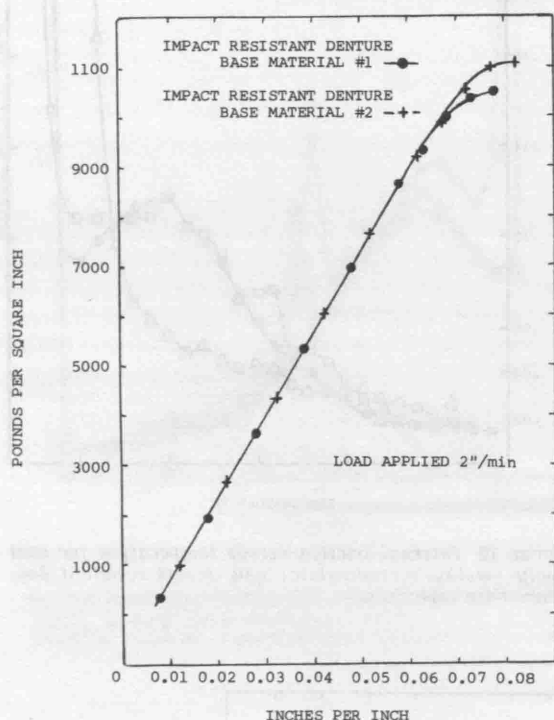


FIGURE 17. Stress strain curves for two impact resistant denture base materials.

To convert from psi (pounds per square inch) to N/m^2 (newtons per square meter), multiply by 6895.

5. Equipment for Torsion Pendulum Measurements

Many authors have written about equipment for measuring low frequency mechanical properties [8, 11, 17, 22, 26, 31, 34-42]. In March, 1962 a basic torsion pendulum design was described before the Dental Materials Group of the International Association for Dental Research. This device utilized a light beam and a galvanometer scale for visual data recording. Figure 18 is a photograph of the torsion pendulum enclosed in a Lucite wall chamber to prevent drafts. Figure 19 shows a cutaway sketch with the pendulum attached to the top of the machine and the sample surrounded by a chamber which can be cooled by liquid nitrogen to about $-180^{\circ}C$ or heated to $+300^{\circ}C$. Beneath the temperature control chamber an inertia bar is attached to the pendulum via a pin vice. On the inertia bar there is a mirror to deflect a light beam and thereby show the amplitude of vibration on

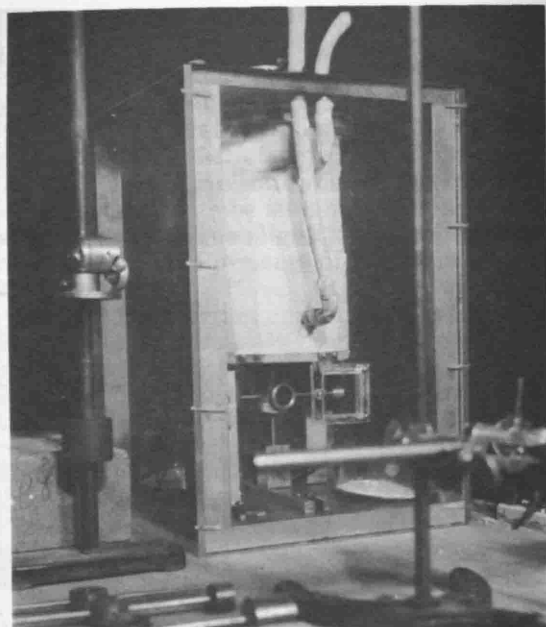


FIGURE 18. Torsion pendulum equipment enclosed within Lucite chamber.

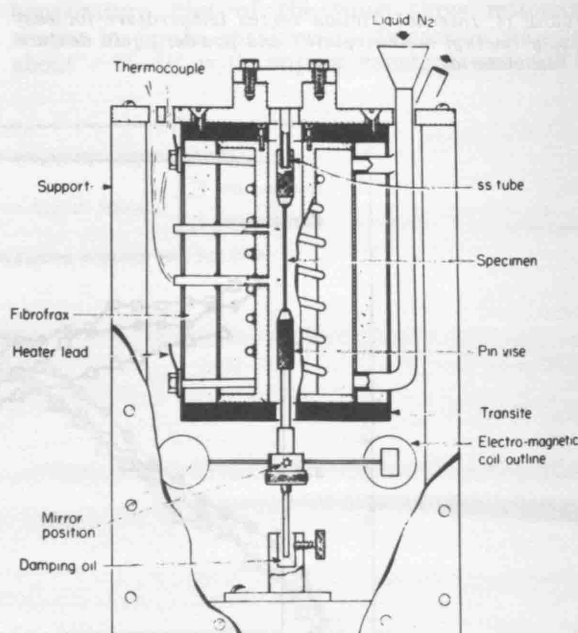


FIGURE 19. Cutaway sketch of equipment shown in figure 18.

the galvanometer scale. Figure 20 shows a photograph of the equipment with a zirconium arc lamp light source. The frequency was determined with a stop watch and the readings on the galvanometer scale were recorded vocally on a tape recorder.

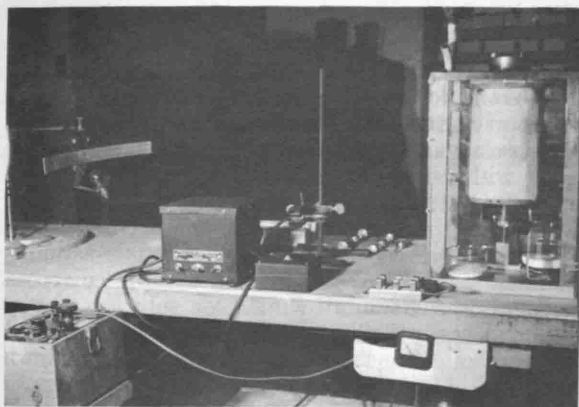


FIGURE 20. Torsion pendulum equipment with zirconium arc lamp.

Oscillations were started by the electro-magnetic coils located near the ends of the inertia rod. Precession in the oscillation was damped out by the damping oil at the bottom of the pendulum. The pin vices supporting the specimen were attached to thin-walled stainless tubing which had the strength and rigidity to function properly mechanically, but were poor conductors and minimized thermal variations.

In designing equipment to operate above two cycles per second, it is necessary to use a recording device.

For measuring very low damping materials, high sensitivity is needed. This can be provided by operating in a vacuum and thereby eliminating air resistance. Blum [8] developed a very sensitive instrument and recorded with fused quartz a value for $\tan \delta$ of 0.000013 at a vacuum of $0.5 \mu\text{m}$ of mercury. This suggests that fused quartz is an excellent material for calibrating the internal friction of an instrument itself.

For further improvement in temperature distribution, Douglas et al. [36] recommended the use of a chromel-alumel thermocouple rather than copper-constantan because of the high conductivity of the latter. To eliminate residual magnetic effects from the starting electro magnets, they used copper wire coils wound on plastic forms and a piece of silicon iron transformer sheet attached to the inertia bar.

Nielsen [42], in his design to eliminate the effect of tensile stress, placed the fixed end at the bottom of the pendulum, with the inertia member at the top, supported by a fine wire and counter weight.

It is desirable to have all nonaxial rotation eliminated. This requires good alignment, a good starting system, and a means of maintaining concentricity. This has been done by bearings (which

have their own friction) and by damping oils. Damping oils will eliminate precession but offer virtually no resistance to the axial rotation of a smooth cylindrical rod.

The challenge of recording the oscillations of a torsion pendulum offer the ingenious instrument designer ample opportunity. For most sensitivity the optical system recorder seems best. One technique is to send a light beam by a mirror attached to the inertia bar to a sheet of photographic paper on a revolving drum. Development of the paper will then produce a record of the oscillations of the pendulum. A variation of this used by Turley [22] employed ultraviolet light reflected to ultraviolet sensitive paper. This can eliminate the need for development of the paper.

Weir [34] described in detail an optical device for recording the amplitude of oscillation using two photocells close together near the zero deflection point. The principle of his recording is based on the fact that for constant frequency in a sinusoidal oscillating system, the velocity at zero deflection is proportional to the amplitude. Thus the time it takes the light beam to travel between cells is proportional to the amplitude. The period can be determined by noting the total elapsed time in one cycle. A digital recorder in conjunction with a microsecond interval time meter was used to record the data.

Plajek et al. [37] used a constant light source aimed at the mirror with a shadow device that would cut off part of the beam in proportion to the amplitude. Thus the emf that was generated from the photocell was of a sinusoidal form in proportion to the frequency and amplitude of the oscillation of the pendulum.

Gillham [41] utilized an inertia disc of glass with varying opacity such that a light beam passing through it to a photocell will be of varying intensity with the angle of rotation.

Klein [40] described a torsional pendulum utilizing an electromagnetic pickup. This was accomplished by attaching a permanent magnet to the pendulum which induced a current in a coil mounted adjacent to it on the fixed portion of the instrument. The induced voltage was then recorded.

Nielsen [42] allowed the "fixed" end of the pendulum to have a small motion by restraining it with relatively rigid spring rods. The motion is proportional to the amplitude of the inertia member and is measured by a linear differential variable transformer. He reported recording values of $\tan \delta$ as low as 0.003.

The Plas-Tech unit shown in figure 21 was used for some of the data reported in this paper. The instrument has a fixed bottom member with a counterweight support system to compensate for length changes. The inertia member at the top is supported by a frictionless bearing in a rotary differential variable transformer which is used to

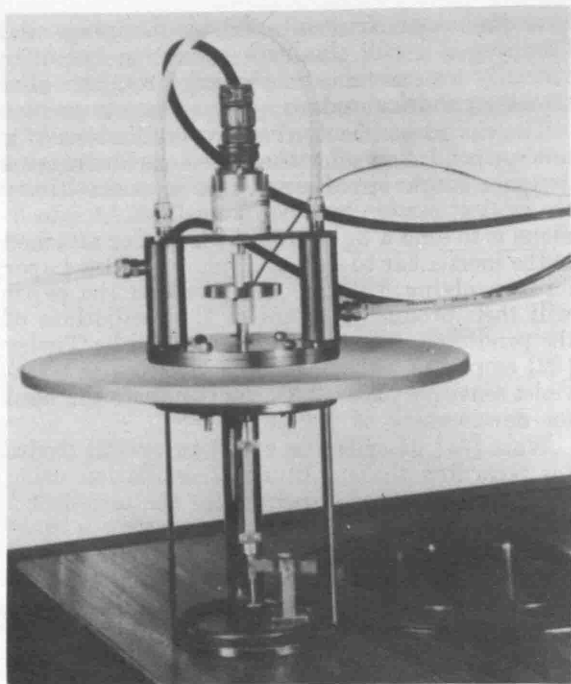


FIGURE 21. Example of commercially available torsion pendulum equipment.

(Courtesy of Plas-Tech Equipment Corporation, Natick, Mass.)

supply a voltage proportional to the amplitude to a recorder.

Heijboer [26] utilized a recording system wherein a specially conductive paper on a rotating drum was marked by an electric spark from the oscillating inertia member of the pendulum, thus recording the motion of the pendulum.

Rodriguez et al. [35] and Plajcek et al. [37] presented designs of equipment for recording the internal friction of weak elastic materials such as gels. In one case a conical plate type of viscosimeter is used to hold the sample, and an air bearing is used to support the weight and minimize friction. In the other case a disc-like specimen was held between two plates and was the elastic member of the pendulum system.

Maxwell [39] described a nonresonant driven device to allow continuous variation of temperature and frequency at a controlled strain. The use of a controlled strain instead of a controlled stress is important in nonlinear viscoelastic materials. The instrument tests a cantilever beam of circular cross section, held in a collet and rotated at the desired speed about its cylindrical axis. A load is applied at the unsupported end causing a fixed deflection. Each portion of the beam then will be alternately under tension and then compression. If the beam is made of a viscoelastic material there will be a lag in the strain relative to the force, and a deflection normal to the applied force will

tend to take place. This deflection can be eliminated by applying a force perpendicular to the initial force direction. The ratio of the force normal to the desired deflection to the deflecting force itself yields $\tan \delta$. These can both be measured by strain gauges. The advantages of this system are a wide range of frequencies with a single specimen geometry and with simple recording devices.

Gillham [41] described the torsion braid pendulum. Basically the technique used is a multifilament substrate with the sample disposed through the strands by melt or solution (or by other means). This allows a material to be tested beyond conditions wherein it can support its own weight (i.e., at high temperatures or in its reaction periods). The use of a multifilament system allows more material to be tested, better stress transfer, and minimizes the modulus of the substrate.

6. Future Work

One obvious project from the brief work reported in this paper is to further understand the nature of the low temperature peak in the pearl polymer used. If this is a surface phenomenon it should be proportional to particle size. A series of tests with different sieve fractions from the same polymer should verify this. If it is a bulk property, then a systematic review of the suspension agents, stabilizers, catalysts, etc., will have to be made to determine just what produces this effect.

Of interest to dentistry is energy absorption. It has often been speculated that the ridges could be protected if the shock of mastication could be absorbed. Indeed soft liners have been proposed for this. With internal friction measurements it would be possible to develop a material of very high damping capacity at the mouth temperature region with a broad range of frequency absorption. Whether this is better than rubbery materials that are of low damping capacity is not known. Clinical tests would be required. However, recording the internal friction of the denture materials at a variety of frequencies in the mouth temperature range would allow a characterization of the material that might profitably be coordinated with clinical data.

The torsional braid pendulum should be of value in characterizing all types of setting reactions. It would be possible to get nearly continuous data on the modulus and the damping capacity of the material versus time at a fixed temperature or at a programmed rate of temperature change. This should be applicable to dental cements, amalgam, impression materials, resin, etc.

There is evidence that the internal friction of a composite material is affected by the bond between the resin and the matrix. This would offer a means of quantitatively evaluating the bond and then testing again after exposing the composite to various environments, thermal cycling, etc. The

data will give not only the internal friction changes but also the modulus changes.

High strength materials for denture base use are of obvious interest. A significant amount of work has been done correlating toughness with internal friction curves. Experiments might be done developing low temperature peaks of various magnitudes and correlating the data against the toughness of the material, the tensile strength of the material, and, most important, against the creep of the material. When there is significant drawing taking place in absorbing the energy of impact, there will also be distortion. There is a level of distortion that is not acceptable, and some brittleness would be more suitable.

An intriguing possibility of utilizing the torsion pendulum is as a means of following the progress of polymerization in self-cure systems. Following the shrinkage is unrewarding because the specimen will shrink by polymerization but also by loss of monomer either through volatility or leaching in saliva. The modulus and internal friction curves will be very sensitive indicators of the degree of polymerization. It would be interesting to make self-cure and heat-cure samples and note the change in internal friction curves of both with time after storage in 100 °F (38 °C) water. Presumably, in the case of the heat-cure material where polymerization is virtually complete, the principle effect will be a plasticizing of the system by absorbed water. In the case of the self-cure material there will be that plasticizing effect, but coupled with it will be a leaching of the monomer and a continued polymerization of the monomer with time.

In analyzing ceramic materials there is a problem of the specimen geometry. With a low frequency pendulum, specimens are needed of the order of one square millimeter in cross section and perhaps 5 to 10 cm in length. Most of the work done in ceramics has been done with drawn glass fibers. To fire a ceramic to these dimensions is difficult. To draw a glass fiber from a ceramic melt would not be satisfactory because the microstructure of a material would be significantly altered. One approach is to fire a specimen oversize and machine it to the proper dimensions. Another approach would be to use refractory investments to make a mold of about the right dimensions that would support the ceramic during the firing operation. A third approach would be to use a two component system—e.g., porcelain on gold. By knowing the data of the gold system by itself, the information relative to the porcelain can be approximated. Internal friction measurements should be an excellent method of determining changes in firing and repeated firings such as solution, crystal melting, and devitrification.

There has been a great deal of interest to date in the nature of the porcelain to gold bond. Evidence has been presented to show that there is ionic diffusion taking place during the firing reaction

aiding in the bond. The torsion pendulum is quite sensitive to ionic diffusion in glassy structures as was shown above.

This suggests that a method could be developed to identify the degree of diffusion and identify the activation energy for diffusion. Experiments in metal and ceramic design could then be conducted to optimize this diffusion process. The degree of diffusion in the porcelain gold system is probably small and located near the interface. In a system of high interface area, it might be possible to get sufficient diffusion to be measurable. One approach would be to disperse in a ceramic mix a fine gold alloy powder and then fire at the appropriate temperature. The electron probe could be used as before to determine the species of ions taking part in the diffusion, and the internal friction curves at several frequencies could be used to give a measurement of the amount of diffusion and the activation energy of diffusion process.

It should be possible to use internal friction measurements to help determine the causes of physical property changes noted in implant materials. For instance, embrittlement through cross-linking would yield a different spectrum than embrittlement through degradation. It would be worthwhile testing the internal friction of materials as a function of time of implantation.

7. References

- [1] Nielsen, L. E., *Mechanical Properties of Polymers* (Reinhold Publishing Corp., N.Y., 1962).
- [2] Braden, M. and Stafford, G. D. Viscoelastic properties of some denture base materials, *J. Dental Res.* **47**, 519 (1968).
- [3] Zener, C., *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948).
- [4] Ryder, R. J., *The Internal Friction of Simple Alkali Silicate Glasses Containing Alkaline Earth Oxides*, Ph. D. Thesis, Pennsylvania State University, 1959.
- [5] Fitzgerald, J. V., Anelasticity of glass: I. Introduction, *J. Am. Ceram. Soc.* **34**, 314 (1951).
- [6] Fitzgerald, J. V., Anelasticity of glass II. Internal friction and sodium ion diffusion in tank plate glass, a typical soda-lime silica glass, *J. Am. Ceram. Soc.* **34**, 339 (1951).
- [7] Kirby, P. L., Internal friction in glass Part II: Flexural and torsional vibration, *J. Soc. Glass Technol.* **38**, 383 (1954).
- [8] Blum, S. L., Some physical factors affecting the internal damping of glass, *J. Am. Ceram. Soc.* **38**, 205 (1955).
- [9] Forry, K. E., Two peaks in the internal friction as a function of temperature in sodium silicate glasses, *J. Am. Ceram. Soc.* **40**, 90 (1957).
- [10] Hoffman, L. C. and Weyl, W. A., A survey of the effect of composition on the internal friction of glass, *Glass Ind.* **38**, 81 (1957).
- [11] Shelby, J. E. and Day, D. E., Mechanical relaxations in mixed alkali silicate glasses, I. Results, *J. Am. Ceram. Soc.* **52**, 169 (1969).
- [12] Fitzgerald, J. V., Anelasticity of glass No. III, effect of heat treatment on the internal friction of tank plate glass, *J. Am. Ceram. Soc.* **34**, 388 (1951).
- [13] Fichter, R., Damping in metals. *Schweiz. Arch.-Ann. Suisses* **24**, 65-78 (1958).

- [14] Nowick, A. S., *Anelastic phenomena in metals and nonmetallics*, Internal Friction, Damping, and Cyclic Plasticity, ASTM Special Technical Publication No. 378 (American Society for Testing and Materials, Philadelphia, Pa., 1965).
- [15] Kaelble, D. H., *Micromechanisms and phenomenology of damping in polymers*, Internal Friction, Damping and Cyclic Plasticity, ASTM Special Technical Publication No. 378 (American Society for Testing and Materials, Philadelphia, Pa., 1965).
- [16] Boyer, R. F., The relation of transition temperature to chemical structure in high polymers, *Rubber Chem. and Technol.* **36**, 1303-1421 (1963).
- [17] McCrum, M. G., Read, B. G., and Williams, G., *Anelastic and dielectric effects in polymeric solids*, (John Wiley and Sons, Inc., N.Y., 1967).
- [18] Nielsen, L. E., Dynamic mechanical properties of high polymers, *SPE J.* **26**, 525 (1960).
- [19] Deutsch, K., Hoff, E., and Reddish, W., Relation between the structure of polymers and their dynamic mechanical and electrical properties, Part I: Some alpha substituted acrylic ester polymers, *J. Polymer Sci.* **13**, 565 (1954).
- [20] Nielsen, L., Effect of chemical heterogeneity in copolymers on some physical properties, *J. Am. Chem. Soc.* **75**, 1433 (1953).
- [21] Cuddahy, E. F., and Moacanin, J., Dynamic Mechanical Properties of Some Cured Epoxy Resin. *Am. Chem. Soc., Division of Organic Coatings and Plastic Chemistry Papers*, (April 1968).
- [22] Turley, S. G., Effect of Polymer Structure on Impact Properties. *Am. Chem. Soc., Division of Organic Coatings and Plastic Chemistry Papers*, (September 1967).
- [23] Heijboer, J., Dynamic mechanical properties and impact strength, *J. of Polymer Sci. Part C* **16**, 3755-3763 (1968).
- [24] Boyer, R. F., Dependence of mechanical properties on molecular motion in polymers, *Polymer Eng. and Sci.* **8**, 161-185 (1968).
- [25] Matsuoka, S., Aloisio, C. J., and Daane, J. H., Some aspects of brittle failure in polymers, *Applied Polymer Symp.* **5**, 103 (1967).
- [26] Heijboer, I. J., Modulus and damping of polymers in relation with their structure, *Plastica* **19** ii, 489 (1966).
- [27] Maeda, M., Tanaka, K., Hibi, S. and Kakei, K., Mechanical properties of FRP, Part I, *Journal of the textile machinery society of Japan* **13**, 58-67 (1967).
- [28] Galperin, I., Dynamic mechanical properties of a TiO₂ filled cross-linked epoxy resin from 20-90° C, *Am. Chem. Soc. Div. of Polymer Chem. Preprints* **7**, 890 (1966).
- [29] Reinhardt, J., Dynamic mechanical behavior of a polyester during cross-linking, *Plastics & Polymers*, **36**, 541 (1968).
- [30] Malpass, V. E., Damping behavior and in-service performance of impact plastics, Paper presented at Seventh International Symposium on High Speed Testing, Boston, Mass. (March 1969).
- [31] Myerson, R. L., The Internal Friction of Linear and Cross-Linked Phosphate Glasses and Methacrylate Polymers, M.A. Thesis, M.I.T. May 1961.
- [32] van Wazer, J. R., *Phosphorous and its Compounds*, I (Interscience Publishers, New York, 1958).
- [33] Myerson, R. L., Effect of cross-linking on mechanical damping and stiffness of methacrylates, *I.A.D.R. Abstracts of the 40th General Meeting*, p. 89 (1962).
- [34] Weir, F. E., Use of a new torsion pendulum for polypropylene property evaluation, *SPE Transactions* **2**, 302 (1962).
- [35] Rodriguez, F., Van Brederode, R. A., and Cocks, G. G., A recording air-bearing torsion pendulum, *J. Appl. Polymer Sci.* **22**, 2415-2420 (1968).
- [36] Douglas, R. W., Duke, P. J., and Magurin, O. V., On the network contribution to the anelasticity of glasses, *Phys. and Chem. of Glasses* **9**, 169 (1968).
- [37] Plajek, D. J., Vrancken, M. N., and Berge, J. W., A torsion pendulum for dynamic and creep measurements of soft viscoelastic materials. *Trans. of the Soc. of Rheology* **II**, 39-51 (1958).
- [38] Copley, G. J., A simple photocell counter for the determination of the logarithmic decrement of the torsion pendulum, *J. Sci. Instr.* **43**, 845-846 (1966).
- [39] Maxwell, B., An apparatus for measuring the response of polymeric materials to an oscillating strain, *ASTM Bulletin* **76-80** (July 1956).
- [40] Klein, J., A method for recording torsion or bending oscillations in damping experiments on high polymers, *Plaste Kautschuk* **13**, 20 (1966).
- [41] Gillham, J. K., Thermomechanical properties of polymer by torsional braid analysis, *Appl. Polymer Symp.* **2**, 45 (1966).
- [42] Nielsen, L. E., A recording torsion pendulum for the measurement of the dynamic mechanical properties of plastics and rubbers, *Rev. of Sci. Instr.* **22**, 690 (1951).

Ultrasonic Methods for Determination of Mechanical Properties

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Elastic characteristics, shear modulus, Young's modulus, bulk modulus and Poisson's ratio for materials can be determined by a variety of ultrasonic methods, most of which involve the measurement of the velocity of sound in the material. The methods are precise, rapid, nondestructive and applicable to small specimens. As a number of reports in the literature indicate, ultrasonic methods offer particular advantages to the study of dental materials and mineralized tissues.

Key words: Dental amalgam; dental materials; elastic properties; mechanical properties; nondestructive testing; ultrasonic techniques.

1. Introduction

The most commonly reported mechanical property of dental materials is strength, usually compressive or tensile. However, strength is not a measure of the reaction of a material within its functional range. To obtain some characterization of the mechanical reaction of a material to the forces encountered in use, Young's modulus is often determined. Generally, Young's modulus is calculated from a stress-strain curve obtained by loading a specimen in a testing machine and measuring the change in length with increase in load. While the modulus determined in this way is usually considered a measure of the elastic characteristics of the material, the data often represent a combination of properties: elastic, retarded elastic, and viscous with varying magnitudes of time and stress dependence. This is illustrated in the stress-strain curves for dental amalgam shown in figure 1 [1].¹

It is evident that even with low stresses, the behavior of dental amalgam is not purely elastic. A plot of the strain of dental amalgam versus time when under constant stress (fig. 2) indicates that at least three types of response to mechanical force are present, an instantaneous elastic response, a retarded elastic response, and a viscous response [2].

To determine the magnitude of the instantaneous elastic response, it is necessary to isolate this particular property of the material.

Time dependent responses such as viscous creep and retarded elasticity can be eliminated or reduced to a negligible level if the stress can be applied and removed rapidly enough. One method

of accomplishing this in some cases is by introducing sonic or ultrasonic waves into the material. Essentially this causes small volume elements of the material to be cyclically strained as a series of stress waves is propagated through the specimen. The velocity of the stress wave depends upon the mass or density of the particles or small volume elements of the material which are displaced and upon the elastic characteristics of the material which provide the forces tending to restore the particles to their equilibrium positions.

In addition to minimizing time dependent responses, ultrasonic methods have other advantages. They are rapid and nondestructive, and they permit repeated measurements on the same specimen

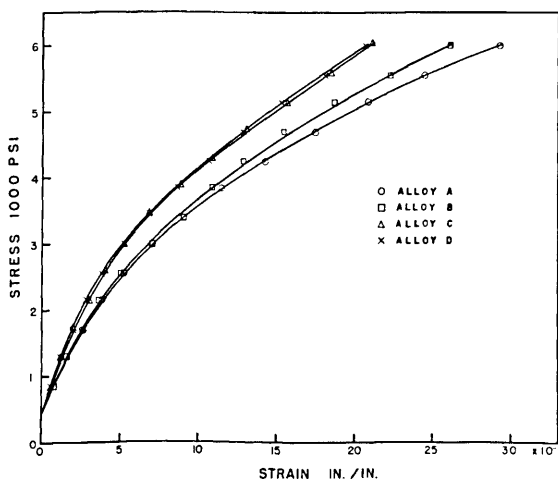


FIGURE 1. Typical stress-strain curves of various amalgams in tension, using 0.003 in/min head speed and 7 day old specimens [1].

To convert psi to MN/m² multiply by 6.895×10^{-3} .

¹ Figures in brackets indicate the literature references at the end of this paper.

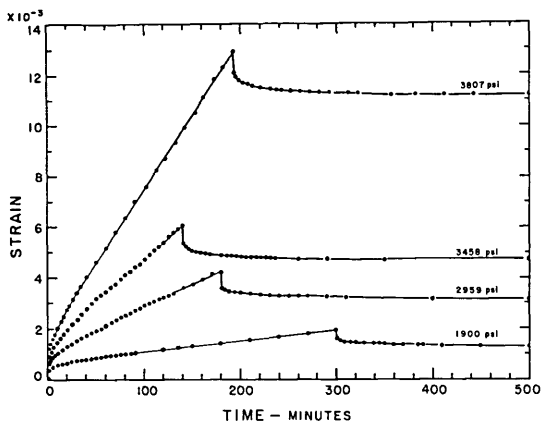


FIGURE 2. Creep and recovery of amalgam loaded in tension [2].

To convert psi to MN/m² multiply by 6.895×10^{-3} .

as it is aged or subjected to temperature change or other treatments. Ultrasonic methods can be applied to small and brittle specimens on which other methods of stress application and strain measurement may be difficult. Also, ultrasonic methods are particularly suitable for measuring elastic coefficients in different directions in anisotropic materials.

For measuring the mechanical properties of materials, low amplitude or low energy ultrasonic waves are employed, and the effects of the medium on the wave are observed. High amplitude waves which would produce a permanent change in the specimen are avoided.

There are two types of stress waves which are particularly useful for determination of mechanical properties. These (fig. 3) are the compressional or longitudinal wave in which particle motion in the medium is parallel to the direction of propagation of the wave, and the shear or transverse wave in which the particles vibrate at right angles to the direction of propagation of the wave.

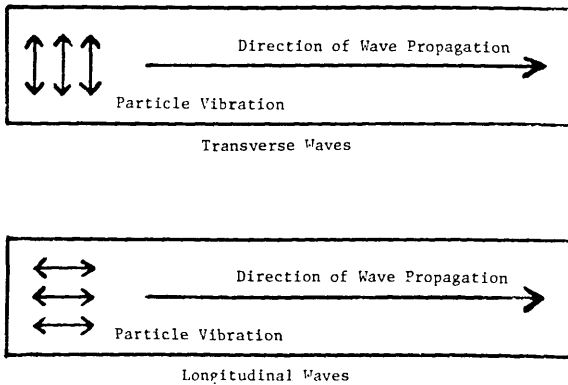


FIGURE 3. Two types of ultrasonic stress waves used for determination of mechanical properties of materials.

2. Velocity and Modulus Determinations

For plane waves in an elastic isotropic homogeneous medium [3], the velocities of the transverse and longitudinal waves can be shown to be:

$$V_T = \sqrt{\frac{G}{\rho}}$$

and

$$V_L = \sqrt{\frac{E(1-\gamma)}{\rho(1+\gamma)(1-2\gamma)}}$$

where

ρ = density
 G = shear modulus
 E = Young's modulus
 γ = Poisson's ratio

When the wave length is large compared to specimen dimensions [4], the equations for propagation in an infinite elastic medium do not apply. For example, for wave propagation parallel to the sides of a thin isotropic plate

$$V_L = \sqrt{\frac{E}{\rho(1-\gamma^2)}}$$

For propagation in an isotropic rod with radius small compared to wavelength [4], the longitudinal wave velocity is

$$V_L = \sqrt{\frac{E}{\rho}}$$

Where frequencies employed are high enough so that the wavelength is small compared to specimen dimensions [3], the shear modulus, Young's modulus, the bulk modulus and Poisson's ratio can be determined from the velocities of the longitudinal and transverse waves, and the density of the material as follows:

Shear modulus $G = \rho V_T^2$

Young's modulus $E = \rho V_T^2 \left(\frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \right)$

Bulk modulus $K = \rho \left(\frac{3V_L^2 - 4V_T^2}{3} \right)$

Poisson's ratio $\gamma = \frac{V_L^2 - 2V_T^2}{2(V_L^2 - V_T^2)}$

From these equations, it is evident that determination of elastic constants is essentially a problem of determination of the velocity of sound in the material. Various methods can be employed for determining the velocity of stress waves. One of the most widely used is the pulse-echo technique, which has been described in numerous papers and books

[3, 4, 5, 6]). In this method (fig. 4), a quartz crystal, or other transducer driven by a pulsed oscillator, is used to introduce the wave at one of two parallel faces of the specimen. The same transducer, or a similar one at the opposite face of the specimen, is used to receive the mechanical vibration and produce an electrical signal which, after amplification, can be observed on an oscilloscope. Unless the attenuation of the specimen material is very high, the stress wave will echo back and forth through the specimen a number of times, and signals representing each double transit will be observed.

If a piezoelectric quartz transducer is used, the crystal may be cut with axes oriented so as to produce either longitudinal vibrations (X cut) or transverse vibrations (Y or AC cut) in the specimen. The crystal can be driven at its natural frequency or at an odd harmonic by a pulsed oscillator tuned to the required frequency. The time interval from one pulse to the next is made long enough to allow the echoes to die out between pulses. The transducers can be coupled to the specimen with a thin film of oil or a viscous resin.

A waveform generator (fig. 4) can be used to control the pulse repetition rate and supply a trigger signal to initiate both the pulse and the oscilloscope sweep. The rectified echo signals, after passage through a broadband amplifier, may be displayed on an oscilloscope (fig. 5) with a calibrated time scale and the time between echoes determined. The frequency, pulse length and pulse repetition rate may vary over a wide range.

Accuracy of the velocity determination will depend on the quality and quantity of echoes which can be observed, which, in turn, depend upon the attenuation of the signal by the specimen material, the presence of spurious signals which may result from reflection from sides of the specimen with the probability of mode conversion from longitudinal to transverse waves or vice versa, and on the precision of specimen preparation. Specimen parallelism to 2 parts in 10^4 or better is recommended, although less accurate parallelism may produce usable results for some purposes. Under

favorable conditions, velocity determinations with a sensitivity of 0.1 percent and an accuracy of 1 percent can be obtained [5].

In another pulse method, the sing-around technique (fig. 6), the signal received when the stress wave has passed through the specimen is used to trigger the next pulse from the oscillator, and the pulse repetition frequency is measured. Since time delays other than that required for the stress wave to pass through the specimen are ordinarily comparatively small, the period of the system is essentially the transit time. For accurate determinations, these other delays must be taken into account. With this simple system, velocity changes of less than one part in 10^5 can be detected [5].

Refinements of the sing-around method have been made to provide sensitivity to velocity changes of a few parts in 10^7 [7]. These refinements consist of using the signal after a specific number of echoes rather than after the first transit to retrigger the transmitter and also using a specific cycle within the pulse. This method is particularly

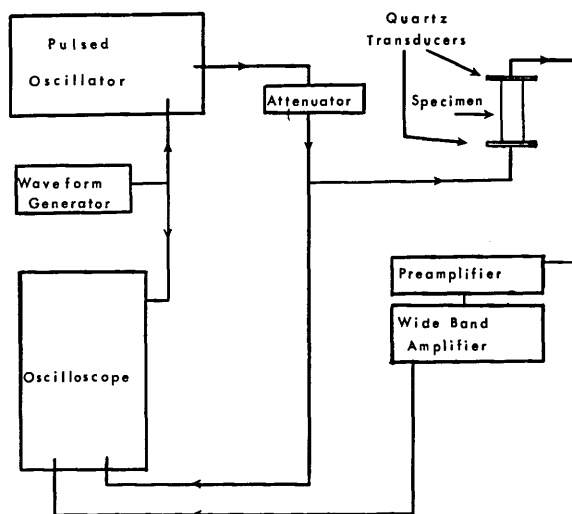


FIGURE 4. Typical pulse echo system.

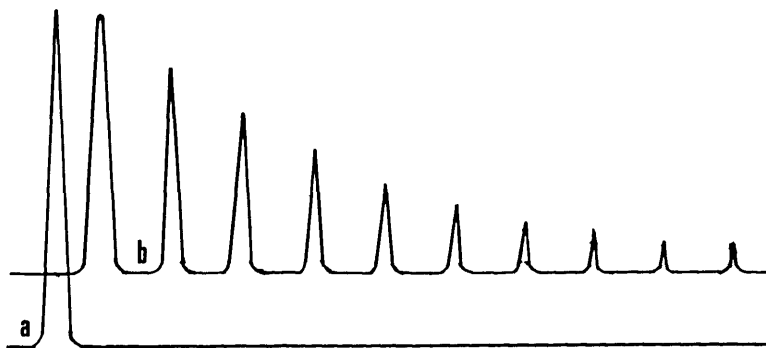


FIGURE 5. Pulse echo pattern, a—input pulse, b—pulses after passage through specimen.

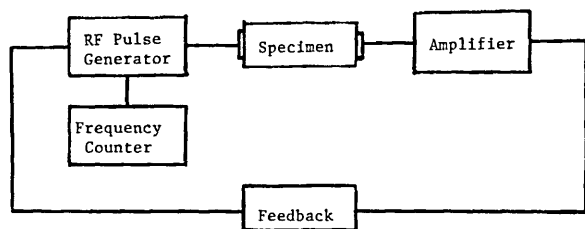


FIGURE 6. Simplified diagram of sing-around system.

useful when the interest is in measurements of small changes in velocity rather than in an absolute value.

Interference methods can be used for measuring velocities. In optical interferometers, such as the type used in measuring the setting expansion of amalgam and in ultrasonic interferometers in a liquid medium, the number of wave lengths between two reflecting surfaces is changed by a continuous variation of path length. Such a system is not feasible for ultrasonic measurement of the properties of solids since path length cannot be readily varied. A similar effect can be obtained, however, by a continuous variation of frequency and consequent change in wave length. For example, sets of two gated, phase-coherent pulses from a continuous wave oscillator may be spaced in time so that the second pulse which has passed once through the specimen arrives at the receiving transducer at the same time as the first pulse which has echoed and passed three times through the specimen [3]. If the oscillator frequency is then adjusted, the phase relationship of the pulses will vary and when the signals are added a series of nulls will be produced. The velocity can be determined from the frequency difference necessary to pass from one null to the next. If the phase change on reflection from the ends of the specimen can be neglected

$$V = 2l(f_2 - f_1)$$

where l is the length of the specimen and f_1 and f_2 represent the frequencies at successive null positions. If the specimen material causes relatively high attenuation of the ultrasonic wave, a continuous wave interferometric method can be used [3]. Here, the signal from the receiving transducer is compared with the signal being fed into the transmitting transducer and again phase change is observed as frequency is varied.

Resonance methods can also be used for velocity determinations. Such methods generally are used with frequencies in the lower ultrasonic range. At the natural frequency of a half-wavelength specimen bar, the longitudinal velocity is

$$V_L = 2lf$$

and Young's modulus is

$$E = \rho (2lf)^2.$$

One experimental arrangement [8] which has been used for such resonance determination involves the use of a three-component system, shown in figure 7, consisting of a quartz crystal driver with the specimen of closely matched resonance frequency cemented to one end and a second quartz bar, also closely matched in frequency, cemented to the other end of the driver to act as a piezoelectric gauge.

Another method of velocity measurement, analogous to optical index of refraction measurement, is based on the determination of the angle of refraction of a stress wave as it passes from a liquid medium into a solid specimen or on the determination of the focal length of an ultrasonic lens made from the specimen material [3].

Velocity measurements can also be made by reflection methods [3]. If ultrasonic pulses are reflected from the surface of a solid immersed in a liquid medium, the reflection coefficient can be defined as follows:

$$\alpha_r = \frac{P_r}{P_i} = \frac{\rho_2 V_2 - \rho_1 V_1}{\rho_2 V_2 + \rho_1 V_1}$$

where

P_r and P_i represent the pressure amplitudes of the reflected and incident pulses, respectively;

V_1 and V_2 represent longitudinal wave velocities in the incident (liquid) and reflecting (solid) media;

ρ_1 and ρ_2 represent densities of the liquid and solid media.

Instead of making absolute measurements of the reflection coefficient, the amplitude of the pulse

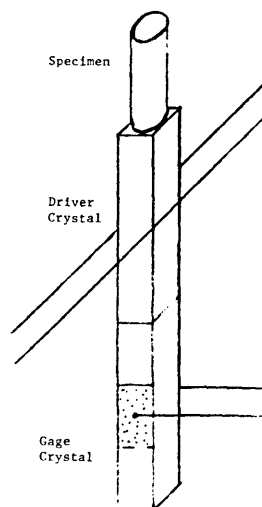


FIGURE 7. Three component resonance system [8].

reflected from the test specimen may be compared with the amplitude of the pulse reflected from a specimen for which the reflection coefficient is known. In this case

$$\alpha_{r2} = \alpha_{r1} \left(\frac{A_2}{A_1} \right)$$

where A_1 and A_2 represent the amplitudes of the pulses reflected from the known and unknown materials, respectively. From the reflection coefficient and the density of the test material, the velocity of the longitudinal wave and the acoustic impedance, ρV , can be calculated. This method can be used with materials which have a high attenuation. It has the advantage also that only one flat surface is required on the specimen. The accuracy is reported to be of the order of 5 percent [3].

3. Attenuation of Ultrasonic Waves

The attenuation of ultrasonic waves may be used to determine the internal friction of a material. Internal friction may be defined as the energy loss per cycle in an element of volume divided by 2π times the maximum energy stored in the element per cycle or as the tangent of the angle by which the strain lags behind the stress. When energy losses per cycle are not high [6]

$$Q^{-1} = \tan \alpha = \frac{\Delta E}{2\pi E} = \frac{\Delta A}{\pi A} = \frac{1}{\pi} \ln \frac{A_1}{A_2} = \frac{\delta}{\pi}$$

where E = energy
 A = amplitude
 δ = logarithmic decrement

The attenuation of ultrasonic stress waves in materials and loss interactions are discussed in detail by Truell, Elbaum, and Chick in a recent book, *Ultrasonic Methods in Solid State Physics* [5]. In brief, energy losses may be divided into two categories, those that are dependent on the physical characteristics of the specimen material, and those that are characteristic of the method of measurement. The latter group includes such effects as coupling losses, losses due to non-parallelism of specimen faces, phase effects in the transducers, and diffraction and mode conversion effects in the specimen. The losses that are of interest, those that are characteristic of the material, are of two main types, scattering effects and absorption effects. Scattering losses are caused by lattice defects or other discontinuities in the medium. The relative size of wavelength and defect and the defect density will determine whether or not the scattering can be measured. Absorption losses include dislocation damping losses, thermoelastic losses, conduction electron damping losses, phonon-phonon interactions, ferromagnetic resonance effects, paramagnetic resonance effects, and nuclear spin energy interactions.

The attenuation of ultrasonic waves in materials can be determined by a number of methods. With the pulse-echo technique, attenuation is measured by comparison of the amplitude of successive echoes. Losses which occur at each reflection also must be taken into consideration. Effects of coupling losses may be determined by making measurements with a transducer at only one end of the specimen and comparing with results obtained when an identical dummy transducer is coupled to the opposite end of the specimen [5]. By making measurements on specimens of different lengths, effects other than the increased path length can be kept constant and the attenuation calculated from measurements on the different specimens. Reflection of the wave from the sides of the specimen may result in mode conversion from transverse to longitudinal waves or vice versa, and result in energy loss and apparent attenuation. Such effects will depend on wavelength and specimen size.

When the attenuation is small, it can be determined from the decay curve of free vibrations in the specimen [6]. The resonance apparatus described for determination of velocity has as a primary use the determination of internal friction. It can be shown [8] that the logarithmic decrement of the specimen in such a system is proportional to the ratio of the driver crystal voltage to the gage crystal voltage

$$\delta = K \left(\frac{V_d}{V_g} \right)$$

where the constant K is a characteristic of the system. After K has been determined from the free decay of the system, the logarithmic decrement can be determined under different strain amplitudes or other specimen conditions by measurements of the two voltages.

The internal friction can also be determined from the amplitude frequency curve in the region of resonance from the relation

$$Q^{-1} = \frac{\Delta f}{f}$$

where Δf is the total spread from one side of resonance to the other where the amplitude has dropped to $\frac{1}{\sqrt{2}}$ times the resonance amplitude [6].

4. Applications of Ultrasonic Methods to Dental Materials

Ultrasonic methods have been used to measure the mechanical properties of a number of dental materials. Dickson and Oglesby [9] reported the elastic constants of dental amalgams in which the mercury content was varied by varying the condensation pressure. Specimens 8mm in diameter by 6 to 15mm in length were prepared as shown in

table 1. Measurements were made by a pulse-echo technic with a frequency of 5.5 MHz, a pulse length of 0.5 to 1.0 μ s and a pulse repetition rate of 6 KHz. Elastic constants obtained for an amalgam containing about 48 percent mercury are shown in table 2. As the plot in figure 8 shows, the relationship between Young's modulus and mercury content was essentially linear over the range investigated.

Using a resonance method with the three component system of specimen, driver crystal, and gage crystal, Larson [10] investigated the Young's modulus and internal friction of amalgam. The frequency was in the 50 KHz range. Young's modulus values of 8.5×10^6 to 10.6×10^6 psi (5.9×10^4 to 7.3×10^4 MN/m²) were found with mercury contents varying from 30 to 60 percent. A peak in both modulus and internal friction was reported in the 45 to 50 percent mercury ranges.

As would be expected, the Young's modulus values obtained for amalgam by the rapid strain rates inherent in ultrasonic methods are considerably higher than those reported from conventional stress-strain curve procedures. However, using a diffraction grating strain gage which permitted stress-strain curve data to be obtained in 3 to 4 seconds, Gardner, Dickson, and Kumpula [11] obtained a modulus value of 8×10^6 psi (5.5×10^4 MN/m²) which does not differ greatly from those obtained by ultrasonic methods.

TABLE 1. Amalgam Specimen Preparation [9]

11 to 8 Hg/Alloy ratio
20 s trituration, Wig-L-Bug
3 to 6 mixes of two pellets
Condensed in steel die
8 mm diameter by 6 to 15 mm length
5,000 to 25,000 psi (35 to 172 MN/m ²)
35 to 49 percent Hg content

TABLE 2. Elastic constants of amalgam [9]

Property	Value	Range*
Hg content.....	48.6%	0.7
Young's modulus.....	9.09×10^6 psi	0.06×10^6
Shear modulus.....	3.41×10^6 psi	0.03×10^6
Bulk modulus.....	9.12×10^6 psi	0.22×10^6
Poisson's ratio.....	0.334	0.005

*Range of three values.

To convert psi to MN/m² multiply by 6.895×10^{-3} .

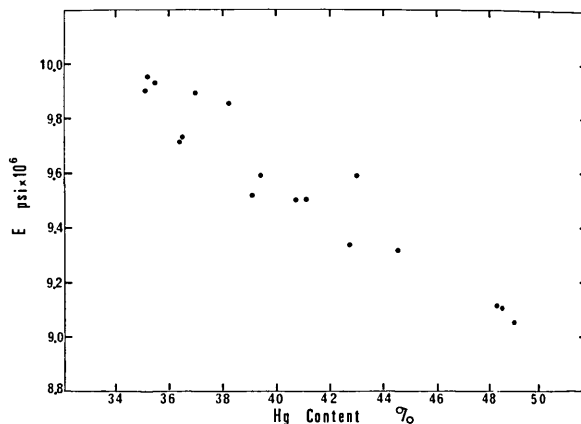


FIGURE 8. Effect of mercury content on Young's modulus of dental amalgam [9].

To convert psi to MN/m² multiply by 6.895×10^{-3} .

In our laboratory, the pulse-echo method has been employed to measure the elastic characteristics of experimental composite quartz or glass-filled resins. The attenuation of the ultrasonic wave in these materials is high and often no suitable echoes are obtained so that the procedure is reduced to measurement of a single transit time. Effects of time delays other than transit time are eliminated by measurements on specimens of various lengths. Data on Young's modulus for an experimental restorative material are given in table 3 [12].

The elastic properties of apatites were investigated by Gilmore and Katz [13] using an ultrasonic interference technic. Powdered specimens of hydroxyapatite, fluorapatite, chlorapatite, and sodium chloride-hydroxyapatite composites were studied when subjected to pressures of up to 50 kbar. Transducers were mounted on the back faces of tungsten carbide pistons, as shown in figure 9, and interference was obtained between reflections from the near and far specimen-piston interfaces.

TABLE 3. Elastic moduli of experimental composite resin restorative material [12]

(In 10^6 psi)

Modulus	Method	Powder-liquid ratio (grams powder to 0.4 ml liquid)		
		1. 10	1. 35	1. 45
E	Stress-strain curve.....	1. 2	1. 3	1. 4
E	Ultrasonic.....	2. 5	2. 6	2. 4
G	Torsion pendulum.....	0. 7	0. 8	0. 8
G	Ultrasonic.....	1. 0	1. 0	0. 9

To convert psi to MN/m² multiply by 6.895×10^{-3} .

X-cut quartz
transducer

Piston

Specimen

Y-cut quartz
transducer

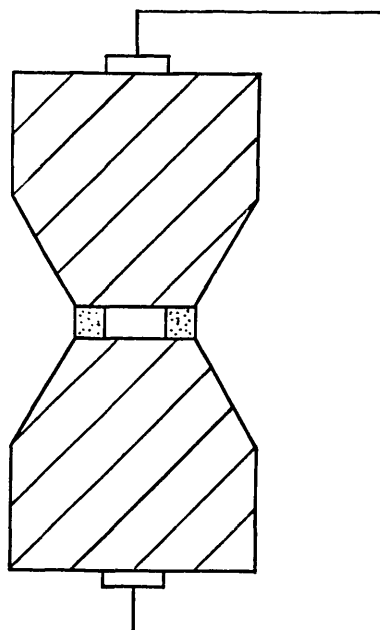


FIGURE 9. Diagram of transducer, piston and specimen arrangement for determination of moduli under high pressure [13].

Values obtained for some of the apatites, as well as values for bovine dentin and enamel, are given in table 4. Moduli of the apatites were found to increase linearly with pressure in the higher pressure ranges.

Lees [14] reported values for the specific acoustic impedance of bovine enamel and dentin obtained by the reflection coefficient method using specimens mounted in acrylic resin. A pulse of 60 ns length was reflected from the specimens in water. The signal amplitude was compared with that of a pulse reflected from stainless steel under similar conditions. Values obtained for acoustic impedance (product of density and sonic velocity) were in general agreement with values obtained by other ultrasonic methods.

The elastic coefficients of animal bone have been investigated by Lang [15] using an ultrasonic pulse method for measurement of velocities. Analysis of the crystallographic structure of compo-

TABLE 4. Elastic moduli of Apatites [13]
(In 10^6 psi)

	E	G	K
Hydroxyapatite.....	15.7	7.7	12.5
Fluorapatite.....		7.5	13.8
Chlorapatite.....		6.3	10.0
Dentin.....	3.0	1.2	2.6
Enamel.....	10.7	4.4	6.7

To convert psi to MN/m^2 multiply by 6.895×10^{-3} .

nents of bone and the piezoelectric and pyroelectric characteristics of bone suggested that bone should behave elastically as a hexagonal single crystal, and the elastic stiffness coefficients were determined on this basis. Young's and shear moduli found for axial and transverse bone directions, in dried bovine femur and phalanx and fresh phalanx, are given in table 5.

TABLE 5. Elastic moduli of bovine bone [15]
(In 10^6 psi)

	Phalanx		Femur
	Fresh	Dried	Dried
E (axial).....	3.19	4.42	3.77
E (transverse).....	1.64	2.31	2.60
G (axial).....	0.78	1.09	1.18
G (transverse).....	0.65	0.94	1.07

To convert psi to MN/m^2 multiply by 6.895×10^{-3} .

5. Summary

A variety of ultrasonic methods are available for determining the elastic characteristics of materials. These methods are precise, rapid, non-destructive, applicable to small specimens, and they measure a specific property of the material. As a number of recent reports in the dental literature indicate, they offer particular advantages to the study of dental materials and mineralized tissues.

6. References

- [1] Rodriguez, M. S., and Dickson, G., Some tensile properties of amalgam. *J. Dental Res.* **41**, 840 (July-August 1962).
- [2] Oglesby, P. L., Dickson, G., Rodriguez, M. S., Davenport, R. M., and Sweeney, W. T., Viscoelastic behavior of dental amalgam. *J. Res. Nat. Bur. Stand. (U.S.)*, **72C** (3) 203-215 (1968).
- [3] Filipczynski, L., Pawlowski, Z., and Wehr, J., *Ultrasonic Methods of Testing Materials* (Butterworths, London, 1966).
- [4] Hueter, T. F., and Bolt, R. H., *Sonics* (John Wiley & Sons, Inc., New York, 1955).
- [5] Truell, R., Elbaum, C., and Chick, B. B., *Ultrasonic Methods in Solid State Physics* (Academic Press, New York, 1969).
- [6] Mason, W. P., *Physical Acoustics—Principles and Methods* (Academic Press, New York, 1966).
- [7] Forgacs, R. L., Improvements in the sing-around technique for ultrasonic velocity measurements, *J. Acoust. Soc. Am.* **32**, 1697 (December 1960).
- [8] Marx, J., Use of the piezoelectric gauge for internal friction measurements, *Rev. Sci. Instr.* **22**, 503 (July 1951).
- [9] Dickson, G., and Oglesby, P. L., Elastic constants of dental amalgam, *J. Dental Res.* **46**, 1475 (Nov.-Dec. 1967).
- [10] Larson, R. V., Internal Friction Damping in Dental Amalgam, Thesis, Dept. of Mechanical Engineering, University of Utah (August 1967).

- [11] Gardner, T. V., Dickson, G., and Kumpula, J. W., Application of diffraction gratings to measurement of strain of dental materials. *J. Dental Res.* **47**, 1104 (Nov.-Dec. 1968).
- [12] Barton, J. A., Jr., Burns, C. L., Chandler, H. H., and Bowen, R. L., An experimental intermediate-restorative composite material. (To be published in *J. Dental Res.*)
- [13] Gilmore, R. S., and Katz, J. L., Elastic properties of apatites. *Proceedings of International Symposium on Structural Properties of Hydroxyapatite and Related Compounds*, National Bureau of Standards, Sept. 1968. To be published.
- [14] Lees, S., Specific Acoustic Impedance of Enamel and Dentin. *Private Communication* (1968).
- [15] Lang, S. B., Elastic coefficients of animal bone, *Science* **165**:287 (July 18, 1969).

Stress Analysis of Dental Structures

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Because of the complex geometry of dental structures, most stress analysis studies in dentistry have been experimental. Brittle coatings have provided generally semiquantitative information on the magnitude, direction and sign of surface stresses of fixed bridges, removable partial dentures, complete dentures and the mandible under various loading conditions. Data from electrical resistance strain gages attached to the metal surfaces of pontics on a gold bridge with various load applications are shown. Applications of both two and three dimensional photoelastic techniques are illustrated. This method, which provides information on the magnitude, direction and sign of boundary and internal stresses is dependent upon how well the model represents the real structure. Other stress analysis methods involve photoelastic coatings, thermophotoelasticity, moiré fringe patterns, holography and x-ray diffraction.

Key words: Brittle coatings for stress analysis; dental materials; denture, artificial, stress analysis; photoelasticity, dental applications; porcelain-gold restorations, stress analysis; stress analysis of dental structures.

1. Introduction

A complete stress analysis of a dental structure would include the determination of the magnitude of the principal stresses, their direction and sign (tension or compression) at all points. Fortunately, from the standpoint of time, a complete stress analysis is rarely required for evaluation of design or for fracture analysis.

Theoretical stress analyses of highly simplified dental structures have been carried out, but simplifying assumptions such as rectangular blocks for pontics and supporting restorations and ends of fixed bridges that are free, resulted in unrealistic calculations. The most sophisticated study to date, considered the roots of anterior teeth to be parabolas of revolution, the periodontal ligament to have designated physical properties, and the boundary stresses were calculated as a function of Poisson's ratio [1].¹ As more information becomes available about the properties of human tissue and restorative materials, it is expected that with the use of computer programs, analytical stress analysis of dental structures will be possible. At present, however, experimental stress analysis of dental structures which have complex geometry is simpler, less time consuming, and more reliable than analytical stress analysis.

Within the time available, I plan to discuss experimental stress analysis techniques which have been applied to dental problems, to point out their advantages and disadvantages, and to discuss briefly experimental techniques that as yet have not been described in the dental literature.

2. Experimental Stress Analysis Using Brittle Coatings

Brittle coatings have been used for many years by industry to indicate the position and direction of the maximum tensile strain and stress [2, 3]. The early work involved the study of mill scale on steel, oxidation layers on bright steel, anodized layers on aluminum and the application of dried coatings of lime and Portland cement prepared from water slurries. Brittle coatings were not used extensively until the development of resin coatings which are prepared by spraying a part with a solution of limed wood rosin K, dibutyl phthalate, and carbon disulfide. The strain sensitivity of the lacquers is controlled by the amount of plasticizer and the method is able to detect strains of about 0.0007 in/in (700 $\mu\text{m}/\text{m}$). The dried coating, if properly applied, contains uniform finely dispersed air bubbles and the sensitivity is essentially independent of the thickness between 0.004 and 0.008 in (100–200 μm). When the coated structure is loaded, cracks appear in the coating at the point of maximum tensile strain and proceed perpendicular to the tensile stress. When temperature and humidity control is used and corrections are made for creep of the lacquer, quantitative values for the magnitude of strain can be obtained. These two quantities may be the only measurements necessary for the stress analysis, and the method has been used successfully to predict fatigue failures. It has the advantages that the tests can be made on the actual structure and with for practical purposes, an infinitely large number of strain gages. Compressive strain and stress can be determined by allowing the lacquer to creep under a load less than

¹ Figures in brackets indicate the literature references at the end of this paper.

that required to produce cracks. After sufficient creep occurs, the load is removed rapidly and the crack patterns observed. Compressive strain also can be measured by preparing the coating while the structure is under load; on unloading, the cracks that appear indicate the compressive strain. Thus, magnitude, direction, and sign can be determined; the method is limited to surface strain which may not be too serious since failures are initiated at surfaces.

A typical example of the use of a brittle lacquer coating in determining the surface strain on the metal framework of a mandibular partial denture when loaded on the left posterior saddle area is shown in figure 1 [4]. The relationship of the load to the location of the cracks and the direction of the tensile strain in the saddle, minor connectors and major connectors can be seen. Of particular interest is that the maximum tensile strain occurred at the left finishing line and that the major connector is under biaxial tensile strain.

3. Experimental Stress Analysis Using Resistance Strain Gages

Electrical resistance strain gages, of wire, foil, or semiconductor type, are described in textbooks [5] and all have been used in dental research [6]. The wire gages are rugged but their large size limits their use to appliances having large, relatively plane surfaces. The semiconductor gages are noted for their high output but their size again, presents problems. The foil gages have been the most practical for small areas on dental bridges and partial dentures. Unless rosette gages are used, some prior information is needed about the direction of the stress in the area where the gage is to be cemented. Of course, the problem of rosette gages is their rather large size. Strain gages can measure the magnitude, sign, and depending on the type of gage, the direction of the strain. A large

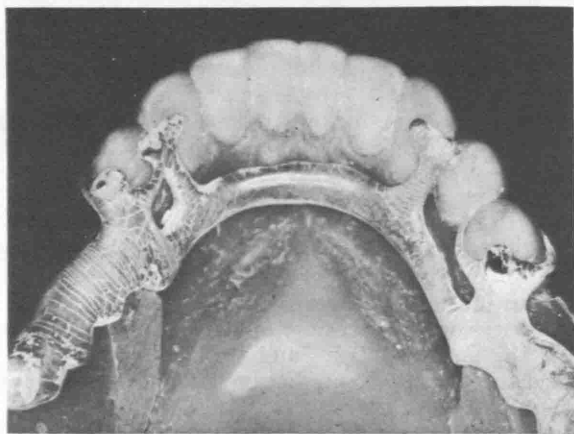


FIGURE 1. Mandibular partial denture framework coated with a brittle lacquer and loaded on the left posterior portion of the saddle.

number of gages may be necessary in a complex structure to obtain a reasonably reliable stress analysis, and thus, an overall idea of the stress distribution may be difficult to obtain.

A gold bridge with strain gages attached to the metal surfaces of the pontics is shown in figure 2 [7]. The sign and magnitude of the strain for various loads and positions of loading are shown in figure 3 for the gage on the molar pontic. As the occlusal loading site was moved from the anterior to posterior position, the gage recorded first

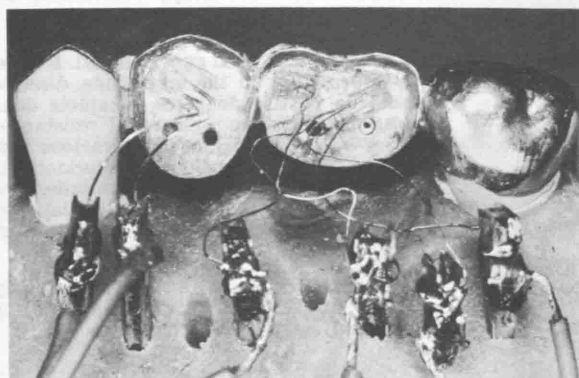


FIGURE 2. Foil strain gages attached to a four-unit gold alloy posterior bridge.

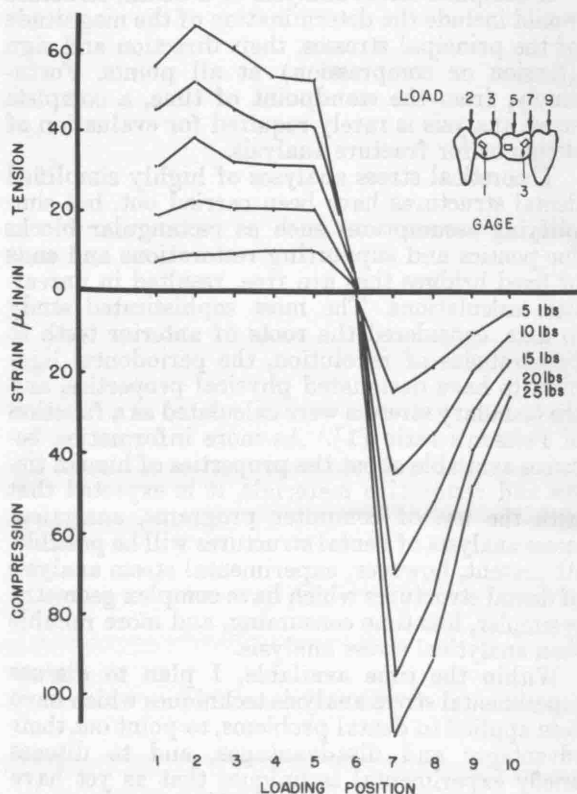


FIGURE 3. Strain versus loading position for the gage on the molar pontic of the four-unit gold alloy posterior bridge.

tensile and then compressive strain. Experience has shown replacement of the gage in as nearly as possible the same position results in strain-position curves of the same general shape, but not identical magnitude; this condition results from being unable to cement the second gage in exactly the same location and orientation as the first. Of course, care must be taken in cementation and the gage must be protected if it is to be used in an adverse environment.

The strain gage method permits the measurement of surface strains of low magnitudes. (Special gages are available for fatigue measurements.) As will be shown later, they are readily used in impact as well as static loading.

4. Experimental Stress Analysis by Photoelastic Techniques

Numerous researchers in dentistry have used photoelastic methods to study stresses in dental structures [6], however, only the more recent papers will be referred to in the following discussion.

The photoelastic method for stress analysis can be divided into two-dimensional, three-dimensional, reflection, and scattered light techniques [8-10]. A schematic sketch of a transmission polariscope is shown in figure 4. In general, the method involves the use of a plastic model or coating which is birefringent under stress. When plane polarized light is used to examine the plastic, two sets of interference lines (fringes) are observed, one is the loci of constant stress direction (isoclinics) and the second is the loci of constant difference between the principal stresses (isochromatics).

They can be identified using white light since the isoclinics are black and move as the polarizer and analyzer are moved. Also, in circularly polarized light (quarter-wave plates used) only the isochromatics are observed. The magnitude of the difference in the principal stresses can be measured by determining the order of the fringe and knowing the fringe constant and thickness of the plastic. The sign may be determined by inspection in white light by noting the order of the color of the fringes or by using various compensators such as the Cooker or Babinet. The boundary stress may be calculated directly, since one or the other of the principal stresses must be zero. The separation of the principal stresses in the interior of the model may be accomplished by additional measurements of the lateral strain by determining the isochromatics using both normal and oblique incident light, or by the shear difference method.

A dental application of the two-dimensional method is illustrated in figure 5 which shows a mesial-distal section of a three-unit bridge [11]. The plastics were selected to have as nearly as possible the same ratio of the elastic moduli as tooth structure and gold. Only the isochromatics are shown and the fringes in the areas of the soldered joint show high tensile stress concentrations and high compressive stresses in the contact area. Only minimal stress is in the gingival portion of the pontic, although maximum tensile stress would be predicted from a simple beam in transverse bending. The boundary stresses can be obtained simply by noting the fringe order, the sign, and multiplying the fringe order by the fringe constant and dividing by the thickness of the model. The separation of the principal stresses has been

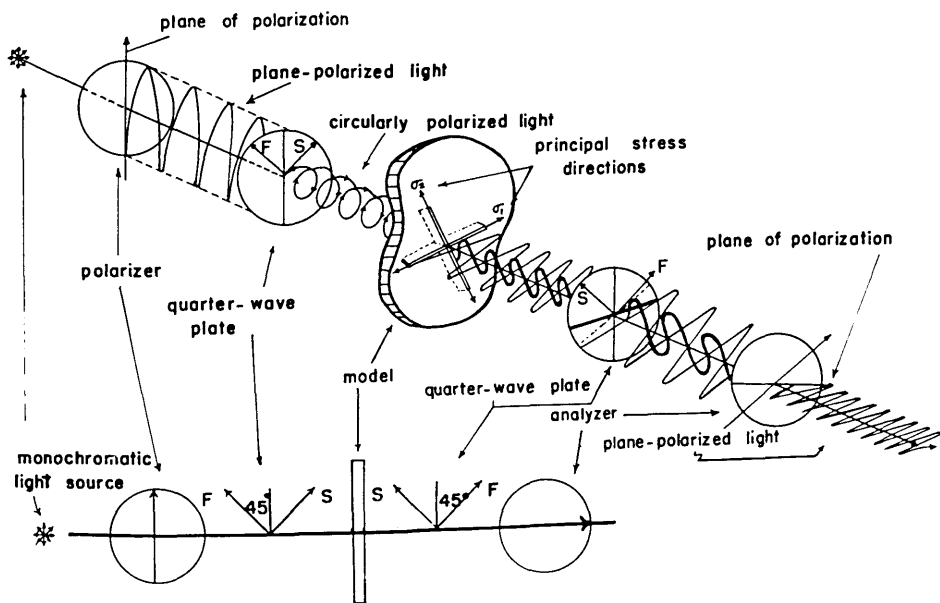


FIGURE 4. Schematic of a transmission polariscope.

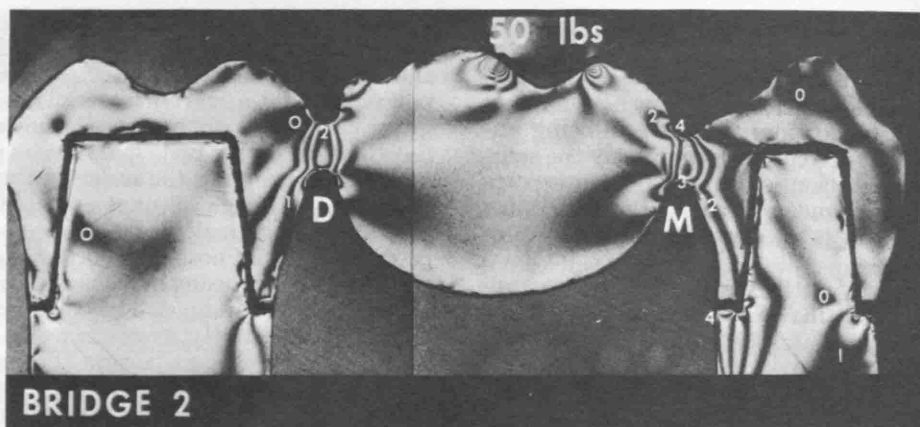


FIGURE 5. Isochromatic fringes in a two dimensional model of a mesial-distal section of a three-unit bridge.

carried out using the shear difference method of graphical integration and the results are shown in figure 6.

The advantages of this method are that the magnitude of boundary and internal stresses can be measured as well as their direction and sign. The disadvantages are related to the model and how closely or remotely it represents the real structure.

An additional example of two-dimensional photoelasticity is shown in figure 7 [12]. The model represents a porcelain fused to gold restoration cemented to dentin; it was constructed of three plastics having moduli in approximately the same ratios as the restorative materials. Of particular

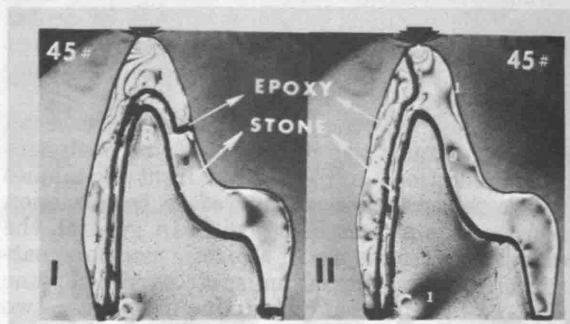


FIGURE 7. Two-dimensional photoelastic model representing a labial-lingual section of porcelain fused to gold restorations; the plastics representing the gold and porcelain were cemented with epoxy cement which in turn was luted to the plastic representing dentin with dental stone.

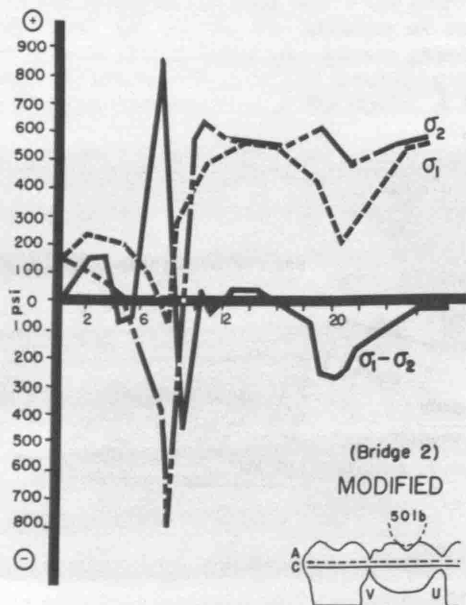


FIGURE 6. Separation of principal stresses along a line midway between A and C for the model in figure 5.

interest is the low state of stress in the dentin section of the model.

The three-dimensional technique takes into account the contribution of the third dimension of an object to the stress distribution. In this technique a three-dimensional model is prepared by machining from plastic or by casting into a mold. The model is subjected to a load and heated slowly under load and finally cooled to room temperature thus freezing the stresses in the model. The model may be sliced without release of the frozen stresses as seen in figure 8. Using surface slices and two-dimensional slices and sub-slices, the principal stresses may be determined using the previously mentioned methods.

The three-dimensional method may be completely reliable for homogeneous solids, but there may be serious discrepancies in the model for heterogeneous solids or composites. In the study of dentures by Klotzer [13] the problem does not exist since the properties of denture and photoelastic plastics are similar. Papirno, Colin, and Kaufman [14] have made progress toward the solution

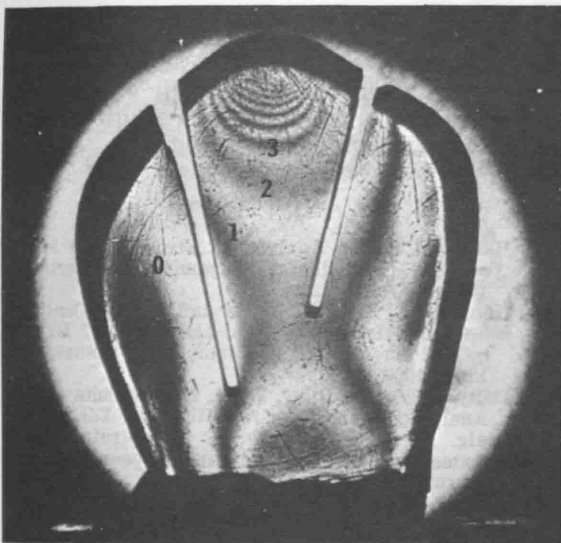


FIGURE 8. A slice from a three-dimensional model which has been subjected to a stress freezing cycle; isochromatic fringes are shown.

of the problem by the use of plastics of different moduli for the restoration and tooth structure.

The use of photoelastic coatings on the actual structure is a more recent method for studying surface stresses. The coating is prepared by pouring a catalyzed resin into a thin sheet and when it has jelled it is adapted to the part to be studied. After the polymerization is complete, the coating is removed and then cemented to the structure with a reflective plastic cement. The structure is loaded and illuminated with polarized light. In this method the polarized light passes through the coating, is reflected off the cement surface and observed with an analyzer. Fringes are observed and interpreted in a manner similar to transmission photoelasticity. A gold bridge coated with photoelastic plastic and loaded occlusally is shown in figure 9. The first-order fringe is easily visible as the brightest fringe. The highest stress concentration was observed in the area of the soldered joint with the highest orders being nearest the center. The pontic and even the area near the site of loading was under low stress. If the photoelastic coating is thin and of low modulus compared to the underlying structure the reinforcing effect of the coating can be ignored and the stress in the coating will be essentially that in the surface of the structure. If these factors cannot be avoided, corrections must be made. The magnitude, sign, and direction of the stresses can be determined as usual, and separation of the principal stresses is accomplished by the oblique incidence method. The method has the distinct advantage that the actual structure can be used and questions about the reliability of the model are avoided.

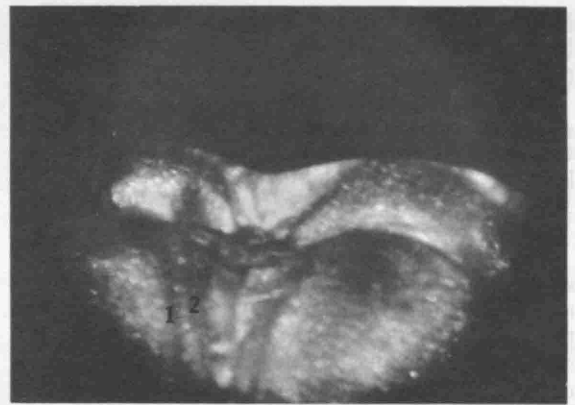


FIGURE 9. Isochromatic fringes in a photoelastic coating on a gold alloy bridge.

5. Additional Techniques in Stress Analysis

The three techniques, brittle coatings, strain gages, and photoelasticity can be used under conditions of impact, as well as static loading. The strain gage recording system must have a high frequency response in order to measure the maximum transient strains; a storage type oscilloscope is particularly useful for these measurements. An example of the strain on the mesial area of the molar pontic of a four-unit gold alloy bridge as a result of an impact on the lingual cusp is shown in figure 10 [15]. The maximum strain did not occur until the third oscillation and the initial strain was compressive followed by tensile strain. The maximum strain was 192 microinches/inch ($192 \mu\text{m}/\text{m}$) and the maximum stress was 2690 lbs/in² (18.6

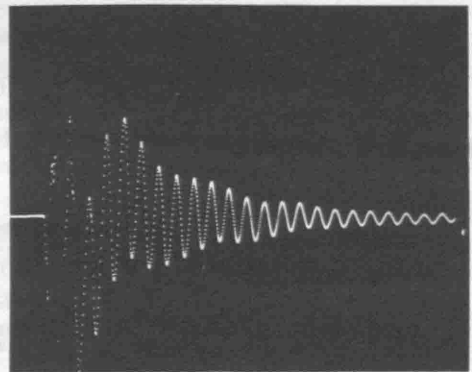
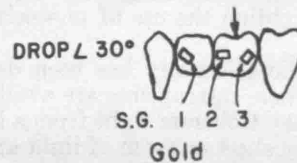


FIGURE 10. Strain as a function of time on the mesial area of the molar pontic resulting from an impact blow on the lingual cusp of the first molar pontic; total time was 4.5 ms.

MN/m²), and the strain decayed with time. Similar measurements showed that torsional, as well as transverse modes of vibration occurred.

The simplest dynamic technique for photoelastic stress analysis involves a spark light source and a delay circuit connected to the loading device. The load is applied and a photoelastic stress pattern is photographed at predetermined delays after loading.

Thermophotoelasticity also has been used to study stresses resulting in plastic models from thermal shock [16]. Various arrangements for the application of heat have been used including liquids and metal resistance strips. This method could be used to examine the stresses in dental restorations resulting from thermal shock.

Moiré fringe patterns have been used to study surface deformation. This is simply the comparison between a deformed grid and an undeformed master grid used as a length standard [17]. The method is applicable to high temperatures, large elastic and plastic strains, long term strain properties of materials, and of two and three dimensional analysis of transparent models using embedded grids. The method is best suited to flat surfaces and the preparation of a grid on curved surfaces such as dental restorations has limited its application in dentistry.

Holography has been used in stress analysis to determine isochromatic, isoclinic and isopachic (loci of constant sum of the principal stresses) fringe patterns in two dimensions [18, 19]. Combination isochromatic and isopachic fringe patterns have been obtained which give directly a solution for the individual principal-stress components. A double exposure method for measuring surface stresses on dental restorations offers promise as a means of avoiding the use of photoelastic coatings.

Scattered light photoelasticity has been developed to the point where instruments are available commercially [20, 21]. Coherent light from a laser is focused into a thin sheet or beam of light and it is passed through a plastic model in an immersion tank under load and the scattered-light fringes are observed. The patterns can be interpreted to give solutions to three-dimensional problems. This technique is comparable to locating a polarizer or analyzer in the interior of the model and stress information can be obtained without stress-freezing or slicing the model.

The distance between atoms may be used as gage lengths in the x-ray diffraction of crystalline solids, and strains may be determined by measuring changes in these interatomic distances. The method can be used to measure residual surface stresses without drilling holes to relieve the stress. The method can give the sum of the principal stresses in the surface layer and in fine-grained alloys, the accuracy is about 2,000 lbs/in² (14 MN/m²) and in coarse-grained alloys it has a much lower accuracy.

6. Summary

In summary, a number of recently developed stress analysis techniques, as well as standard methods offer real promise in the solution of the numerous related problems in dentistry.

7. References

- [1] Haack, D. C., *An Analysis of Stresses in a Model of the Periodontal Ligament*, Dissertation (Kansas State Univ., 1968).
- [2] Hetenyi, M., *Brittle Models and Brittle Coatings*, 636-62, In Hetenyi, M. ed., *Handbook of Experimental Stress Analysis* (John Wiley & Sons, New York, 1950).
- [3] Dally, J. W., and Riley, W. F., *Experimental Stress Analysis*, 91-139 (McGraw-Hill, New York, 1965).
- [4] Craig, R. G., and Peyton, F. A., *Strain on the framework of a mandibular free-end partial denture under load*, J. Biomed. Mater. Res. 1:263-74 (Jan. 1967).
- [5] Dally, J. W., and Riley, W. F., *Experimental Stress Analysis* 366-514 (McGraw-Hill, New York, 1965).
- [6] Peyton, F. A., Asgar, K., Charbeneau, G. T., Craig, R. G., and Myers, G. E., *Restorative Dental Materials* 138-9 (Mosby, St. Louis, 1968).
- [7] Tillitson, E. W., Craig, R. G., and Peyton, F. A., *Experimental Stress Analysis of Gold and Chromium Alloy Bridges*, I.A.D.R. Dental Materials Group microfilm, Washington, D.C., March 1967.
- [8] Dolan, T. J., and Murray, W. M., *Photoelasticity I. Fundamentals and Two-Dimensional Applications* 828-923, In Hetenyi, M. ed., *Handbook of Experimental Stress Analysis* (John Wiley & Sons, New York, 1950).
- [9] Drucker, D. C., *Photoelasticity II. Three-Dimensional Photoelasticity* 924-76, In Hetenyi, M. ed., *Handbook of Experimental Stress Analysis* (John Wiley & Sons, New York, 1950).
- [10] Dally, J. W., and Riley, W. F., *Experimental Stress Analysis*, 143-333 (McGraw-Hill, New York, 1965).
- [11] El-Ebrashi, K. M., Craig, R. G., and Peyton, F. A., *Photomechanics and Stress Concentrations in Fixed Dental Restorations*, I.A.D.R. Dental Materials Group microfilm, San Francisco, March, 1968.
- [12] Craig, R. G., El-Ebrashi, M. K., and Peyton, F. A., *Stress Distribution in Porcelain Fused to Gold Alloy Crowns and Preparations Using Photoelasticity*, I.A.D.R. Dental Materials Group microfilm, San Francisco, March, 1968.
- [13] Klotzer, W., *Über polarisationsoptische Untersuchungen an Prothesenmodellkörpern*, Deut. Zahn. Zeit. 21:894-901 (1966).
- [14] Paprino, R., Colin, L., and Kaufman, E. G., *Properties and Preliminary Three Dimensional Photoelastic Results Using Room Temperature Curing Resins*, I.A.D.R. Dental Materials Group microfilm, San Francisco (March 1968).
- [15] Tillitson, E. W., Craig, R. G., and Peyton, F. A., *Experimental Stress Analysis of Dental Bridges Using a Dynamic Method*, IADR Dental Materials Group microfilm, San Francisco, March, 1968.
- [16] Leven, M. M., and Johnson, R. L., *Thermal stresses on the surface of tube-sheet plates of 10 and 33½ percent ligament efficiency*, Exper. Mech., 4, 356 (1964).
- [17] Zandman, F., *The transfer-grid method, a practical moiré stress-analysis tool*, Exper. Mech., 7, 19 A (1967).

- [18] Fournery, M. E., Application of holography to photoelasticity, *Exper. Mech.* **8**, 33-8 (1969).
- [19] Hovanesian, J. D., Brcic, V., and Powell, R. L., A new experimental stress-optic method: Stress-holo-interferometry, *Exper. Mech.*, **8**, 362-8 (1968).
- [20] Srinath, L. S., and Frocht, M. M., The potentialities of the method of scattered light, *International Symposium on Photoelasticity* (Pergamon Press, New York, 277-93, 1961).
- [21] Jenkins, D. R., Analysis of behavior near a cylindrical glass inclusion by scattered-light photoelasticity, *Exper. Mech.* **8**, 467-73 (1968).
- [22] Barrett, C. S., X-ray Analysis, In Hetenyi, M., ed., *Handbook of Experimental Stress Analysis* (John Wiley & Sons, Inc., New York, 1950).

Relations Between Mechanical Properties and Clinical Behavior

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A dilemma in the field of dental materials is that in many instances the critical physical properties that are relevant to the failure of restorative materials have not been identified or when identified the limiting values which separate successful from unsuccessful materials have not been established. To determine the critical property relevant to clinical marginal fracture of dental amalgam restorations, dynamic creep and other physical properties including compressive, tensile and transverse strength and transverse deflection of nine amalgam alloys were determined. Clinical evaluation of restorations made using alloys widely separated in dynamic creep showed that marginal fracture was associated with the rheological properties of dynamic creep, static creep and slow compressive strength, but showed little relationship to the other physical properties measured. Although the relationship between creep and marginal fracture may not be a cause and effect mechanism, creep appears to be reasonably predictive of clinical marginal fracture.

Key words: Amalgam, dental; correlation of laboratory and clinical evaluations; creep of dental amalgam; dental materials; dynamic creep; fracture, marginal of dental amalgam; mechanical properties of dental materials; rheological properties of dental amalgam.

If an engineer were to be taken into a clinical operatory, a tooth which had been restored with a certain material were pointed out to him, and he were asked to comment on the efficacy of the restoration, what questions would he be likely to ask? First he might ask the general question whether the material was performing satisfactorily. Specifically he might ask the following questions about the material:

1. Is it maintaining its shape, color and appearance?
2. Is it biologically compatible?
3. Is it truly restoring the tooth to its original function?
4. Is it doing these things over a long time period?

If the answer was yes to all of these questions, he might lose interest in the conversation and leave. If the answer was no, he would probably become interested and ask how is the material performing unsatisfactorily. Specifically what are the modes of failure. Let us assume that we can supply our engineer with an answer to this question. If so, he would probably start to think in terms of physical properties and try to identify in his mind which property or properties might relate to the mode of failure outlined.

The dilemma in the field of dental materials today is that, by and large, we have been unable to identify these critical physical properties that are relevant to the failure of restorative materials. In figure 1, this dilemma is outlined. Furthermore, where we have identified a pertinent physical property, we have not been able to assign limiting

values which can separate the successful from the unsuccessful material.

Once the relevant property is identified, the procedure for improving the material is fairly straightforward, although there may be many difficult and unsolvable problems along the way. The identification of this relevant property can function as follows:

1. It would allow us to identify the actual mechanism of failure.
2. It would give us a means of designing this weakness out of the material.
3. It would allow us to utilize laboratory methods of screening material modifications for possible improvement.
4. It would allow us to conduct clinical trials on only those modifications which show the greatest promise.

I would like to show you an example of how we, at the Dental Materials Science Department of the University of Oregon, have attempted to follow this approach of identifying a relevant physical property. The example is that concerned with the marginal fracture of dental amalgam which is perhaps the most significant failure mode for this material.

Initially, a laboratory test was devised which was thought to parallel the situation confronted by an amalgam restoration in the mouth. Cyclic compressive loading, which was considered to relate to the way in which masticatory forces are applied to amalgam restorations under clinical conditions, was applied to an amalgam test specimen. In addition, water at 37 °C was circulated around the specimen during the test. The deforma-

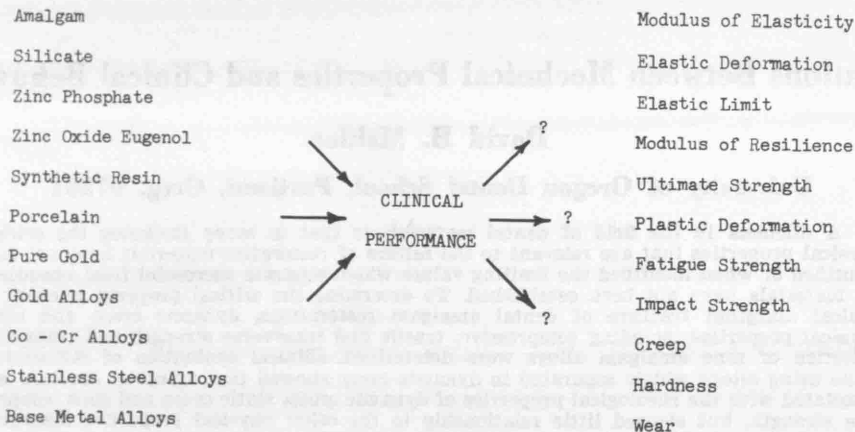


FIGURE 1. Dental restorative materials; clinical performance and mechanical properties.

tion of the specimen was recorded during the testing procedure using a linear transducer wired to a recorder. The parameter measured was the dynamic creep of the specimen over a fixed time interval of testing. A schematic of the test system is shown in figure 2. The results of testing 9 commercially available amalgam alloys are shown in figure 3. The first most obvious result was that amalgam alloys having relatively small differences in conventional physical properties showed a very marked difference in dynamic creep properties.

The next step was to determine the clinical significance of these differences. In view of the many difficulties attendant with clinical testing, it is important to maintain as simple an experimental design as possible. Therefore, it was considered appropriate to evaluate the clinical performance of the two alloys at opposite ends of dynamic creep behavior, Alloys A and I. If no difference in clinical performance could be observed, then this property would have little relevance to clinical

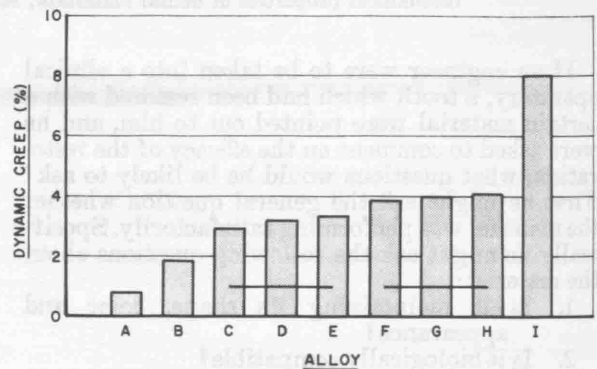


FIGURE 3. Dynamic creep of nine commercial dental amalgam alloys.

behavior and there would be little point in testing alloys in between. Alloy B was also selected for evaluation in case this property did prove of significance since the dynamic creep value for Alloy B was close to but significantly different from Alloy A.

The procedure consisted of placing these three alloys under conditions which produced amalgam restorations having physical characteristics close to those of the laboratory test specimens. This was accomplished by determining the Hg content of representative restorations of the three alloys placed by dentists cooperating on the project. Laboratory test specimens were prepared at these same Hg contents. After one year of service, occlusal photographs were taken of these restorations. Marginal fracture was noted in many of the restorations and the entire group of photographs was separated into five groups of marginal frac-

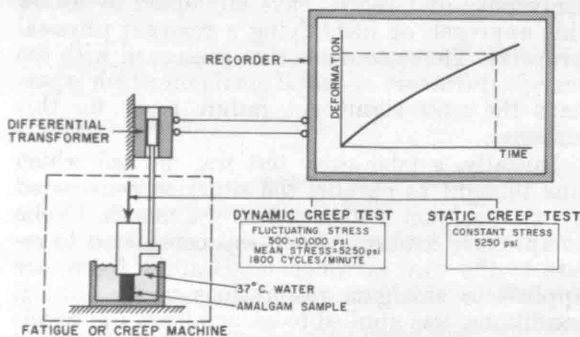


FIGURE 2. Schematic of systems for dynamic and static creep testing.

ture as shown in figure 4. The data were subjected to a Ridit analysis which is shown in table 1. The table entries are the numbers of restorations assigned to each category by three evaluators. Alloy N, which corresponds to Alloy B, having a dynamic creep value slightly higher than Alloy A in figure 3, was taken as the standard distribution with a mean value of 0.50. Alloy D, which corresponds to Alloy A, having the lowest creep value, (fig. 3), had a mean value of 0.39 which was clearly differentiable from Alloy N with a significant "t" value of 3.2. Alloy M having the highest creep value of all alloys tested and which corresponds to Alloy I in figure 3, had a mean value of 0.81 with a significant "t" value of 10.2.

In simple terms, the results of the clinical evaluation showed that Alloy D, having the lowest dynamic creep value, had the least amount of marginal fracture; Alloy N, having a slightly higher dynamic creep value, had a slightly higher incidence of marginal fracture; and Alloy M, having the highest dynamic creep value, had an extremely high incidence of marginal fracture.

In order to test the uniqueness of this relationship of dynamic creep to marginal fracture, other mechanical property tests were conducted as well. These included compressive strength, tensile strength, transverse strength, transverse deflection, flow as determined in accordance with American Dental Association specification No. 1, and static creep. The results of these tests together with the marginal fracture results are shown in figure 5. Arrows have been drawn in the direction of superior characteristics and the "t" values for comparisons are shown with the arrows. From figure 5, it is seen that only the rheological properties of dynamic creep, static creep, and slow compressive strength relate in the proper direction to marginal fracture.

Although the relationship between creep and marginal fracture should not at this time be considered a cause and effect mechanism, this property appears reasonably predictive of the clinical phenomenon of marginal fracture. Additional work is being conducted to strengthen this hypothesis.

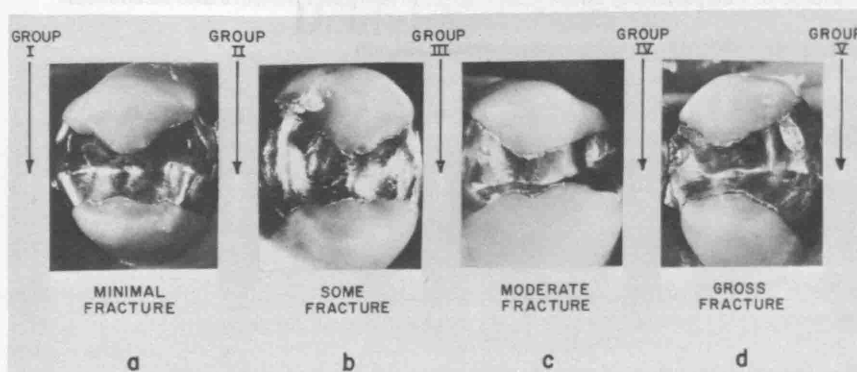


FIGURE 4. Classification of marginal fracture of amalgam restorations.

TABLE 1.—Ridit analysis of marginal fracture

		I	II	III	IV	V	Total
Alloy N.....	Evaluator A.....	8	35	8	4	1	56
	Evaluator B.....	15	15	16	7	3	56
	Evaluator C.....	10	20	21	4	1	56
Alloy D.....	Evaluator A.....	18	33	6	1	0	58
	Evaluator B.....	22	19	14	3	0	58
	Evaluator C.....	19	26	11	2	0	58
Alloy M.....	Evaluator A.....	1	5	18	22	6	52
	Evaluator B.....	0	1	11	13	27	52
	Evaluator C.....	2	5	19	18	8	52

	\bar{X}	$S\bar{X}$	t
Alloy D compared to Alloy N	0.39	0.032	3.2
Alloy M compared to Alloy N	0.81	0.026	10.2

	<u>Alloy D</u>		<u>Alloy N</u>		<u>Alloy M</u>
Marginal Fracture	.39	← 3.2 →	.50	← 10.2 →	.81

Compressive Strength (psi)	61400	← 2.5 →	59500	← 9.7 →	51900
Tensile Strength (psi)	6940	← 4.2 →	7930	← 0.7 →	7770
Transverse Strength (psi)	13220	← 6.2 →	18030	← 8.4 →	12450
Transverse Deflection (μ)	20	← 1.8 →	23	← 6.8 →	32
ADA Flow (%)	0.50	← 2.6 →	0.65	← 19.4 →	3.91
Dynamic Creep (%)	0.86	← 6.4 →	1.85	← 23.7 →	8.76
Static Creep (%)	0.76	← 8.0 →	2.36	← 20.3 →	8.37
Slow Compressive Strength (psi)	38500	← 7.3 →	34600	← 30.6 →	23400

FIGURE 5. Comparison of alloys with respect to marginal fracture and mechanical properties.

(psi × 0.00689 = MN/m²)

VI. Development of Improved Methods for Evaluating Dental Materials

Need for Research To Develop Performance Characteristics

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To develop the most important characteristics of restorative materials, an understanding of the processes by which margins of such restorations become damaged is needed. Bulk and margin properties should be correlated. The mechanical forces developed in mastication and chemical attack by the oral environment are important factors. Tensile strength appears a more meaningful data than either shear or compressive strength. Research for selection of proper tensile test procedures is needed. Cracks and voids in specimens complicate their strength behavior. The role of temperature in laboratory evaluation is important. The mechanisms of corrosion and erosion of dental restorations requires further research.

Key words: Clinically related strength properties of dental materials; dental materials; dental materials, correlation of bulk and marginal properties; dental materials, performance characteristics; dental restorations, the role of oral environment factors in stability thereof.

1. Introduction

The purpose of a dental restoration is to re-establish the patient's ability for chewing and speaking while also attention must be given to the esthetic requirements. The quality of the restoration must be on such a level that a long lifetime is guaranteed. When limited only to the materials which are used to restore teeth, it may be said that the lifetime of the filling is restricted by the appearance of recurrent caries in the adjacent tooth structure. In many cases a correlation can be detected between the recurrent caries and the adaptation of the filling. The adaptation of the filling can be decreased by damage to the margin of the filling. Such a defect however is seldom discovered by the patient himself. In most cases the dentist will trace the defect with the help of a radiographic photograph, which shows the recurrent caries.

When determining the quality of a filling, attention should be directed to the junction between filling and tooth structure. The adaptation must be so good that local caries will not occur and the quality of the margin must be on such a level that chewing and biting forces, as well as the chemical attack by the oral environment, can be resisted.

2. Desirability of Establishing a Correlation Between Bulk and Margin Properties

Many authorities have shown that the margins of amalgam fillings are inferior to the body-part. Also zinc phosphate cement may show such discrepancies. When cementing a crown or inlay, the

fluid part of the cement runs faster to the margin than the more viscous material, which may result in a weaker material at the margin. It seems possible that silicate cement may show such phenomena also.

The discrepancy between the margin and the other part of the filling is correlated to the clinical manipulation of the material. It is well known that in order to get a better amalgam filling, the cavity must be filled to excess and then carved or reduced to the right level. The degree of over-filling depends on several factors such as cavity design, the plasticity of the material, and the skill of the dentist. Therefore, it may be concluded that in clinical cases there will not be an exact correlation between the properties of the margin and the body-part of the filling. As the properties of the filling materials are determined on a rather large specimen, which most likely shows the characteristics of body-material, it is questionable if the quality of the filling, particularly of the margin, might be predicted in this way.

Research is needed to determine the correlation between body and margin properties. If the different brands of a dental material do not show the same correlation between the body properties and margin properties, it would be useful to test the material on a powder-liquid ratio which correlates with the composition of the margin.

3. Relation of Properties and Forces Applied Orally

When it must be decided if a material can be used successfully for a restoration, consideration must be given to the chemical and physical forces

to which the material will be subjected. In general, a distinction can be made between mechanical forces, i.e., chewing and biting forces, which are applied to the occlusal part of a filling, and a chemical attack on the whole filling. Consideration must also be given to the fact that as long as the filling is not hardened, the adjacent soft tissue and the pulp may be irritated by the toxic nature of some ingredients.

The materials which are used for occlusal fillings require such strength that fracture or deformation will not occur. It is very difficult to establish the exact requirements because there is a large diversity in tooth shape and in the forces which can be developed. Only a qualitative approach seems possible. In relation to the chewing muscles average forces can be developed in the magnitude of 100 to 200 kgf (980 to 1,960N). Also forces of 800 kgf (7,800N) are known, but these are exceptional.

When a force of about 200 kgf (1,960N) is supported by the multi-cusp contact area between the teeth and their antagonists which is approximately 2 cm², a stress of 100 kgf/cm² (9.8MN/m²) results. Such a stress is far below the compressive strength of all filling materials. Amalgam may show a flow-deformation if the stress remains for a long time. When the force is carried by only one tooth, a higher stress is possible. Then, the magnitude of the force depends on the distance to the temporomandibular joint. The maximum force might be about 35 kgf (340N). However, it is questionable if such a force is, in fact, accepted by the tooth. Normally the force is restricted by a pain reflex.

A more practical approach to assessing the magnitude of the forces, developed on chewing, has been to utilize electronic measuring devices, mounted in the elements of a partial prosthesis. These measurements indicate that chewing forces on first molars approximate 6 to 7 kgf (60 to 70 N). It seems reasonable to assume that with natural teeth higher forces might be developed. When the chewing force is doubled, e.g. 14 kgf, (140N) and the contact area between the tooth and the antagonist with food in between is established on 0.14 cm², then a stress is applied of 100 kgf/cm² (9.8MN/m²).

As the stresses ordinarily developed are far below the compressive strength of the filling materials, it is most likely that fracture will occur only in exceptional circumstances. When looking for an explanation of a fracture of a fully supported margin, it is reasonable to find it in a stress concentration which is caused by hard substances that may exist in the food. For example, vegetables may contain some sandgrit. The stress realized by biting upon this grit is hard to calculate, because this depends on the size and shape of the grit and the magnitude of the developed force. During chewing, when the hard substance comes between

the teeth, the movement of the jaw will be stopped by the reflex from the proprioceptive receptors which are settled on the end of the fibers which support the teeth. The reflex goes through the brain and can be suppressed. When a high force is needed to mill the food the proprioceptive receptors will react at a different level and the force transmitted by the unexpected hard particles might be rather high.

On the other hand, the movement of the jaw itself is realized by a very small force. In fact the force is increased as soon as the contact between the teeth is realized. This means that when biting on a large particle, the chewing will be interrupted before a high force is developed. If it is accepted that hard substances in the food are a main reason for damage to the margin of fillings, it is clearly desirable to develop information pertaining to the magnitude of the developed forces. Especially when the hard substances are small, a large stress may develop. By such a phenomenon, fracture will not occur very often but each incidence may result in a carious attack.

In many cases the filling and the margins do not possess a perfect shape. A perfect adaptation seldom occurs and many times at the margin the filling is not coincident with adjacent tooth structure. Such a situation is much more dangerous for the occurrence of a fracture, because the filling is no longer fully supported. It is questionable if this is a matter of any importance to the specialist in dental materials. When the filling extrudes because the dentist incorporated moisture in the zinc-containing amalgam, the inferior result is the responsibility of the dentist.

Whenever there are phenomena which cannot be controlled by the dentist, they deserve much attention. It is very desirable to be informed in a quantitative way about the influence of the dimensions of the gap between filling and tooth structure, on the loss in strength of the margin, and on the chance for recurrent caries. Such knowledge will assist in the determination of the requirement for dental materials.

Fillings are mainly subjected to compressive forces. However, even in the case of a perfect adaptation, in addition to the compressive stresses developed in the filling, tensile and shear stresses will also be realized. The nature of the stress causing the fracture is difficult to tell because the ratio between the magnitude of the different stresses is not known, but experience shows that the resistance against compression is much higher than the resistance to tensile forces. When the margin of the filling is not perfect, it is likely that greater tensile and shear stresses are developed. Therefore, it is difficult to decide which mechanical property is the criterion that should be used to evaluate the filling material. Research is needed to solve this problem. In relation to this, it might be useful to study the phenomena which initiates the fractures.

4. Theory of Fracture in Compression and Tensile Testing [1-4]¹

The compression test has been used most frequently. It is assumed in this test that fracture is realized by shear stresses. It is believed an ideal fracture shows two cones, respectively containing the bottom and the top surface of the specimen. This shape of fracture is explained by shear stresses which are maximal in the planes at an inclination of 45° with the direction of loading. This theory, especially when applied to fracture of brittle materials, is no longer accepted by the specialists in fracture phenomena. New theories have been introduced since repeated failures have been reported of Polaris rocket motor casings at stresses well below design value. An early tensile fracture is based upon the existence of cracks, which cause stress concentrations, according to the theories of A. A. Griffith [3], published in 1920. The materials that are used in the Polaris rocket have a high strength but do not possess much ductility. It seemed that a new property must be introduced: namely the stress intensity factor with the formula $K = \sigma\sqrt{\pi a}$, wherein "a" is one half of the length of the crack.

Because most of the dental filling materials are brittle by nature and contain cracks and porosities, it might be useful to consider these newer theories. Comparing the appearance of the fracture planes respectively caused by tensile forces and compression forces, it is suggested that brittle fracture can only be realized by tensile forces. Further investigations showed that most fractures under compressive forces run in an axial direction. This was also the case with a single crystal of sodium chloride which was oriented in such a direction that oblique fracture planes with a certain inclination were expected. Although a scratch on the surface initiated a crack in an oblique direction, the fracture propagated in the direction of loading. Thus it may be stated that the fracture is realized by tensile stresses and initiated by cracks which cause stress concentrations. However, the influence of the crack is not the same in every case. In the direct tensile test, the stress concentration depends only on the longest axis of the assumed elliptical crack, which increases during fracturing, while in the compressive test the stress concentration depends on the ratio of both axes of the ellipse and on the inclination. In the direction of fracturing under compression, however, only the crack itself is important; and during fracturing the stress is not increased nor decreased.

For dental purpose a test must be selected which indicates the strength of the margins. It seems very probable that a tensile test will offer the best correlation. Besides the direct tensile stress, which is not very favored by reason of the difficulty in fab-

ricating a proper specimen, the cleavage test and the flexure test have been used. The resulting strength values, however, are not on the same level, therefore, research is needed to select the proper test. Also, the existence of porosities should be taken into consideration. The appearance of the fracture surface might give indication of the source of rupturing.

5. Role of Temperature in Property Evaluation

In most cases strength measurements are made at room temperature, although the materials are subjected to forces at mouth temperature. This may lead to wrong results for materials with a low fusion temperature, such as the amalgams. It is known that amalgams which go from room temperature to mouth temperature show a reduction in compressive strength. The literature gives numbers of 8 percent and 15 percent for the average reduction. Private observations showed a reduction of about 30 percent. This discrepancy may result from variations in the time which the amalgam is allowed to remain at mouth temperature and by the difference in the loading speed. The figures regarding the reduction in strength show that the different brands did not behave in the same way. Thus by this effect it might be concluded that the testing must be performed at least at mouth temperature.

In addition, it must be taken into consideration that higher temperatures are developed while hot food is swallowed, resulting in a temporary decrease in amalgam strength. While the oral cavity temperature decreases rather quickly, it is questionable that the phases of the amalgam come to equilibrium as rapidly. Where such phenomena may cause a weakening effect during a longer time, the chance is increased for damaging of the margins of the filling. In this paper fatigue phenomena are not discussed. However, it may be stated that these are also very important, because they may introduce the initial defect in the filling.

6. Oral Environmental Effects and Laboratory Testing of Dental Materials

The lifetimes of fillings which are not subjected to chewing or biting forces will be related to the chemical attack by the oral environments and to erosion created by saliva, food, and the soft tissues which slide over the fillings. The chemical attack itself can be created by the saliva, the plaque, and eventually by the food. Because the oral environment varies from person to person, it is hard to predict the clinical behavior of a filling. A proper test for measuring the solubility and disintegration of all kinds of cements is desirable. This means research is needed to determine the phenomena which are responsible for the attack on the filling materials. Special attention should be given

¹ Figures in brackets indicate the literature references at the end of this paper.

to the plaque which forms on the filling. Often deep holes are discovered in silicate cement fillings at places where cleaning is difficult. The basis for this effect may be closely related to the theories which are developed to explain caries in the teeth. Although the lifetime of silicate cement is limited, it possesses a special benefit; namely, it decreases the chance for secondary caries. This is explained by the freeing of fluorides during the solution of the cement. If this theory can be proved by proper experimentation, it could be concluded that a certain solubility of the cement is required. Consequently, then a test is also needed which will show the solubility of fluorides: when the cements do not contain fluorides it is senseless to require a certain solubility.

It may be assumed that solubility phenomena will tend to create a decrease in the volume of inserted silicate cements. An increase of the volume of filling materials may also occur such as is evidenced by amalgams which are coated with a corrosion product. If a coherent layer on the metal is not formed, the formation of the corrosion product will go on. The growing forces are large and could lead to a deformation of the metal, when the corrosion product has no way to escape. Such phenomena might occur with the amalgam fillings. When the flow property indicates that small forces lead to a deformation of the filling which is followed by a loss of adaptation, then damage of the margins is more likely to occur. An investigation of the behavior of the corrosion product might be very useful.

Many times a small inlay that is not subjected

to chewing forces, is dislodged from the cavity. It is not likely that this dislodgement is a result of the formation of a corrosion layer upon the gold alloy; thus attention must be directed to the zinc phosphate cement. When this cement is exposed to acetic acid, a reaction product is noticed which appears on the surface of the specimen. It is difficult to tell if this also happens when the cement is in contact with lactic acid. However, it seems useful to research the development of reaction products on cements and on the forces which are consequently being developed.

Finally, in discussing filling materials, attention must be directed to ingredients which might irritate the soft tissue and the pulp of the tooth. It is very important to know if an irritation will be temporary or if it will lead to a more serious complication. The latter will depend on several factors such as the concentration of the toxic ingredient and the time it is in an active state. According to these aspects research that may lead to the creation of a safety test would be very useful and beneficial to dentistry.

7. References

- [1] ASTM STP 381, Symposium on Fracture Toughness Testing and its Application (1965).
- [2] ASTM STP 410, Plane Strain Crack Toughness Testing of High-Strength Metallic Material (1967).
- [3] Griffith, A. A., The phenomena of rupture and flow in solids. *Phil. Trans. Roy Soc. London, Ser. A.*, 221: 163-198, (1920).
- [4] J. Gramberg: The Ellipse-with-Notch Theory to explain Axial Cleavage Fracturing of Rocks, (to be published).

Need for Correlation Between Laboratory Testing and Clinical Research

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Although priority must be given to basic and clinical research in preventive dentistry, this does not eliminate the need for research on materials and methods for restorative dentistry which is in itself a preventive measure. There is an urgent need for collaborative and correlative studies involving properties of materials to be studied in the laboratory and tested in the clinic. Clinical research with materials is slow, and with the present incomplete information on oral environment and function, it is often difficult to assess properly the results, but there is no alternative. With sound clinical research on a larger and more penetrating scale, data and information may be obtained, that will make it possible to set up more meaningful test procedures in the laboratory. And that is the goal: to be able to characterize the dental material in the laboratory and correctly predict its clinical performance.

Key words: Aging processes, relation to dentistry; clinical research, dental; correlation of laboratory and clinical results; dental materials; dentistry, preventative; dentistry, restorative; epidemiological information, dental.

1. Introduction

I regret to have to report a failure. And this on behalf of the dental profession. Oral health is obviously our responsibility—but with the measures we have in our therapeutic arsenal we have failed to uphold the oral health of the population. There are many of us in the dental field—about 275,000 qualified dental practitioners spread all over the world. And we will increase our members to 300,000 within the next decade. In that same decade the world population will have increased to and superseded the 3-billion line.

These few figures indicate, of course, the reason for our failure. In fact, they imply that we as a profession are facing an impossible task if we, as we mainly do today, limit our activities to those which we learned and were trained for at the dental schools; that is to provide for removal and healing of pathologic processes and to restore anatomically—and hopefully also functionally—the damaged tooth or dentition. Within the limitation mentioned we have intricate and sometimes near-to-impossible problems to face. And still this is not enough. The responsibility of our profession goes far beyond that. Its ultimate goal is to find ways and means to provide oral health to large populations without relying upon chairside restorative procedures.

Priority should and must be given basic and clinical research in preventive dentistry. There can be no objection to this; obviously a noncarious tooth is better than a restored one. It should also be underlined that effective preventive measures provide the only means with which we can expect

to cope with the situation of the fast-growing population.

If we thus give highest priority to prevention, where does that leave us as clinicians and researchers in the field of restorative dentistry? There are three answers to that:

1. It will take a long time to develop effective and far-reaching preventive methods.
2. Already today we have experience of the fact that preventive measures are not fool-proof; that is, that a certain degree of failure has to be expected with any future method.
3. Traumatizing injuries, malformations, and congenital deformations will always provide demand for restorative dentistry.

Actually, these answers reach rather far into the future. The immediate answer is simply: The restorative procedure is in itself a preventive measure and should consequently be incorporated in the list. And today and tomorrow the restorative procedures are those, which will occupy most of the dentist's time. Or, I should rather say conservative procedures, as preventive measures are always incorporated. I have only to mention scaling.

2. Epidemiological Information

There should also be another foundation laid down and that is our knowledge today of oral status, need for restorative treatment, and possibly also demand for treatment. There are, unfortunately, only a limited number of scientifically sound epidemiological studies done in this field. Therefore, we can today only give rather rough figures. It could be outlined this way; every fifth person

above 16 has no natural teeth. Between one and two of the remaining four wear full upper and/or partial removable dentures. At the most, three out of one thousand adults have noncarious dentitions.

The need for treatment is high—it points towards a dentist-population ratio of one to five hundred. The awareness of need for treatment seems to be 60–80 percent of the need registered. But the demand for treatment is still considerably lower. It is a sad picture we gain from epidemiological studies in so-called well-developed countries. It is also a picture that heavily underlines the fact that restorative procedures have to be used for a very long period yet—even if the incidence of caries and periodontal disease is quickly and drastically reduced. What we actually lack are more penetrating epidemiological studies set up on a larger scale and internationally directed, so that geographical as well as environmental differences can be traced.

3. Nature and Implication of Current Restorative Treatment

Now, let us consider the restorative treatment given. We define restorative in its widest sense, that is the endeavor for optimally restored function irrespective of degree of dental deficiency. And here the interesting question to be asked is: Will the treatment given have to be revised and if so how long will it last?

Records on dental treatment show consistently one and the same picture. In the adult patient the restorations due to primary lesions are in the minority. Today the clinician is mainly concerned with revision of earlier therapy. Due to secondary lesions, restoration breakdown and changes in the properties of remaining tooth substances, revision of the former treatment will involve more extensive restorative measures, which in due time will be followed by even more extended therapy. Thus dental treatment breeds extended dental treatment.

Any process or any measures that can delay the deterioration of therapy given will in actual fact increase the productivity of the profession. Just one example: You have in the United States around 100,000 dentists. If just one silicate filling per dentist would have an increased longevity from four to five years, you would save 50,000 man-hours to be used for dental treatment otherwise not available. We have to think in terms of productivity irrespective of whether we are considering preventive dentistry or restorative dentistry. In both instances we are after the same thing: lasting results.

4. The Deficiency in Our Knowledge of Oral Function

The problem we deal with in clinical dentistry is the impaired tooth and the consequent defective dentition. Here all the questions arise, which have

to be solved in order to perform a correct treatment and restoration. It should be underlined that all problems derive from the clinic and the answers finally end up in the clinic.

You may comment that I am saying a mouth full, and you are right. We cannot today furnish the laboratory researcher with sufficient clinical and biological data, so that suitable laboratory studies under simulated mouth conditions can be performed. Actually, we know only the gross picture of oral function. It is still debated, whether tooth contact occurs during the early chewing cycles, the time period, the direction, and the force during later contacts. Debate is also going on concerning mandibular movements and contact during sleep. All have a bearing on methods and materials in restorative dentistry.

It is only recently that some understanding has been reached of tooth deformation and periodontal performance under load. Studies of the elastic deformation of the tooth, initiated by Körber and collaborators, have indicated among other findings minor bending by lateral forces. This work, started in vivo and repeated in the laboratory, has considerable importance as background for developing materials to be used in the tooth-restoration system.

Especially in this field of elastic deformation clinical studies and laboratory investigations of model systems may close the now existing gap between the basic materials scientist and the clinical researcher. What is absolutely necessary is a clear picture of the behavior of the tooth and its various components in order to define requirements for the restorative material as well as the restoration. Here the very close collaboration between clinician, biologist, and physicist may yield the information sought after. Important steps have already been taken; I may remind you of the work by Stanford on the physical properties of hard tooth substances.

5. Proper Assessment of Clinical Performance, A Requirement for Improvement

Under the situation we have at present—that is incomplete information on oral environment and its changes with various factors—it is not possible in laboratory testing to predict the detailed performance of a material in a tooth-restoration system. Obviously certain indications can be made, but only the clinical test will yield the final answer. It is consequently my firm belief that laboratory testing without evaluation of clinical performance is unsatisfactory.

It should not be necessary to point out that the same rigid research rules apply in clinical testing as in laboratory testing, but evidently there is some confusion among the clinicians as to this. In reality, the mouth is the clinician's laboratory; he is,

however, limited in his approach to evaluation methods, but there is no limitation to the requirements on the strictness in registration of the variables.

As to selection of patient material for clinical studies, the aim of the study is important. We have in a few studies deliberately selected patients with high carbohydrate intake with bad oral hygiene—this in comparative studies where two different restorative procedures were performed intraindividually. The reason for this is obvious; an acceleration of deteriorating factors decreases the observation period. For optimal performance a patient group with other characteristics, for instance low caries incidence and good oral hygiene, may be the choice.

There are several studies at present where these circumstances are somewhat combined. In a small group of patients (50) the treatment is given by two well-trained operators, and the registrations of bilateral restorations are done collaboratively. In a considerably larger group of patients many clinicians (15) perform the treatment according to their individual methods. In this group only a few variables are registered. All registrations are, however, done by two observers trained for these studies. With such an organization we hope to obtain information on how the restorations stand up under different circumstances. Laboratory tests are done according to related specifications and comparisons are to be made later. I am mentioning these studies merely to underline the fact that the clinical investigation has to be carefully planned and that the patient material is one very important variable.

6. Consideration for Aging Processes in Clinical Studies

There is another problem that we as clinical researchers have come to be aware of during the last 10 to 15 years. About 10 percent of our population in Sweden is 65 or older. I understand that the percentage of older individuals in the U.S. is similar to that in Scandinavia, that is one out of

ten belongs to the age group above 65. Aging can be described as decreasing cellular metabolism and steadily reducing function of the central nervous system. We as clinicians register this in decreased function of the stomatogastric system. Saliva production is reduced; the quality and composition of saliva changes towards more mucous consistency and less mineral content and reduced surface tension. The motor activity is decreased, the threshold sensitivity increases, and function as a whole seems to be on a more primitive or basic level.

Aging presents certain fundamental psychological factors as the most pronounced problems for the dental clinician to deal with. However, in recent publications on gerodontology, suggestions have been made that restorative procedures and selection of materials should be viewed in the light of the properties of aging tissues. This is particularly important regarding the hard tooth substances, where changes toward increased brittleness may provide a basis for specific properties of the restorative material to be used.

Again, I am actually asking for future collaborative work regarding oral environment changes with aging, this in order to gain a more sound basis for the search for suitable materials or for the selection of procedures in restorative treatment of the aging patient.

7. Conclusion

It is obvious that there is an urgent need for collaborative and correlative studies involving properties to be studied in the laboratory and given the final check and test in the clinic. It is, however, quite obvious that clinical research with dental materials is time-consuming and slow, but today there is no way out of that. With sound clinical research on a larger and more penetrating scale, data and information may be obtained that will make it possible to set up more meaningful test procedures in the laboratory in the future. And that is, of course, the goal: to be able to characterize the dental material and in laboratory testing correctly predict its clinical performance.

Biological Evaluation of Dental Materials

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Biological evaluation of dental materials includes (1) screening for toxic or other untoward effects of the materials, and (2) clinical evaluation of materials that pass the screening tests. Screening tests must take into account the functional requirements of various types of and service conditions for dental and auxiliary materials. Methodology for evaluation of clinical performance of materials must include examiner training and calibration in the use of rating scales. Emphasis is placed on the need for correlation of laboratory properties with clinical performance.

Key words: Biological evaluation of dental materials; clinical evaluation of dental materials; correlation of laboratory and clinical performance; dental materials; restorative materials; toxicity tests.

1. Introduction

Biological evaluation of materials used in dentistry includes (1) screening for toxic, allergic, or other untoward effects of the materials and (2) clinical evaluation of restorations, appliances, or devices, the materials for which have passed the appropriate screening tests.

Maybe we should first discuss the definition of a dental material. About a year ago I sent out a circular letter to initiate action on the part of the Subcommittee on Biological Testing which was formed under the auspices of the FDI Commission on Dental Materials, Instruments, Equipment and Therapeutics. Many respondents accepted these working definitions but as those of you who have followed Dr. Paffenbarger's excellent and exemplary work for the FDI Commission will know, the greatest value in balloting of such circular letters lies in the votes of the dissenters, and, as it has often been demonstrated in Dr. Paffenbarger's *modus operandi*, the negative votes and the thoughtful and thorough objections constituted the real substance of the discussions on definitions and classifications.

Although I cannot, in this short presentation, pay tribute to all of the people who gave of their time and thought to constructive dissent, I must mention the excellent suggestions of Dr. Baume and Dr. Petzold from Switzerland, Alan Grant, Dr. Thonard, and Alan Docking from Australia, Dr. Shoemakers and Dr. Van de Woerd from the Netherlands, Kramer from the United Kingdom, Fischer from Germany, and several from the Scandinavian countries. Also, several people in the United States, from military services, from industry, and from universities, came through with ex-

cellent comments and criticisms—and, as you would expect, George Paffenbarger topped them all with his closing comment: "Don't shoot me now—wait until I'm a year older." This letter, incidentally was dated November 21, 1968, so I guess Dr. George is safe for another 44 days.

Previous speakers, including Dr. Schoonover and Dr. Greulich, have made reference to Webster's and Dorland's dictionaries. I am sure that I should have done the same before I sent out my working definitions. Now, however, I'm not going to quote Webster and Dorland—but Paffenbarger and Petzold, and I'm not talking about their abridged version either! In fact, I don't believe they have an abridged version! According to the best authority that I can find, this is it:

Dental Material: Any substance specially intended for use in dentistry:

- (1) to replace tooth structure or tissue lost or missing in part or in whole by injury, disease, malformation, or by restorative dental procedures;
- (2) in the construction of appliances to alleviate malformations and to restore and improve esthetics and function.

Similarly, the definition of Dental Device has been clarified, improved, and refined to: "Any restoration, appliance, instrument, machine, or equipment especially intended for use in dentistry." Dental instrument is: "Any manual or powered hand-held tool used in dentistry."

Dental Drug: Any chemical compound or non-infectious biological substance, not used for its mechanical properties, which may be administered to or be used on or for patients:

- (1) as an aid in preventing, diagnosing, and treating diseases, injuries, malfunctions,

and malformation of the teeth, jaws and mouth;

- (2) to relieve pain or suffering or to control or improve any physiological or pathological condition.

Finally, Dental Therapeutic is: any dental drug, dental material, or dental device used for preventing, diagnosing, and treating diseases, injuries, and malformations of the teeth, jaws, and mouth.

Obviously, there are some overlappings—these definitions do not segregate all of the categories that I had hoped to divide up into neat little packages in my so-called working definitions. Some agents will fall into more than one category, and, as I have gone through comments from all over the world in response to that first circular letter, I can see that, indeed, the dissenters carried the day and gave us sharper and better definitions upon which we can build an international system for biological testing.

The classification of dental materials on the basis of functional requirements for the various types and service conditions leads to meaningful screening tests at various biological levels. The classification developed by Ray Bowen in his work as Secretary of the Subcommittee on Toxicity Tests under the Specification Committee of the Dental Materials Group of the IADR does, with minor modifications, appear to be internationally acceptable, and the next step, then, is to prescribe the screening methods that apply to the functional requirements.

An acute systemic toxicity test, a short duration inflammatory reaction test, a long duration tumor production and chronic inflammatory test, an allergic response test, an eye irritation test, a mucous membrane irritation test, and a pulpal irritation test can be prescribed selectively in appropriate order and combinations to meet the needs on a realistic basis.

In spite of the shortcomings of that first circular letter on biological testing that was sent out about a year ago—or perhaps because of these shortcomings—this first effort has produced such a wealth of good comments that I am indeed optimistic about future progress in this area, and quite a number of those present here today deserve the credit for it.

2. Motivation for Clinical Evaluation of Dental Materials

Evaluation of the clinical performance of dental materials has, until a few years ago, been based upon testimonials. The need for establishment of sound clinical research methodology has been emphasized by many investigators and I personally must confess to having used the phrase: "The clinical importance of these findings is not established" in several reports of laboratory studies of dental materials. Therefore, when the Division of Dental Health approached me to establish an ap-

plied clinical research program on Dental Materials and Technology, I saw the opportunity to do something about this, and I guess that this is the reason you have to listen to me today!

Most of you are probably aware that there are some inherent advantages in studying dental materials in the laboratory, as compared to clinical investigations. In the laboratory, one can design the experiments much neater—one can determine the number of specimens necessary to obtain statistically significant results, and then proceed to make the specimens under well-controlled conditions using the advice that one of my physics professors gave me: you make all of the variables constant and make all of the constants zero! Your specimens stay in their box until they are tested, and you end up with a fairly well organized piece of work that you can count on for the next IADR meeting and a subsequent neat publication. Not so with clinical evaluation! One of the first objections I was faced with was the comment: "Are you telling me that you will evaluate dental restorations placed by a number of operators?" Indeed I planned to do just that. My scientific friends would then say: "Don't you realize that you will have operator variables?" My early answer was: "Yes sir, I guess I will but has it ever occurred to you that operator variables do indeed exist in clinical dentistry?" The response from not one but several scientific friends can be summarized in a comment like: "Don't be smart—what I meant to say was, all you will find is that there is more difference between operators than between materials!" I thought about that and came to the conclusion that this could very well be so but, on the other hand, maybe this would be valuable information, at least if well documented. I don't recall finding this kind of information in the literature. Perhaps it would be important to know that differences between materials were less important than operator variables—particularly if one knew what were the operator variables that lead to this conclusion.

I am mentioning these comments and discussions merely to illustrate the philosophy and the viewpoints that motivated me to take on the attempt to make clinical evaluation of dental materials a legitimate and, hopefully, meaningful discipline.

3. Application of Research Methodology to Clinical Evaluation of Dental Materials

How does one evaluate a dental restoration—how does one move from testimony to research methodology? Dave Mahler today showed one approach and I believe that my approach will be useful both by itself and as a supplement to his method. In clinical practice, every dentist is making evaluations every time he has a patient in the chair. He looks at each existing restoration and makes a decision that leads to one of four courses of action: He either decides that the restoration

is okay—no action needed; or else he decides that there is some doubt about the restoration. He may decide that he isn't going to do anything now, but that he would like to see the patient six months from now for another evaluation; a third decision would be that of replacing the restoration for preventive reasons and, the last course of action would be that of replacing the restoration because it is esthetically or functionally unsatisfactory. It looks bad or damage is occurring around it.

How do we, as practicing dentists, arrive at these judgments? Which are the factors that we consider? What are the criteria? A thorough analysis of the elements that enter into such judgments was precisely the basis for development of rating scales for clinical evaluation of the performance of restorative materials, as these rating scales are used today by the Materials and Technology Branch of the Division of Dental Health, both in intramural and extramural or cooperative projects.

The criteria for clinical evaluation, as we used to call them, were formulated, in their first version, in the fall of 1964 in a work session that lasted into the wee hours of the night, and I would like to mention the names of my three co-workers from this session, two of whom are here today: Dr. Björn Hedegård who, as most of you know, conducted one of the first—and finest—studies on restorative direct resin materials, Dr. Richard L. Webber and Dr. R. J. McCune of the Materials and Technology Branch. Jim McCune wasn't quite satisfied with the early effort, so he proceeded to take over the Materials and Technology Branch about 9 months

ago so that he could revise the whole system and show up the efforts of the previous administration of the Branch!

As a result, the clinical evaluation system now consists of rating scales for: (1) Color Match; (2) Cavo-Surface Marginal Discoloration; (3) Anatomic Form; (4) Marginal Adaptation, and (5) Caries.

To illustrate the type of judgments that are made to measure the clinical performance of paired anterior and paired posterior restorations fabricated from contrasting dental restorative materials, reference is made to figures 1 and 2. Figure 1 shows the categories chosen for color match while figure 2, similarly, describes the categories, or ratings, used to evaluate marginal adaption.

A similar system is used for arriving at ratings for Cavo-Surface Marginal Discoloration (fig. 3), Anatomic Form (fig. 4), and Caries (fig. 5), so that for each restoration, a total of 16 judgments or choices are made, resulting in 5 ratings. Each of two examiners carries out such an evaluation independently and calls off the ratings to the recorder. When the two examiners arrive at a different rating for any one category, the recorder will request a resolution of the disagreement by joint examination. Such disagreements are usually the result of one examiner discovering a discrepancy or defect that was overlooked by the other examiner and are easily resolved by trained examiners. In addition to the ratings for each pair of restorations, a ranking procedure is used whenever the two

COLOR MATCH

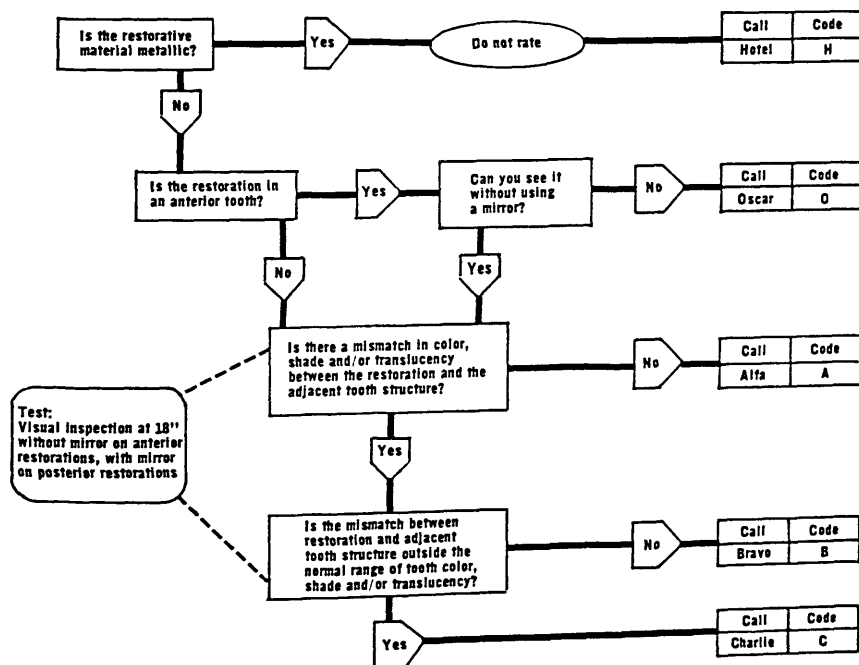


FIGURE 1. Color match.

MARGINAL ADAPTATION

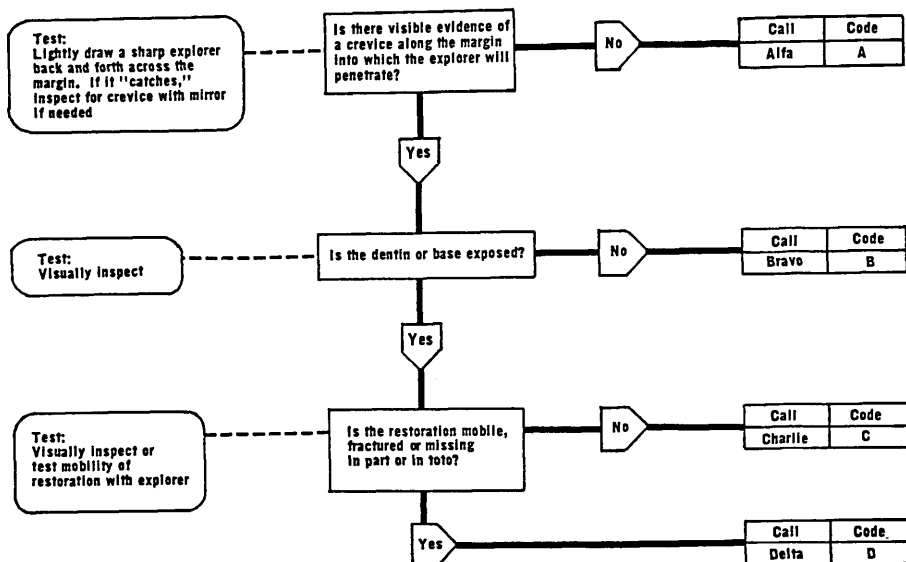


FIGURE 2. Marginal adaptation.

CAVO SURFACE MARGINAL DISCOLORATION

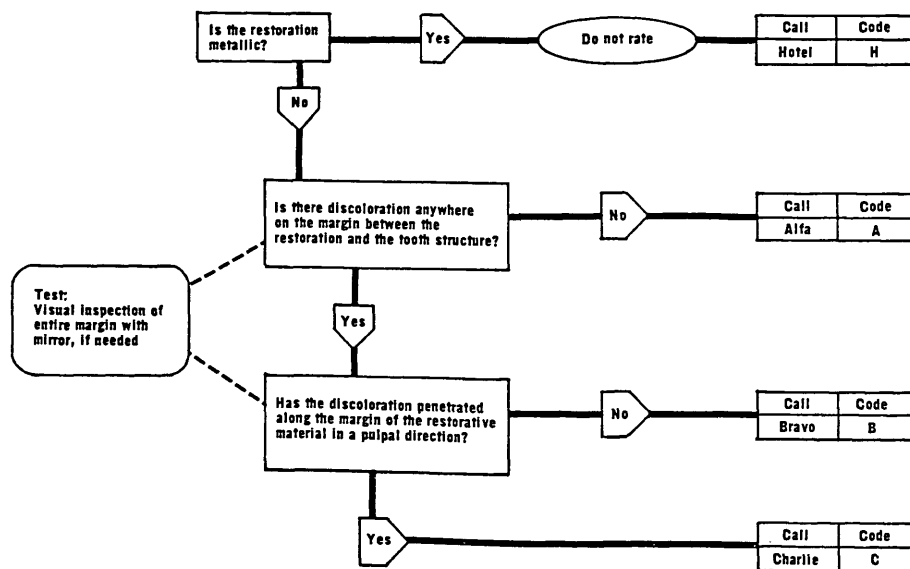


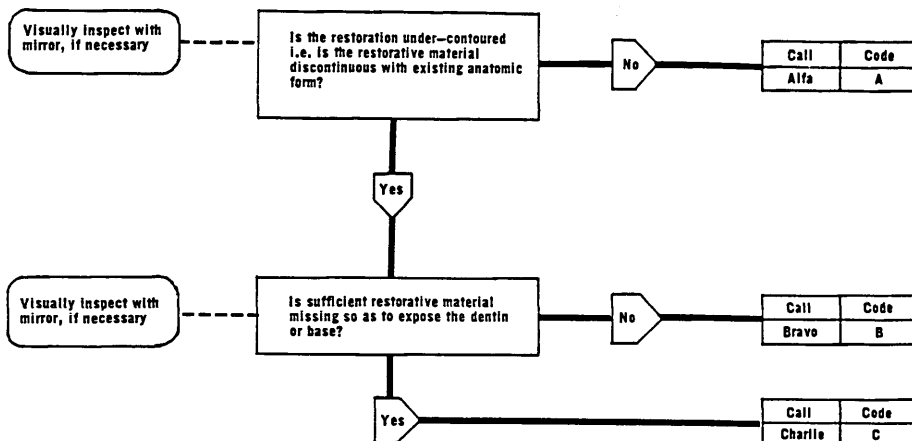
FIGURE 3. Cavo-surface marginal discoloration.

paired restorations receive the same rating by both examiners for any one characteristic.

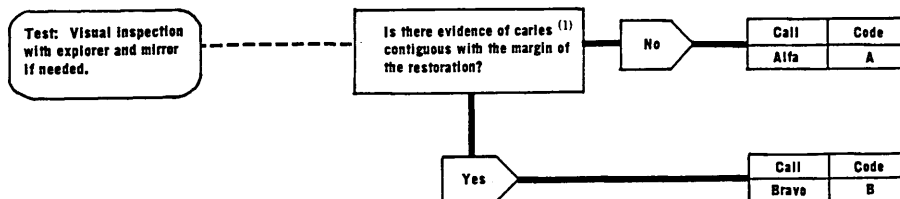
Clinical evaluation studies are planned according to a set of procedures that include strict adherence to the research protocol and use of specific procedure records (figs. 6 and 7), evaluation records (fig. 8), and other forms (figs. 9 & 10) that permit effective utilization of data processing equipment. The computer program not only provides tabulation of statistical data but generates

the evaluation records and performs complex editing procedures to guarantee the accuracy of stored information. The system is based upon the concept of a research team consisting of a dentist, a dental assistant, and an observer-recorder, and the role of each person is defined in the protocol for the study.

Twice annually, the Materials and Technology Branch conducts a training, calibration, and testing session for its clinical staff to maintain per-

FIGURE 4. *Anatomic form.*

CARIES



(1) An area at the restoration margin is carious if an explorer "catches" or resists removal after insertion with moderate to firm pressure, and is accompanied by one or more of the following:

- a. Softness
- b. Opacity at the margin, as evidence of undermining or demineralization

c. Etching or a white spot as evidence of demineralization
An area at the margin is also considered carious if the explorer does not "catch," but conditions b or c are present.

FIGURE 5. *Caries.*

formance standards. These sessions have also been attended by personnel from cooperating institutions both from the United States and other countries.

To supplement the clinical evaluation of paired restorations fabricated from contrasting restorative materials or of restorations placed with contrasting techniques, an attempt is being made to design test methodology that will provide meaningful correlation of laboratory data with the clinical findings. Time does not permit a discussion of this phase of the work but we are in this respect following similar guidelines as those Dave Mahler laid down so beautifully this morning.

4. Conclusion

It is not feasible to describe fully in this short presentation all aspects of the clinical evaluation

scheme that has been developed over the past five years at the Dental Health Center. I have no hesitation to admit that we have made mistakes along the way—but we have benefited from some of these mistakes by being forced to review procedures and judgments. I hope, however, that I may have succeeded in arousing your curiosity or even interest in the system and that those of you that might be inclined to venture into the magic world of clinical research have obtained some information that may help you avoid making the same mistakes that we have made along the way.

I would like to conclude on an optimistic note by quoting a recent pronouncement by my Division Director, Dr. Viron L. Diefenbach; it is particularly apropos to describe the status of clinical research: "The best part of our future lies ahead of us."

DO NOT USE
THIS
COLUMN

PROCEDURE RECORD
POSTERIOR RESTORATIVE STUDY
MATERIALS AND TECHNOLOGY BRANCH, DIVISION OF DENTAL HEALTH, NIH

1-3 _____

4-5 _____

6-9 _____

STUDY NAME	
10-29 PATIENT'S NAME (TYPE OR PRINT)	
LAST	FIRST
30 SEX (CIRCLE)	31-36 DATE OF BIRTH
M F	MONTH DAY YEAR
37-42 DATE RESTORATIONS PLACED	
MONTH DAY YEAR	

INSTITUTION
PATIENT'S ADDRESS
DENTAL ASSISTANT
OBSERVER/RECORDER
OPERATOR

43-44 _____

TYPE OF PAIR	TOOTH NUMBER	SURFACE(S) (CIRCLE)	CLASS (CIRCLE ONE)	BASE CODE	LINER CODE	MATERIAL CODE
45	46-47	48-49	50	51-53	54-56	57-60
T		M D F L O	1 2 3 4 5			
C	61-62	63-64	65	66-68	69-71	72-75
		M D F L O	1 2 3 4 5			

76 _____ (T)

77 _____ (C)

78 _____

79 BLANK

80 3

END OF KEYPUNCH

TIME TRITURATION STARTED

TRITURATION TIME

LAPSE TIME

INSERTION TIME

DELAY TIME

TIME REQUIRED FOR INITIAL CARVING

TIME INITIAL CARVING COMPLETED

DAY FINAL POLISHING PERFORMED

TIME REQUIRED FOR FINAL POLISHING

WAS AN IMPRESSION MADE?

TEST		DO NOT USE THIS SPACE	CONTROL	
HOURL	MIN.		HOURL	MIN.
MIX 1	MIX 2		MIX 1	MIX 2
SEC.	SEC.		SEC.	SEC.
SEC.	SEC.		SEC.	SEC.
SEC.	SEC.		SEC.	SEC.
SEC.			SEC.	
SEC.			SEC.	
HOURL	MIN.		HOURL	MIN.

MO. DAY YR.		MO. DAY YR.
MIN. SEC.		MIN. SEC.

☐ YES

☐ NO

M.T. BR. FORM 65-9
(REV. 02-29-69)
PENDING APPROVAL

FIGURE 6. Procedure record posterior restorative study.

DO NOT USE
THIS
COLUMN

PROCEDURE RECORD
ANTERIOR RESTORATIVE STUDY
MATERIALS AND TECHNOLOGY BRANCH, DIVISION OF DENTAL HEALTH, NIH

1-3 _____

4-5 _____

6-9 _____

STUDY NAME

INSTITUTION

10-29 PATIENT'S NAME (TYPE OR PRINT)

LAST FIRST

PATIENT'S ADDRESS

30 SEX (CIRCLE) 31-36 DATE OF BIRTH

M F MONTH DAY YEAR

DENTAL ASSISTANT

OBSERVER/RECORDER

37-42 DATE RESTORATIONS PLACED

MONTH DAY YEAR

OPERATOR

43-44 _____

TYPE OF PAIR	TOOTH NUMBER	SURFACE(S) (CIRCLE)	CLASS (CIRCLE ONE)	BASE CODE	LINER CODE	MATERIAL CODE
45	T 46-47	48-49 M D F I L	50 1 2 3 4 5	51-53	54-56	57-60
	C 61-62	63-64 M D F I L	65 1 2 3 4 5	66-68	69-71	72-75

76 _____ (T)

77 _____ (C)

78 _____

79 BLANK

80 2

END OF KEYPUNCH

TIME MIX STARTED

MIXING TIME

LAPSE TIME

INSERTION TIME

TIME MATRIX HELD

DELAY TIME

TIME REQUIRED FOR INITIAL FINISHING

TIME INITIAL FINISHING COMPLETED

DATE FINAL FINISHING PERFORMED

TIME REQUIRED FOR FINAL FINISHING

WAS AN IMPRESSION MADE?

TEST		DO NOT USE THIS SPACE		CONTROL		
HOUR	MIN.			HOUR	MIN.	
SEC.				SEC.		
SEC.				SEC.		
SEC.				SEC.		
SEC.				SEC.		
SEC.				SEC.		
SEC.				SEC.		
HOUR	MIN.			HOUR	MIN.	
MO.	DAY	YEAR		MO.	DAY	YEAR
MIN.	SEC.			MIN.	SEC.	

☐ YES

☐ NO

M.T. BR. FORM 65-6
(REV. 02-29-69)
PENDING APPROVAL

FIGURE 7. Procedure record anterior restorative study.

EVALUATION RECORD

ANTERIOR AND POSTERIOR RESTORATIVE STUDIES
MATERIALS AND TECHNOLOGY BRANCH
DIVISION OF DENTAL HEALTH, U. S. P. H. S.

PATIENT'S NAME

DATE EVALUATED

19

MONTH

YEAR

STUDY
NUMBER

INSTITUTION
NUMBER

PATIENT'S
NUMBER

DATE
PLACED

TYPE OF PAIR	CRITERIA	COLOR MATCH	CAVO-SURFACE MARGINAL DISCOLORATION	ANATOMIC FORM	MARGINAL ADAPTATION	CARIES
	EXAMINER					
	EXAMINER					
	FINAL RATING					
R A N K	EXAMINER	0 1 2	0 1 2	0 1 2	0 1 2	0 1 2
	EXAMINER	0 1 2	0 1 2	0 1 2	0 1 2	0 1 2
REASON NOT EVALUATED		<input type="checkbox"/> TOOTH MISSING <input type="checkbox"/> RESTORATION MISSING <input type="checkbox"/> RESTORATION REPLACED		<input type="checkbox"/> PATIENT MOVED <input type="checkbox"/> OTHER (EXPLAIN)		REMARKS:

TOOTH NUMBER	EXAMINER					
	EXAMINER					
	EXAMINER					
	FINAL RATING					
R A N K	EXAMINER	0 1 2	0 1 2	0 1 2	0 1 2	0 1 2
	EXAMINER	0 1 2	0 1 2	0 1 2	0 1 2	0 1 2
COLUMN 80	REASON NOT EVALUATED	<input type="checkbox"/> TOOTH MISSING <input type="checkbox"/> RESTORATION MISSING <input type="checkbox"/> RESTORATION REPLACED		<input type="checkbox"/> PATIENT MOVED <input type="checkbox"/> OTHER (EXPLAIN)		REMARKS:

FIGURE 8. Evaluation record.

DAILY REPORT OF BATCH NUMBERS AND VARIATIONS OF RESEARCH PROCEDURES

Study Name _____ Study Number _____

Institution _____

Date Work Performed _____
Day Month Year

PART I: Manufacturer's Batch Numbers

Number Placed	Material Used	Manufacturer's Batch Number	
		Base (or solid)	Catalyst (or liquid)
Test	Base		
	Liner		
	Restorative		
Control	Base		
	Liner		
	Restorative		

PART II: Variations of Research Procedure

☐ No Variations in Research Procedures Occured on the Above Date

Signature of Operator _____ Date _____

Variation of Research Procedure (Describe Variations and explain)	Check One	Tooth Number	Surface & Class	Patient's Name
	Test Tooth <input type="checkbox"/>			
	Control Tooth <input type="checkbox"/>			
	Test Tooth <input type="checkbox"/>			
	Control Tooth <input type="checkbox"/>			
	Test Tooth <input type="checkbox"/>			
	Control Tooth <input type="checkbox"/>			

COMMENTS: (Include recommendations for the further conduct of this research)

FIGURE 9. Daily report of batch numbers and variations of research procedures.

PATIENT PARTICIPATION AGREEMENT

As part of an effort to develop better materials and procedures for use in dentistry, new and conventional dental materials, techniques, and devices are being investigated in controlled clinical studies. Since such studies involve considerable expense and require up to five years of periodic examinations, only persons willing to cooperate fully in this program will be included. Treatment that falls within the scope of the clinical study will be performed by staff members of _____

in cooperation with the Materials and Technology Branch, Division of Dental Health, National Institutes of Health. Your decision regarding participation will in no way affect your eligibility for dental care customarily provided.

If you are interested in participating in this program, please supply the following:

Name _____ Address _____
(last) (first) (middle)

Birthdate _____ Sex _____ Telephone _____

Name and address of your dentist _____

Date of last dental visit _____

FLUORIDE HISTORY: In drinking water ☐ Topically ☐ Tablets ☐ None ☐

Have you now or have you ever had: _____	YES	NO
Rheumatic Fever _____	<input type="checkbox"/>	<input type="checkbox"/>
Heart Trouble _____	<input type="checkbox"/>	<input type="checkbox"/>
High or Low Blood Pressure _____	<input type="checkbox"/>	<input type="checkbox"/>
Diabetes _____	<input type="checkbox"/>	<input type="checkbox"/>
Tuberculosis _____	<input type="checkbox"/>	<input type="checkbox"/>
Asthma or Hayfever _____	<input type="checkbox"/>	<input type="checkbox"/>
Allergy to any drug or medicine _____	<input type="checkbox"/>	<input type="checkbox"/>
Hepatitis (Jaundice) _____	<input type="checkbox"/>	<input type="checkbox"/>
Reaction to 'local' anesthetic _____	<input type="checkbox"/>	<input type="checkbox"/>
Prolonged bleeding from an injury or tooth extraction _____	<input type="checkbox"/>	<input type="checkbox"/>
Are you taking any drugs or medicine? _____	<input type="checkbox"/>	<input type="checkbox"/>
Are you under the care of a physician? _____	<input type="checkbox"/>	<input type="checkbox"/>

If "yes" to any of the above, please explain

The attending dentist has explained the nature of the study to me and the need to return for periodic examinations. I will do my best to cooperate.

Date

Signature (patient, parent or guardian)

FIGURE 10. Patient participation agreement.

Corrosion Testing in the Mouth

Kazuo Nagai

School of Dentistry, Nihon University, Tokyo 101, Japan

For many years various base-metal alloys were used as substitutes for gold alloys for dental restorations in Japan. The adoption of an official requirement that these alloys should not have a weight loss of more than 3 mg/cm² when immersed in solutions of 0.05 percent hydrochloric acid, 1 percent lactic acid, 1 percent sodium chloride, and 0.1 percent sodium sulfide for three days, prompted a study of corrosion of a copper-zinc alloy and dental amalgam in the mouth. Cast copper-zinc specimens had average weight losses in the mouth in the range of 0.022 to 0.034 mg/cm² per day. Conventional amalgams had losses as small as 0.0063 mg/cm² per day. Weight losses in the test solutions ranged up to 150 times those in the mouth while weight losses in artificial saliva *in vitro* were about twice those in the mouth. It is believed that the lower corrosion in the mouth (which varies from place to place) results from a cleaning and inhibiting action by the saliva.

Key words: Base-metal alloys, dental; copper-zinc dental alloy; corrosion, clinical tests; corrosion of dental alloys; dental amalgam; dental materials.

1. Introduction

Immediately before World War II, and during the intervening years, the dental profession in Japan has not been able to use gold for restorative purposes, the main reason being the critical supply of gold, as well as the economic factor. Consequently, a variety of gold substitute alloys have been developed. Metallurgically, they include alloys of silver, German silver, copper, stainless steel, nickel-chromium, chrome-cobalt, and others. Much research has been accomplished and published on these alloys, and controversy still exists on the acceptability of the alloys in dentistry. In October 1950, the Ministry of Welfare of the Japanese Government issued an official test for corrosion of these alloys. This test required that any gold substitute alloy used in the mouth could not have a weight loss of more than 3 mg/cm² when immersed for three days in solutions of: 0.05 percent hydrochloric acid, 1 percent lactic acid, 1 percent sodium chloride, and 0.1 percent sodium sulfide.

No reason or justification was given to the Profession by the Ministry of Welfare for the composition of the test reagents. No information was provided as to why a dental restorative material should be subjected to this kind of test, nor whether the concentrations of the chemical reagents were appropriate. This is the basic reason why we initiated a series of studies on dental alloy corrosion in the mouth, particularly with the copper-zinc alloy and amalgam. We also wished to confirm the contention that copper alloy was injurious to the human body both locally and systemically. Consequently, the copper alloy and amalgam were placed in the mouth to determine

their actual weight losses due to corrosion, as well as other effects.

2. Corrosion Testing of Copper Alloys

In the first part of my discussion I would like to introduce an investigation on corrosion testing of copper-zinc alloy in the mouth which was reported by Dr. Wakumoto. This test was carried out by four different subjects using four specimens of various shapes and sizes. The position of the specimen in each oral cavity was also varied. The specimen was cast and polished in the usual manner in accordance with the manufacturer's instructions, and placed in the mouth for 50 days. Weight change was measured by electric balance every 10 days.

Figure 1 shows the sizes and shapes of the specimens of subjects A to D. The shaded portion in the figure indicates the copper alloy specimen having different surface area and shape. The result of Wakumoto's report is summarized in figure 2. The vertical axis indicates weight loss in mg/cm², and the horizontal axis indicates time in days. It is obvious from this figure that the result was divided into two groups.

Table 1 shows the weight changes of the copper alloy specimens in the mouth after 50 days and the average value per day. The largest weight loss is 2.697 mg/cm² after 50 days and 0.0539 mg/cm² per day in subject B. The least change is 0.730 mg/cm² after 50 days and 0.0146 mg/cm² per day in subject D. This variation may be due to the individual differences among subjects, and a change of alloy structure of each of the specimens when they were cast.

CORROSION TEST IN THE MOUTH
SHAPE AND SIZE OF Cu ALLOY SPECIMEN
- by WAKUMOTO -

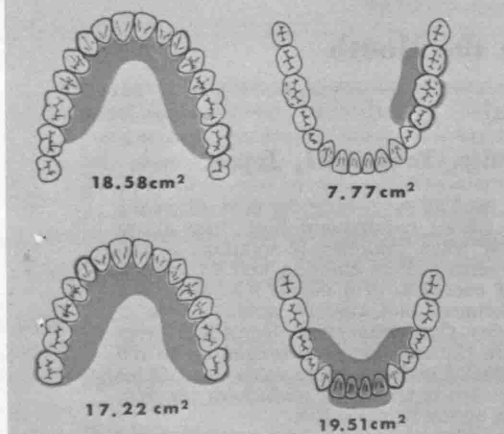


FIGURE 1. Corrosion test in the mouth by Wakumoto.
The shaded portion in the drawing indicates the shape and size of the copper alloy specimen.

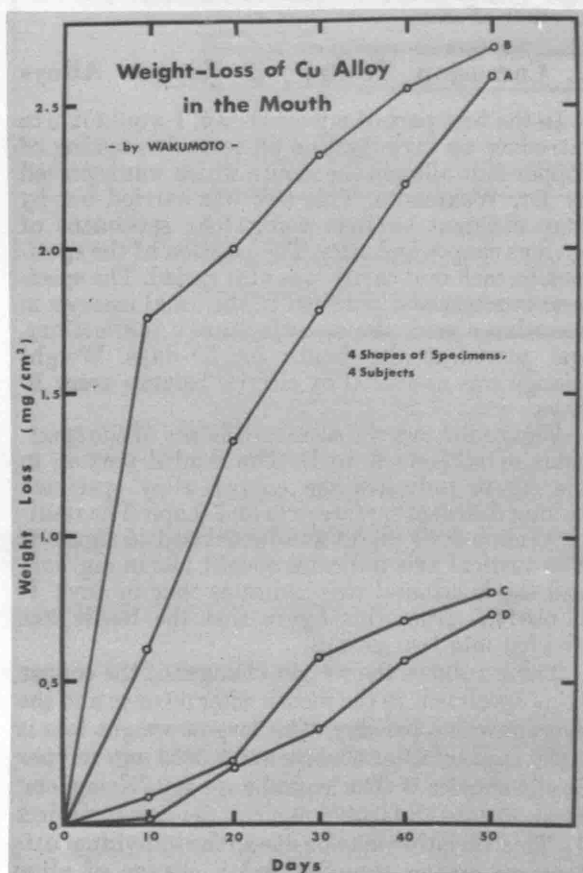


FIGURE 2. Weight loss of copper alloy in the mouth reported by Wakumoto.

TABLE 1. Weight loss of Cu alloy in the mouth for 50 days (by Wakumoto)

Subject	Weight loss (mg/cm ²)	
	After 50 days	For a day
A	2.597	0.0519
B	2.697	0.0539
C	0.802	0.0160
D	0.730	0.0146

In figure 3 the size and shape of specimens is given for the in vivo corrosion test of copper alloy as determined by Dr. Sakuma. This test was performed in order to evaluate the common opinion that the use of copper alloy for dental purposes was harmful to the human body. He wore four specimens which have different shapes and sizes in his mouth.

Figure 4 is a summary of the results of Dr. Sakuma. According to his test, the weight loss of copper alloy in the mouth is between 0.6 and 1.4 mg/cm² after 50 days.

Although specimen C was broken at 40 days (table 2), its weight loss is the largest, being 1.383 mg/cm² for 40 days, which corresponds to 0.0346 mg/cm² a day. The least change in Sakuma's report is 0.611 mg/cm² after 50 days, and 0.0122 mg/cm² per day in specimen A.

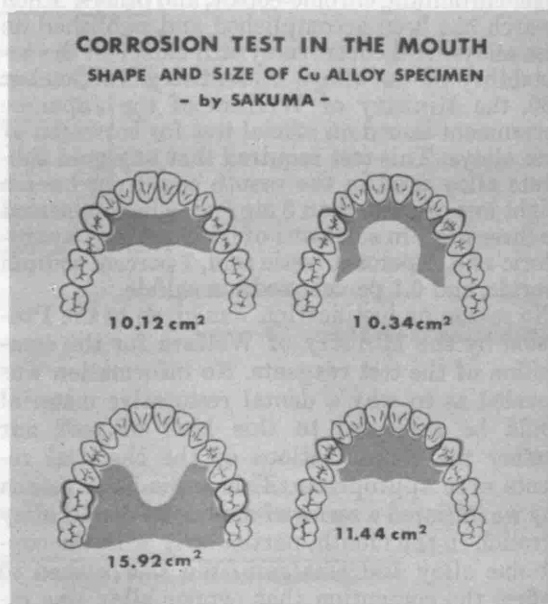


FIGURE 3. Corrosion test in the mouth by Sakuma.
The shaded portion in the drawing indicates the shape and size of the copper alloy specimen

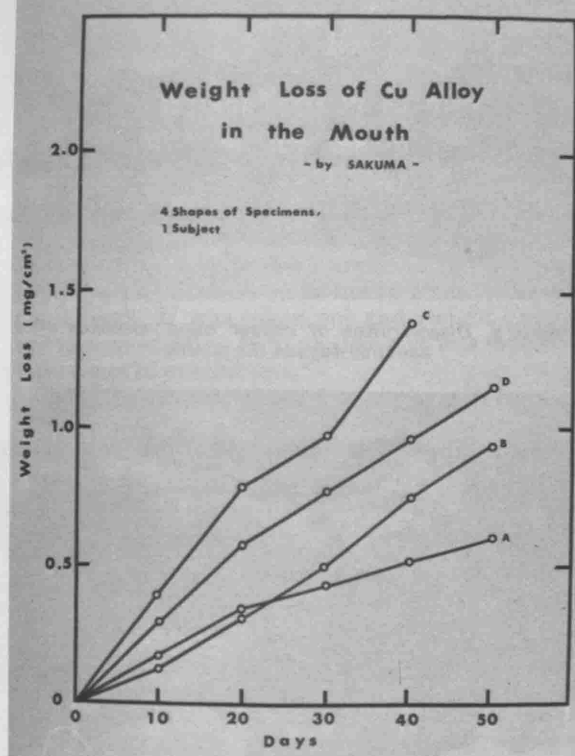


FIGURE 4. Weight loss of copper alloy in the mouth reported by Sakuma.

TABLE 2. Weight loss of Cu alloy in the mouth for 50 days (by Sakuma)

Specimen	Weight loss (mg/cm ²)	
	After 50 days	For a day
A	0.611	0.0122
B	0.941	0.0188
C*	1.383	0.0346
D	1.159	0.0232

*After 40 days

Figures 5 and 6 relate to the in vivo corrosion test of copper alloy by our laboratory. We made three palatal denture specimens using a copper alloy, so that they have nearly the same size and shape. The position of the specimen in the mouth was also designed to be the same. The test was repeated three times in the same mouth.

As is shown in figure 6, our test results have less variation among specimens compared with the two reports described before. This fact proves our contention that the shape and type of the specimen is of less significance in the corrosion test of

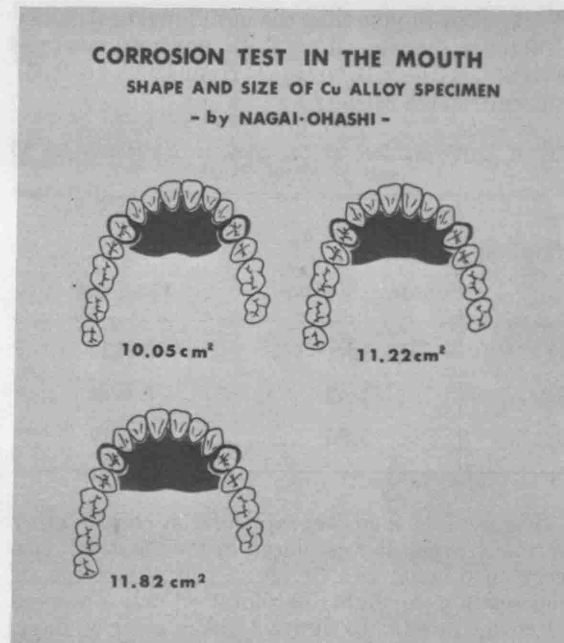


FIGURE 5. Corrosion test in the mouth by Nagai and Ohashi. The shaded portion in the drawing indicates the shape and size of the copper alloy specimen.

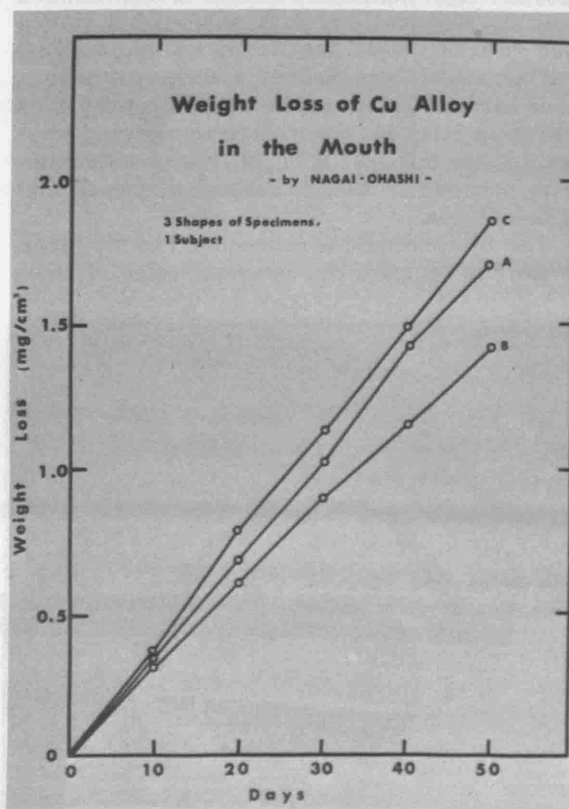


FIGURE 6. Weight loss of copper alloy in the mouth reported by Nagai and Ohashi.

dental alloy in vivo than the individual oral cavity difference among subjects. In our test, average weight loss per day ranges from 0.028 to 0.037 mg/cm² (table 3).

TABLE 3. *Weight loss of Cu alloy in the mouth for 50 days (by Nagai, Ohashi)*

Specimen	Weight (loss mg/cm ²)	
	After 50 days	For a day
A	1.71	0.0342
B	1.42	0.0284
C	1.86	0.0372

Figure 7 is a photograph of the copper alloy specimen when it was placed in the mouth. It has very nice color and brightness at this stage of the testing. A slight discoloration was observed after one month. In figure 8, taken after 50 days, the copper alloy showed more discoloration and less luster.

Figure 9 is a typical example of a copper alloy crown which has been cemented in a patient for about 1 year. Not much corrosion or discoloration was observed on the occlusal surface, but quite a few corrosion spots were found on the proximal surface after it was removed. Generally speaking, it is hard to find the corrosion of a copper alloy crown or inlay by visual inspection during service, but the corrosion is in progress on an unsanitary portion such as the proximal surface or subgingival area.

Let us reconsider the main subject of my paper. When we compare the corrosion value of three

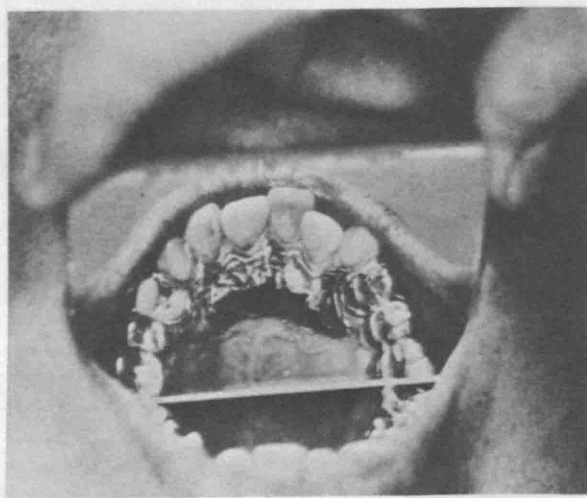


FIGURE 7. *Copper alloy specimen when it was placed in the mouth.*

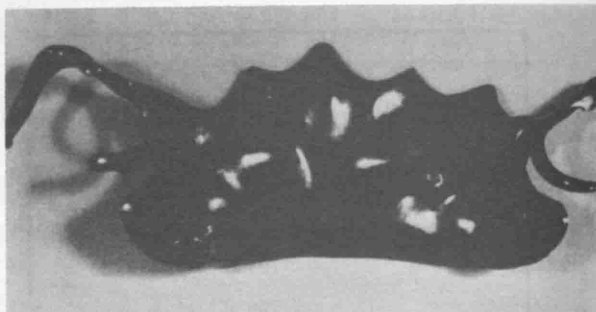


FIGURE 8. *Discoloration of copper alloy specimen after about 50 days in the mouth.*

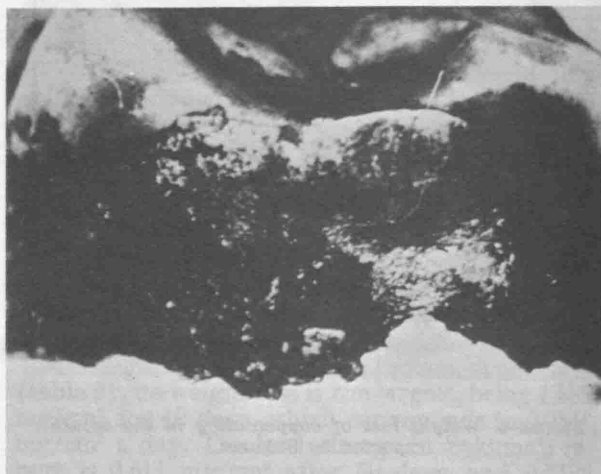


FIGURE 9. *Typical example of a copper alloy crown which has been cemented in a patient for about one year.*

reports (table 4), the average weight loss for a day is 0.0341 mg/cm² by Wakumoto, 0.0222 mg/cm² by Sakuma, and 0.0333 mg/cm² by our laboratory. The largest weight loss is 0.0539 mg/cm² and the smallest 0.0122 mg/cm² in 11 trials. The overall average of the three reports is 0.0299 mg/cm² per day. According to these results, the copper alloy which is commonly supposed to have a high degree of corrosion actually loses weight in the mouth much less rapidly than was thought.

TABLE 4. *Comparison of weight loss of Cu alloy in 3 reports*

Wakumoto's Report		Sakuma's Report		Nagai-Ohashi's Report	
Subject	(mg/cm ² /day)	Specimen	(mg/cm ² /day)	Specimen	(mg/cm ² /day)
A	0.0519	A	0.0122	A	0.0342
B	0.0539	B	0.0188	B	0.0284
C	0.0160	C	0.0346	C	0.0372
D	0.0146	D	0.0232		
Average	0.0341	Average	0.0222	Average	0.0333

Overall average = 0.0299 (mg/cm²/day)

3. Corrosion Testing of Conventional Amalgam

In the next part of this paper, I would like to discuss tests carried out by our laboratory on the corrosion of a conventional type amalgam in the mouth. A cylindrical specimen, 4 mm in diameter, was made according to the manufacturer's instructions and after 24 hr was polished to be 4 mm long. The specimen was imbedded in the occlusal surface of an acrylic resin artificial tooth for an upper partial denture so as not to contact the opposite teeth. It was taken out and weight change was measured after 40 days. The test was repeated three times in one subject.

The weight loss of amalgam after 40 days in vivo is shown in table 5. A variation of weight loss between both sides, the right and left, is noted. Average weight loss is 0.250 mg/cm² for 40 days, which is only 0.00625 mg/cm² per day. This value includes the weight loss by erosion or abrasion produced by contact with the tongue and food in addition to the corrosion, so that actual weight loss by corrosion must be less than the result we obtained.

TABLE 5. *Weight loss of amalgam in the mouth after 40 days (by Nagai, etc.)*

Number of test	Weight loss (mg/cm ²)		
	6]	6]	Average
1	0.35	0.21	0.28
2	0.28	0.22	0.25
3	0.27	0.17	0.22
Average	0.30	0.20	0.25

Average weight loss per day = 0.00625 mg/cm²/day.

Finally, in table 6 the weight changes of human enamel, copper alloy, and amalgam in various environments are compared. In addition to the specified chemical reagents, an orange juice of pH 3.2 and artificial saliva prescribed by Greenwood at a pH of 6.8 were used. The weight loss is far greater in vitro than in vivo. By way of example, amalgam decreases its weight in 0.05 percent hy-

drochloric acid solution about 150 times as much as the decrease in the mouth. Even in 1 percent sodium chloride solution, it is about 60 times as great as in the mouth. The results indicating that greater weight loss was observed in artificial saliva than in the mouth are probably due to the fact that human saliva has an inhibitive action to the metal corrosion.

When we compare the alloy weight loss with that of human enamel, the weight loss of human enamel is about 40 times as great as that of copper alloy and amalgam in 0.05 percent hydrochloric acid, and more than 100 times as great in 1 percent lactic acid. Thus the results indicate that the corrosion test in the laboratory as proposed by the Minister of Welfare is far from the actual corrosive behavior in vivo.

4. Summary and Conclusions

The purpose of our studies was to determine the corrosive behavior of dental restorative alloys in the mouth and, at the same time, to examine them from a dental health point of view. The salient conclusions are as follows:

1. Even the copper alloy which is commonly supposed to have a high degree of corrosion, actually has weight loss in the mouth as small as 0.022 to 0.034 mg/cm² for a day.

2. The type of amalgam which is widely used in many countries today has a weight loss in vivo as small as 0.0063 mg/cm² a day.

3. The basic reason why these alloys are not corroded as is generally supposed is that the salivary secretion has the benefit of keeping the mouth clean. It is also due to the fact that the saliva tends to inhibit the corrosion of alloys.

4. As it became clear by our testing that the 1950 Ministry of Welfare corrosion test was not realistic as a means of expressing the corrosive behavior of dental alloys, it was removed from the specifications.

5. Within the same oral cavity, the degree of corrosion varies from area to area, that is, anterior teeth, posterior teeth, occlusal, buccal to lingual, or proximal surface. Observation of the copper alloy restorations after they were removed indicated that the corrosion is most pronounced on the proximal surface.

TABLE 6. *Comparison of weight loss of permanent tooth, amalgam, and Cu-alloy in various environments (mg/cm²/day)*

Mat. \ Env.	0.05% HCl	1% Lactic acid	1% NaCl	Orange juice	Artificial saliva	Oral cavity
Teeth.....	40.60	94.20	-----	-----	-----	-----
Amalgam.....	0.94	0.83	0.39	0.145	0.0102	0.0063
Cu-alloy.....	1.01	0.68	0.073	0.07	0.059	0.0299

VII. Specifications

International Specification Program—Australian Experience

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The Australian dental specifications as a basis for a certification program were developed through the Standards Association of Australia and not within the dental association. Products are accredited by the Australian Dental Association on the basis of meeting these specification tests. The Commonwealth Bureau of Dental Standards assists in preparation of specifications and in accreditation of products. Approximately thirty Australian dental standards have been issued. Participation in international specification work has proved of great benefit especially in the raising and maintenance of the quality of dental goods used by the Australian dental profession.

Key words: Accreditation of dental materials, Australian experience; Australian dental specifications; dental materials; dental standards; specifications, dental.

1. Introduction

If imitation is the sincerest form of flattery, the Australian tribute on this memorable occasion is of special significance. From the beginnings of dental materials research in Australia over thirty years ago an effort has been made to emulate, in a modest way, the highly successful program of the National Bureau of Standards and subsequently the system of specifications for materials and of accreditation of dental products employed by the American Dental Association through the Fellowship it established at the Bureau. Thanks to the inspiration and guidance of the NBS Dental Research Section and the ADA Fellowship there, the Australian effort has proved to be of immense value to the dental profession in that country too. The Commonwealth Bureau of Dental Standards was established in 1947, but the work did not commence then; ten years prior to this, Dr. Howard K. Worner, with his Materials Research Laboratory at the University of Melbourne School of Dental Science, had established a close liaison both technically and personally with members of the staff of the Dental Research Section of the National Bureau of Standards. It was the knowledge and appreciation of the NBS success story that largely shaped the destiny of dental materials research and specifications in Australia.

There are many differences, of course, between the two systems both quantitatively and qualitatively. In size, the Australian program is very much smaller. Although Australia is of comparable size to the main body of the U.S.A., its population is only some twelve million, served by about four thousand dentists. On this basis one could expect something of the order of a twentieth in magnitude. One would almost imagine that such

a small number is below the critical nucleus size for the growth, on a national basis, of a systematic research, standardization, and testing program for dental materials. All the more credit is due to the early foresight of members of university staff and the Australian Dental Association that such a program was not only initiated, but flourished.

2. The Bureau of Dental Standards

The staff of the Bureau of Dental Standards numbers only eight, none of whom are qualified dentists, unfortunately. Physicists, chemists, and metallurgists are included and for clinical opinions or trials the Bureau relies on the dental schools, the Services, and individual dentists either independently or through a Panel of Cooperating Practitioners throughout each State of the Commonwealth.

There are essential differences in organization too in that the Bureau of Dental Standards was established as an activity of the Commonwealth Department of Health; furthermore, the standard specifications on which the certification program is based, were developed through the Standards Association of Australia and not within the dental association as it was in America. It is interesting to note that in recent months the corresponding body in America, The United States of America Standards Institute, has now become very actively involved in the preparation of dental specifications and is to become the national organization through which such specifications are to be promulgated.

In Australia, as in the United States, the national dental association is the body which controls and directs the accreditation program and

issues an official List of Certified Products. It has a special committee for this purpose and for taking action on other matters concerning the quality and supply of dental products available on the Australian market. The Standards Association of Australia, through the help of the dental profession, the industry and the Bureau of Dental Standards, prepares the specifications; and the Australian Dental Association accredits products based on these specifications which they endorse. It is the Bureau of Dental Standards that does the necessary testing, checking, and investigational work required to assist both in the preparation of specifications and in the accreditation of products complying with them.

3. International Participation

Because of the limited local demand, Australia has never been anywhere near self-sufficient in the manufacture of dental supplies. At the outset, therefore, cognizance had to be taken of the fact that a large proportion of dental goods are imported and the accreditation program had to be adapted accordingly. It is only in recent years that the American Dental Association program has included any imported products and these are still very much in the minority. There is a certain amount of dental manufacturing in Australia, particularly in relation to gypsum products, amalgam alloys, gold alloys, waxes, modelling compounds, hydrocolloidal impression materials, orthodontic wires, local anaesthetic solutions, synthetic resin teeth, and a few cements. The large bulk of equipment, instruments, and other fabricated items are imported; also, for every product manufactured in Australia, there are many of the same type available from overseas, in spite of various protective tariffs that may be imposed to foster local production. One of the prime functions of the Bureau of Dental Standards is to assist local manufacturers, many of which are not large enough to support adequate laboratory staff and facilities. At the same time, the Bureau plays an important part in advising importers on the quality of their lines and ways in which they could be improved to meet the specified requirements.

The fact that so much of investigational and testing work is concerned with overseas products and developments has meant that Australia has maintained a keen interest in the progress on dental materials throughout the world; this has led to active participation in international committees both through the Federation Dentaire Internationale and the International Organization for Standardization. This interest has been greatly stimulated and encouraged by personnel of the National Bureau of Standards and of the American Dental Association Fellowship to whom we are greatly indebted for their part in initiating international specification programs.

Participation in the international sphere has proved to be of great benefit to the local specification program and to the raising and maintenance of the high quality of dental goods used by the Australian dental profession.

4. Australian Specification Program

As to the specification program itself, some thirty Australian dental standards have been issued. These cover a wide range of items including mercury, amalgam alloy, zinc phosphate and silicate cements, impression and laboratory plasters, artificial stone, inlay, sticky and modelling waxes, modelling compound, agar and alginate impression materials, impression paste, inlay and denture casting gold alloys, cobalt-chromium casting alloy, casting investment, denture base resin, synthetic resin teeth, local anesthetic solutions, x-ray films, hypodermic needles, hand cutting instruments, and gold and silver solders.

Currently, work is in hand to develop Australian standards for elastomeric impression materials, rubber dam, orthodontic cements, matrix band material, rubber elastics, endodontic instruments, root canal materials, and toothbrushes. Some of the existing specifications are under revision.

The controlling body in the specification program is the Dental Materials Committee of the Standards Association of Australia. This has equal representation of profession and trade together with representation from the Department of Health. It decides on policy and priority, but the drafting work is done through a number of subcommittees appointed for special fields such as gypsum products, impression materials, cements, waxes, casting alloys, synthetic resins, instruments, photographic materials, and, more recently, orthodontic materials, endodontic materials, and toothbrushes. These subcommittees also comprise the profession, trade, and testing authorities, but also bring in industrial experts from the respective fields.

When the need for a specification is recognized, a preliminary draft is prepared for the consideration of the appropriate subcommittee. This draft is usually prepared by the Bureau of Dental Standards and is based on existing overseas specifications and on its own work. When the subject has been well thrashed out in committee and reviewed, a draft is prepared for public criticism. Such drafts are widely circulated and are available to all interested parties.

After consideration of all comments received on the proof issued for critical review, a new draft is prepared and a postal ballot is finally taken. An effort is made to achieve unanimity at this stage. The specification then is printed as an offi-

cial Australian standard, but is always subject to amendment or revision in the light of new knowledge and developments.

The system used by the Standards Association of Australia is modelled largely on that of the British Standards Institution and it appears to work very well in British Commonwealth countries particularly.

It now remains for the Australian specifications to be reconsidered in the light of ISO Recommendations as they appear. An attempt was made on several occasions to reconcile Australian standards with the corresponding FDI specifications, but these have not succeeded because of the expressed

desire of committee members to retain some of the local differences.

The change in status of FDI specifications from a professional association backing to a national basis through ISO members should have a significant influence in dental specification philosophy, not only in Australia, but elsewhere throughout the world.

If any country has endeavoured to emulate the U.S. dental materials program of specification and certification, it is surely Australia and the fruits are apparent in the standard of dental supplies currently in use and in the confidence of the profession and trade in the local program.

Development of European Specifications and Testing

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The development of a European specification program is difficult because of the many differences of race, nationality, politics, and social systems. One of the first problems is the establishment of a common dental terminology. The lack of sufficient data on the relationship of properties and clinical results is another difficulty. However, Europe has a long heritage of standardization in other fields and this has made it logical to think of the ISO as the proper organization to introduce international dental standards into Europe. Many European countries have already achieved promising results on a national basis. Cooperation on a regional or continental level in the development of a specification and certification program will help to provide better dental health for the public.

Key words: Certification; dental specification; European dental specifications; FDI; ISO; terminology, dental.

1. Introduction

The United States of America seems to have a natural propensity to be, in a large number of matters, first in the world. The science of dental materials was no exception. So, we are here to celebrate the fiftieth anniversary of the dental research at the National Bureau of Standards. The joint sponsor of this celebration, the Americal Dental Association, has cooperated in this research for forty-one of the fifty years, and I think we all agree that this was a fruitful wedding.

Unfortunately, European weddings appear to be much more difficult. We, Europeans differ by race, nationality, politics, and social systems. And, when, by accident, we happen to believe in the same God, we do not worship Him the same way. Moreover, I was told, that in some European countries, the dentists themselves were not very strongly united.

This charming variety has made European dental specification programs interesting, because we had to meet nearly the same difficulties as to establish a world wide plan. Firstly, we had to think over a terminology, a philosophy, and a policy. A terminology for our mutual understanding, a philosophy to ascertain and make our general aims common, and a policy to enable us to meet our wide range of national and international difficulties.

2. Terminology

Maybe the worst danger of our time is what we might call "babelization"—using the same word with different meanings. In Europe, we speak a good number of different languages, more than twenty. Even when these languages were restricted to only two, there was no true communication with-

out difficulty. And it appeared dangerous to try to reduce them to only one; in each language, the meaning of a word is, by itself, a convention. In another country, although the term is the same, its conventional meaning may be different. So we have to agree, by mutual concessions, upon an international meaning, at least for important dental terms. Deciding this may help the countries whose language is neither English nor French, to revise their own dental terminology, in the same way they should have revised their political terminology. Problems involving both terminology and classification belong in a specification program and are not simple matters either. We are confronted with just such a problem on the codification of dental burs and the classification of dental equipment.

Apparently, there is still much work to do as concerns terminology, and everyone may have a share of it.

3. Philosophy

A sound and useful philosophy for international dental terminology, classification, and specifications is very difficult to establish—we are ignorant of much of the data we should know. For instance, experience has taught us that, when some physical properties are within certain limits, restorative materials, such as ones based upon zinc, silver, tin, or pure gold, generally give satisfactory clinical results. Of course, the temptation is great to reduce every specification to these physical properties. But we shall have no security whatever about the clinical behavior of such specified materials. On the other hand, specifying chemical composition may, in some cases, hamper progress.

If we agree, for instance, upon a code number signifying that a bur is an inverted cone, we are

bound to specify the ratio between the length of the head and the mean diameter as well as the ratio between the two extreme diameters of the head. The same concerns truncated cones. After that, should we consider as true inverted or truncated cones only the burs complying with the adopted ratios? Such a classification may come to the same inconvenience as the specification of a chemical composition for any dental material. Working out and agreeing upon a common and prospective philosophy will certainly need wide cooperation of experienced specialists and learned scientists.

4. A Policy for Specifications

It must be kept in mind that an international specification will probably not be so easily revised or amended as a national one. Once upon a time, in Washington, a senator was writing at his desk. Suddenly, the door was flung open by a young and excited secretary shouting that a Mr. Charles Lindbergh, alone in an airplane, had succeeded in flying across the Atlantic Ocean, from the United States to France. The disturbed senator stared calmly at his secretary and uttered: "Well, a single man can do anything. Please call again when a commission has flown across the ocean."

It looks like these days have come. Now, dental commissions fly across the oceans, thus making clear that we are in the era of effective and worldwide cooperation in the field of dental specifications.

If we provisionally lay aside dental specifications, international cooperation in the field of standardization is, in Europe, a very old affair. Many European national standards associations are more than fifty years old and celebrations of fifty years of international standardization could have taken place during the past years. Electrotechnical international standardization began with the first years of this century. This includes long established habits and rules that are far too much implanted in the incredible legal and political particularisms of Europe to allow easy pacific changes. And experience proved that, in a good number of cases, national dental federations had neither desire, nor power, to discuss these matters with sufficient force to convince national standards organizations.

Moreover, these standards organizations might think that they were very experienced and had dealt with much more important matters than dental standardization. They have built many European organizations: CEN, European Committee for standardization; COCOR which has the same function for the European Common Market; CENTRI, organization uniting BSI, DNA, and AFNOR to speed up the work of CEN; CENEL, for the coordination of electrotechnical standards, with CENELCOM the same for the common market.

With the exception of the electrotechnical branch, which is related to CEI, all these organizations are very strongly linked with ISO, the International Standards Organization. Whenever an ISO Recommendation exists, and is acceptable to the members of CEN, no further national or regional cooperation work is initiated.

Therefore, it was quite logical to think that ISO was the proper organization to introduce international dental specifications into Europe. And the International Standards Organization Technical Committee 106—Dentistry—was established. Its Secretariat was assigned to the United Kingdom, which took into account the experience of the British Standards Institution both in dental specifications and in European standardization. Geographical, historical, and intellectual conditions have, in the past, made Great Britain able to serve as an abutment to various kinds of bridges established between America and Europe. Dental standardization was no exception: the nine current FDI specifications were soon proposed as ISO Recommendations. The FDI and ISO agreed to inform each other of their intention to standardize such and such material, instrument, or equipment, thus avoiding as far as possible the duplication of work. This agreement between the FDI and ISO, now in procedure of development, is actually a very promising one. The two organizations are, I believe, more and more willing to work together. And many dentists are related to both, thus insuring a good conveyance of our professional ideas and needs. This might well be that fruitful European wedding we were searching for.

5. A Policy for Testing and Certification

Another question is the testing of dental materials, instruments, or equipment according to accepted specifications. Nowadays, many European standards organizations have, upon a national basis, their own mark of approval or certification. To these are submitted all products, national and imported, seeking certification. This may work when products are exported to a rather limited number of countries. But this is not the case for many dental materials. And it would be a heavy charge for the manufacturers to seek certification in every country. For Europe only, more than twenty standards organizations might be involved. This will probably not be tolerable for long.

Europe has to work out a common program for certification. Perhaps on a CEN and FIDE basis, perhaps in other ways. Later on, we could sign and observe agreements with other continental certification programs to obtain cross examination and cross reference upon a continental basis. This would avoid a material being sold with the reference: "this material appears on the North American—or European—list of certified dental materials" when, in fact, the exported quality is

not the same, the manufacturer knowing well that his risk is nil because nobody will test his material.

So, I would suggest that within an FDI or ISO/TC/73/SCI schedule, continents or groups of continents work upon this possibility of cross-testing and cross-referencing dental products. Anyway, this question of continental laboratories has to be solved; there is little hope that a worldwide laboratory will be convenient. Nor can it be expected that national laboratories belonging to small or developing nations be efficient or economically feasible. Europe is a good example of a continent where there is no other possibility. The opinion of certification specialists—particularly of the Working Group CEN/WG 42-Certification of products—is that such objectives will probably be reached through a multilateral recognition of national marks indicating conformity with standards. I believe that continental laboratories are of a paramount importance. Continental dental associations could probably speed up and improve such achievements by inducing their members to exert pressure upon government institutions, or national standards associations.

6. Research, Backbone of Specification

Underlying the importance of research as the backbone of a certification program today would not, I am afraid, be very inventive. In fact, some very simple specifications could make our work easier. For instance, we could decide that all the droppers used for the liquids of our cements should deliver equal drops of a standard liquid. And we might specify that every manufacturer should provide a plastic or metal proportioner for the powder, with the indication of the corresponding number of drops to obtain the standard or clinical consistency under standard hygrometric and thermometric conditions. Such a simple indication

might facilitate our work, and the teaching of dentists and dental hygienists.

Other specifications will be much more difficult to establish. For instance, it was the Swedish Delegation to ISO/TC/106 who called attention to the need of the biological testing of dental materials. Here is a very wide and interesting issue about which we have not much more exploitable knowledge than our forefathers. In fact, we are still “cementing wooden legs to the teeth of our patients.” There is still a lot of work to do. And Europe is like a mosaic, a puzzle of nations. It would be very surprising if each one of these nations were able to explore all the fields of science necessary to improve our specifications. Here again, European and even worldwide cooperation is necessary.

7. Conclusion

In conclusion, I am obliged to say that, in the true meaning of the term, we have then no European specifications and testing program. But, fortunately, many European countries have already achieved a lot of promising results upon a national basis, and, concerning the northern countries, upon a regional basis. In this rather limited paper, I have chosen not to speak of these achievements, although they will certainly prove to be very useful. But, for the future of Europe, as concerns dental specifications and testing, like many other matters, there is no better way than cooperation and coordination. These would be easier to attain if national dental associations would cooperate with their national standards organizations and with government institutions while giving firm support to the FDI and ISO. Organizations acting at the regional or continental level could also speed up and improve coordination. There is no doubt that such cooperation will help provide what we are all seeking: better dental health for the public.

Development of South American Specifications and Testing—Brazilian Experience

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A successful program of specifications for dental materials requires extensive knowledge of and participation in the program on the part of teachers in dental schools. In turn the dental teachers can involve dental industry and dental societies. In Brazil a specifications program in dental materials was initiated by holding annual meetings to which persons recognized as authorities in dental materials were invited to lecture and give assistance in specification aspects. Certification testing of dental materials has been initiated in only two dental schools, but it is planned to have dental materials departments at selected dental schools responsible for three or four materials in a general certification testing program.

Key words: Brazilian experience, dental materials specifications; dental materials; dental specifications; dental specifications and testing, South American.

1. Introduction

During the last 35 years, in many dental meetings throughout South America a great number of speakers talked about the importance and necessity of a national program of specifications for dental materials.

Sometimes theses were approved [1, 2]¹ by General Assemblies, concerning this subject. On other occasions, specific dental materials were tested, according to existing ADA or FDI specifications and many articles were published, only a few of which are referred to here [3, 4, 5].

In Brazil, many theses with titles like "Doutoramento", "Livro-Docente" or "Catedrático", from teachers belonging to prosthetic dentistry or operative dentistry departments, were completed in dental materials departments and, in most instances, ADA or FDI specifications were used as a guidance.

The effort of Degni [3] in 1949 should have been the beginning of a specification program in Brazil. The effort of Pinto [4] in 1962 should also have been the beginning of a regular specification program for dental materials in Argentina.

Why did those two extraordinary leaders in the field of dental materials in South America fail, with regard to a regular specification program?

Why did other people fail, each time they intended to start a specification program, in different countries in South America?

The answer to these questions is precisely what I intend to analyse and later on, when I give you

a brief report about our "Brazilian Experience" during the last four years, I hope this could be of some benefit to other South American countries.

2. Persons and Institutions Involved in a Specification Program

2.1. The Dentist and the Dental School

A specification program has to involve first of all, the dentist. What does he think about a specification program? How much does he care about a specification program? How much does he know about specifications?

I think it is fair to state that the dentist is a product of his dental school. If you want to know about the quality of teaching of any school of dentistry in South America, you should analyse the curriculum, you should find out about integration of teaching programs, you should find out about teaching facilities, but you should also be able to evaluate the teachers themselves! How much do they know about specifications and the complexities of a specification program?

I think that any attempt to start a specification program, in any South American country, in which only a minority of the dental teachers has a fair knowledge about the subject, is going to be a failure.

The whole teaching staff has to have, at least, a reasonable amount of knowledge about the problem, so that the students and later on, the dentists, as a consequence, will have developed the necessary mental attitude to understand and accept such a specification program!

This also means, of course, that the dental societies, consequently will easily accept and work

¹ Figures in brackets indicate the literature references at the end of this paper.

toward the program's acceptance. Without preparation of mental attitude there will be no acceptance.

As we see, our first vicious circle can only be cut, by preparing the teaching staff in our dental schools.

2.2. The Dental Dealer and the Dental Industry

I remember, back in 1954, in Brazil, I was criticized by my colleagues of the teaching staff of my own dental school, because I was introducing my students through lectures, visual aids, and demonstrations to the newly developed elastomeric impression materials. They reasoned: "Why teach it? Those materials are not available from the dental dealers in Brazil."

My colleagues agreed with me, however, when I answered: "The dental dealers do not carry these products because there is no demand for them on the part of the dentist. There is no demand on the part of the dentist, because we teachers, at the dental school, do not mention the product!"

This is another vicious circle that very often happens in South American dental schools.

Through the dental schools, the dental dealer, and especially the dental industry, will get involved in a specification program.

2.3. The Dental Societies

It used to be a policy of past-Presidents of the Brazilian Dental Association, to nominate a Committee of Dental Materials: a President, a Secretary and usually two or three members.

For many years the by-laws of the Brazilian Dental Association contained reference to specifications and a specification program. The simple nomination of a Committee of Dental Materials, however, used to be the beginning and the end of a specification program! I think this is true for many South American dental societies. The mental attitude towards acceptance of such a program, was not prepared. Not even all the dentists realized its importance.

At the same time as the Committee was nominated, new dental schools were created, with teaching staffs, in most instances, not well prepared for teaching. Yet those teachers, would somehow prepare dentists who, of course would join a dental society. I think, around 3,500 dentists graduate each year from the approximately 70 dental schools in South America.

To get the dental societies involved in a specification program, we have to start the work, seriously, with all the dental students.

2.4. The Public Health Dental Services

It is unquestionable that dentistry, all over the world, is seeking new methods, in an effort to extend its service to more and more people. This occurs through Dental Public Health Programs,

either supported by governments or by private institutions.

When it comes to restorative dentistry, what criteria do these institutions use to buy dental materials? You and I know that the research program at the National Bureau of Standards was started in 1919 to answer this question.

Especially with government-supported dental services, many programs in South America are restricted by drastic budget cuts, and very often as a result cheaper dental products are acquired, unfortunately.

2.5. The Government

I agree that the government of any country has to participate in a specification program for dental materials. But on the other hand, I think it is unwise to think that the government of any South American country should start such a program.

In most instances there are not enough funds available to finance adequately the national standards institutions!

There are still so many other important and basic problems to be solved by governments of South American countries that I think we do not have the right to expect them to start a specification program for dental materials. The government must get involved and cooperate, but is not supposed to start the program!

As we can see, specifications committees and sub-committees of national standards institutions need the active participation of dental schools, dental materials groups, the dental profession through state and national dental associations, the associations of dental research, the national and Latin-American associations of dental schools, and the governments.

To be successful, any specification program for dental materials needs the active participation, the cooperation, of the whole group of persons and institutions involved!

3. Brazilian Experience with a Specification Program for Dental Materials

In Brazil, as in any other South American country, we have an excellent starting point: the tremendous amount of excellent work and experience accumulated during the 50 years of your National Bureau of Standards; the excellence of postgraduate courses offered by many dental materials departments in the United States; all the information received through your research associations and institutes; the American Dental Association; the excellent opportunities offered to Latin American dental teachers, through fellowships sponsored by foundations such as the W. K. Kellogg Foundation.

We also based the starting of a specification program in Brazil, on the experience of other institutions, such as the Commonwealth Bureau of

Dental Standards in Australia (22 years), the BSI, the DNA (Deutscher Normenausschuss), the AFNOR (Association Francaise de Normalisation), ISO-TC/106; FDI; the experience of excellent researchers of Switzerland, Sweden, Denmark, and Japan, among others, who were always very cooperative, sending us information.

3.1. The Brazilian Dental Materials Group

Forty-two out of the approximately seventy dental schools in South America are located in Brazil. We felt that it was worthwhile to try to start a specification program through the dental schools in Brazil. The dental school, we think, is the only place in which we can prepare the mental attitude of the future dentist toward the acceptance of a specifications testing program. To achieve this with the 2,100 students who graduate each year from the dental schools in Brazil, we need first of all the understanding, the acceptance, and cooperation of all the dental teachers. The starting point, of course, is the teacher of dental materials, participating actively in the Brazilian Dental Materials Group.

We started the Group (GBMD, Grupo Brasileiro de Materiais Dentários) in September, 1965, when we had our first meeting in Pôrto Alegre, in the State of Rio Grande do Sul. Distances are great in Brazil, and we needed from the beginning the active participation of as many dental materials teachers as possible. For our first meeting, we used, as you might call it, a very good "bait". To deliver a course in dental materials and to present some conferences, we were fortunate to have with us at the time, the world-known authority in dental materials, Dr. Floyd A. Peyton, from the University of Michigan. Besides Dr. Peyton's course, we had group discussions on the following subjects: (1) Dental materials in the dental curriculum: lectures and laboratory course contents; (2) Integration of dental materials with clinical departments; (3) Research in dental materials departments; (4) The establishment of a Brazilian dental materials group and the adoption of specifications.

Over one hundred, most of whom were teachers of dental materials, attended the course and the meeting. Thirty-one dental schools were represented, out of a total of 38 then in existence, in Brazil!

For our second meeting, in 1966, in Belo Horizonte, State of Minas Gerais, we had as our guest lecturer, Dr. Hector Maddalena, Head of the Dental Materials Department in Buenos Aires, Argentina. Again we had a good meeting, with group discussions related to teaching and research in dental materials and specifications.

Our third meeting, in 1967, was held in Piracicaba, State of São Paulo, and we had over 80 members of our Dental Materials Group present. At that opportunity Prof. Degni and staff presented to the group the results of the controlled testing

of amalgam alloys manufactured in Brazil. This information was sent to all teachers of operative dentistry in Brazil, to all the deans of dental schools, to all dental associations in Brazil, to most dental government-supported services and to the dental industry. Our guest lecturer was Dr. Guillermo Mac Pherson, from the dental school of Santiago, Universidad de Chile. Thanks to Drs. Mac Pherson and Maddalena, our group has a good number of members from Argentina and especially Chile.

We divided Brazil into five regions, each having a coordinator who is responsible for special activities related to dental materials in his region. We have one meeting each year and the meeting places are chosen two years in advance.

The fourth meeting was in Fortaleza, Ceará and we had as our special guest lecturer Dr. George C. Paffenbarger who presented to us an excellent course in dental materials. Again we had planned group discussions, related to three main topics: (1) Philosophy of the teaching of dental materials; (2) Integration; and (3) Teacher training in the specialized field of dental materials: teaching and research programs.

There were over sixty teachers present, an excellent attendance, if you consider the great distance of Fortaleza (in the very northern part of the country) to Central and Southern Brazil, where most of the dental schools are. Dr. Paffenbarger has also been a great help to the Brazilian Dental Materials Group and even though, due to his many assignments at the time, he could not accept our invitation to visit the dental schools in the central and southern parts of the country, we believe he has a very good idea of what we are trying to accomplish. Through Dr. Paffenbarger we also wanted FDI to know a little bit more about our activities in Brazil.

Our fifth meeting was held this year, in July, in Baurú, State of São Paulo. I think it was an excellent meeting too, and I am sure Dr. John W. Stanford could tell you more about it than I; he was our special guest lecturer. We appreciated very much his course and his conferences and I would be tempted to say that he probably returned with a better impression of our group than our previous guests: the dental materials teacher is now, I would say, much better prepared than he was four years ago. We notice the great difference, just reading the conclusions of the group discussions!

We make good use of the many excellent articles published in the Journal of Dental Education, especially the ones related to teachers and training programs like the Workshop on Teacher Education [6].

Our staff of the dental school in Pôrto Alegre presented to the group the results of the surveys related to two additional dental materials manufactured in Brazil: investments for gold alloys and alginate impression materials.

I am certain that the dental materials teacher in Brazil is now much better prepared to exert his influence in preparing the mental attitude of the other teachers of his dental school and, through them, of the dental students toward acceptance of a specification program.

We are also noticing the greater interest and greater cooperation of the dental industry in Brazil toward our specification program.

So far, tests with regard to what you might call a "Certification Program of Materials" in Brazil were realized only in the Dental School of the University of São Paulo and in the Dental School of Pôrto Alegre, University of Rio Grande Do Sul. The dental materials departments of those two dental schools are generally considered training centers for dental materials. In São Paulo, especially under the leadership of Dioracy Vieira and Francisco Degni, we have accomplished quite a lot.

Several other dental materials departments from other dental schools in Brazil are being prepared to participate actively in the specification program. The idea is to have those chosen dental materials departments responsible for, say two, three, or four specific materials, in the general testing program. The results are distributed through the Brazilian Dental Materials Group.

Our Group is recognized by the Brazilian Standards Association (ABNT) as their Committee of Dental Materials.

We want the Government to enter the picture, but only later, when we have some concrete accomplishments to show!

To finish my presentation, I would like all of you to know that we of the Brazilian Dental Materials Group are now quite aware of the fact that the enormous prestige of your National Bureau of Standards, of many of your excellent dental materials departments, of your dental research institutions, this enormous prestige, I repeat, was neither easily, nor casually acquired!

4. References

- [1] Degni, F., Especificações e pesquisa, *Rev. Bras. Odont.* **3**, 19-23 (Ago 1945).
- [2] Acuna, R. O., Oficina Chilena de normas para materiales dentales, *Odont. Chilena* **15**, 11-15 (Mar-Abr 1966).
- [3] Degni, F., and Pomes, C., Amalgamas Latino-Americanas, *Rev. APCD* **2**, 13-24 (Jan-Feb 1949).
- [4] Pinto, F. E., Amalgamas Dentales Argentinas, *Rev. Odonto. Arg* **50**, 253-259 (Jul 1962).
- [5] Vieira, D. F., Pastas Zincoenolicas, *Ann. Fac. Farm. Odont. S. Paulo*, **10**, 329-347 (1952).
- [6] Workshop on Teacher Education. Conclusiones: Teacher training and education programs, *J. Dent. Education* **30**, 54-55 (Mar. 1966).

USA Specification and Evaluation Programs

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Reliable and valid laboratory tests which delineate satisfactory materials and rule out unsatisfactory ones are essential to the development of a satisfactory specifications program. Factors guiding the American Dental Association in the formulation of specifications are: Relevant tests; correlation of laboratory, structural, and service tests; and quality of product. An important change in organization for the development of dental specifications involves the formation of the USA Standards Committee for Dentistry, operating under the United States of America Standards Institute. The Certification Program provides a means for recognition of those materials complying with existing specifications. A new evaluation program on dental devices is currently issuing pertinent status reports on the safety and efficiency of such devices. Safety and usefulness are based primarily upon information established under conditions of clinical use.

Key words: Dental materials and devices, specifications for and certification of; dental specifications; specifications; standards, dental.

1. Introduction

Programs for the standardization and evaluation of dental materials have been available to the profession in the United States for many years. In fact it is well known that the basis for establishing dental research in 1919 at the National Bureau of Standards was the need for a laboratory standard for dental amalgam. This was the first attempt to define a material by means of physical and chemical properties.

Until 1966 these programs were conducted by the Association's Council on Dental Research through its Research Division at the National Bureau of Standards. The specification and certification programs for materials, along with other responsibilities, were transferred in 1966 to a new Council on Dental Materials and Devices. The formation of the new Council elevated programs in dental materials and devices to a level within the Association commensurate with their importance.

The Council has the following *By laws*:

To determine the safety and effectiveness of, and disseminate information on, materials and devices which are offered to the public or to the profession.

To encourage the development and improvement of materials and devices for use in dental practice or to improve the oral health of the public.

Some of its duties include the following in addition to standardization and evaluation programs:

1. Preparation of recommendations in radiation hygiene and practice.
2. Formulation of status reports on materials and devices.
3. Revision of the Association's publication *Guide to Dental Materials and Devices*.
4. Guidance on advertising and exhibit standards related to materials and devices.
5. Development and evaluation of new materials and devices or the improvement of existing ones.

Before the program was instituted at the National Bureau of Standards, most evaluations of filling materials were based on service tests in the mouth. Such tests were long drawn out, expensive, usually poorly controlled and, hence, frequently inconclusive. Materials must be tested in the laboratory prior to any widespread use. The laboratory tests should be designed so that they will delineate satisfactory materials and rule out unsatisfactory ones. This terse dictum is difficult to carry out because the design of tests that will accomplish it requires considerable imagination and the necessary research to prove that the tests are reliable and valid. By reliable it is meant that the tests can be repeated by different laboratories with satisfactory agreement in results. By valid it is meant that the laboratory testing will predict the behavior of the materials in service.

The American Dental Association believes that only the highest quality materials obtainable should be used and does not consider the price at which a product is sold as any criterion of its quality. The Association believes that this philosophy is sound and dependable from a public health standpoint, and the current specifications

reflect this policy. Therefore, in designing a specification one has the following in mind:

1. Relevant tests
2. Correlation of laboratory, structural, and service tests
3. Quality of the product

These factors have guided the Specifications Committee of the Dental Materials Group of the IADR, which acted as principal consultant to the American Dental Association in the formulation of specifications or standards during the period 1953 until 1969. Some of its recent programs have dealt with formulating specifications or standards for the following:

1. Dental diamond rotary instruments
2. Dental excavating burs
3. Dental radiographic film
4. Direct filling resins
5. Duplicating materials
6. Endodontic files, reamers, and points
7. Gypsum materials
8. Toxicity tests
9. Zinc silico-phosphate cements
10. Base plate wax
11. Orthodontic wire not containing noble metals

The Specification for duplicating materials became official on November 1, 1968, and was designated American Dental Association Specification No. 20. Final approval of specifications for items 2, 3, and 9 were given in May and June of 1969.

2. Specifications and Biological Toxicity

The formulation of a specification dealing with toxicity tests deserves discussion. In the past, specifications have been designed to evaluate materials on the basis of chemical composition and physical and mechanical properties determined in the laboratory. These tests have been designed to simulate actual service conditions as closely as possible. The degree of the validity of the laboratory test is determined by the degree of correlation between data obtained from laboratory tests and the behavior of the materials in service. The safety of the materials for clinical use has in the past been largely based on the fact that no serious complications arose from clinical use. In other words, no screening tests were available for new materials before they were placed in clinical use.

With the knowledge that new materials were and are being made available to the profession at an increasing rate, the Specifications Committee recommended and the Association agreed that a subcommittee should be established to prepare recommended screening test procedures to be used in the laboratory. The subcommittee is progressing in the development of such recommendations for guidelines to biological testing. These guidelines will be of special assistance to both the manufacturer and the Association in the event of federal legislation regulating medical devices.

3. U.S.A. Standards Committee for Dental Materials and Devices

Of special interest here also is the formation of a USA Standards Committee for Dental Materials and Devices. The recommendation for such a committee originated in the dental trade. The recommendation as presented calls for the phasing out of the duties of the Specifications Committee of the Dental Materials Group of the IADR and a transfer of its duties to a new committee which would operate under the United States of America Standards Institute (USASI). During recent years the United States has become involved in an international standardization program through USASI.² With formation of various committees, subcommittees, and working groups there has been some duplication of effort and, in some instances, mass confusion about the relations of all the organizations involved. The new committee will be called the USA Standards Committee for Dental Materials and Devices, and all other committees will, as such, be disbanded. The American Dental Association will act as the administrative sponsor of the committee through the Council on Dental Materials and Devices and will also handle the duties of secretary. It is believed that the Association as sponsor of and the dental industry as a contributor to such a committee will place organized dentistry in a favorable position in the event federal legislation in the dental device area is passed.

4. The Certification Program for Dental Materials

The Certification Program forms the second part of the program for materials, after specifications have been adopted. Under this program the manufacturer of a dental material certifies that his product complies with the specifications which have been approved as official *Specifications of the American Dental Association* and that he is in compliance with the *American Dental Association Advertising and Exhibit Standards*. If the product is found to comply with the specification, its name is then placed on the *List of Certified Dental Materials* which is maintained by the Council and published periodically in *The Journal of the American Dental Association*.

From time to time, materials on the *List* are tested in the laboratories of the American Dental Association. When a product is found not to comply with official specifications, the manufacturer is notified, and the product is removed from the *List*. No manufacturer may claim participation in the Certification Program except under authorization granted by the Council on Dental Materials and Devices of the Association. The program has

² Name later changed to American National Standard Institute (ANSI).

been increasingly accepted during recent years. Tables 1 and 2 show the growth in the number of specifications and in the number of products on the List.

TABLE 1.

List of Certified Dental Materials	
Year	Number
1929.....	40
1932.....	112
1934.....	145
1936.....	187
1938.....	205
1940.....	225
1942.....	222
1945.....	245
1948.....	270
1951.....	285
1954.....	315
1956.....	305
1958.....	325
1960.....	350
1962.....	345
1964.....	372
1967.....	427
1969.....	475

Number of Manufacturers or Distributors	
Year	Number
1969.....	105

TABLE 2. *New Certifications*

During the period of 1952 to 1964 there were approximately 120 new certifications. The following is a breakdown of results:

Materials.....	120
Complied.....	110
Failed.....	10 or about 8%

Compare this to surveys of certified products:	
Surveys.....	955
Failed.....	5 or about 0.5%

5. Evaluation of Dental Devices

A new program of the Association concerns the evaluation of dental devices, with priority given to those devices which directly relate to the health and safety of the patient, the dentist, and his auxiliary personnel. The program, to date, has consisted of initiation of a series of status reports on the safety and efficacy of devices. These reports summarize the existing information and may or may not arrive at certain specific conclusions, depending upon the amount and quality of the available evidence. At least the reports serve to

acquaint the dentist with the extant knowledge. It is planned that other evaluation procedures, such as specification and certification or acceptance programs, will be utilized in the future. No one type of program will apply to all devices, and, to be of greater value to the profession, the program should include an evaluation of the usefulness and effectiveness of the devices from both a clinical and a laboratory standpoint.

The Council has assigned priority for evaluation of the following classes of devices:

1. Instruments for surgical cutting
2. Devices for removing calculus
3. X-ray machines
4. Oral hygiene devices
5. Desensitizers
6. Pulp testers

The first application of the acceptance program is in the oral hygiene device area. The Council classifies an evaluated device as *Acceptable*, as *Provisionally Acceptable* or as *Unacceptable* under this program. Evaluation of safety and usefulness of a device is based primarily upon information established under conditions of clinical use and not physical standards or specifications. Electric toothbrushes (formerly a device evaluated by the Council on Dental Therapeutics) and oral irrigating devices are the first devices being rated by the Council under the Classification System which follows:

CLASSIFICATION SYSTEM

1. *Acceptance Program:* The Acceptance Program applies to devices for which evidence of safety and usefulness has been primarily established under conditions of use or to devices for which physical standards or specifications do not currently exist. Powered toothbrushes are an example of this type of device. Devices accepted under this program shall be classified as described in the following section.

A. *Classification of devices evaluated by the Council:* After consideration of a device has been completed under the provisions of the 'Acceptance Program', the Council will classify the device as *Acceptable*, as *Provisionally Acceptable* or as *Unacceptable*. Devices will usually be classified as *Acceptable* for a period of three years. Acceptance is renewable and may be reconsidered at any time. If manufacturing ownership of the device changes, the period of acceptance expires automatically.

1. *Acceptable* devices will be listed in *Guide to Dental Materials and Devices* and the manufacturer or distributor may use an authorized statement as specified in Section V, "Announcement and Maintenance of Acceptance or Certification", of these provisions.

2. *Provisionally Acceptable* devices consist of those which lack sufficient evidence to justify classification as *Acceptable*, but for which there is reasonable evidence of safety and usefulness including clinical feasibility. These devices meet the other qualifications established by the Council on Dental Materials and Devices. The Council may authorize the use of a suitable statement to define specifically the area of usefulness of a device classified as *Provisionally Acceptable*. Classification in this category is reviewed each year and is not ordinarily continued for more than three years.
3. *Unacceptable* devices are those which are dangerous to the health of the user, obsolete, markedly inferior, or useless. These devices do not meet the standards outlined in the "Provisions for Evaluation of Dental Devices."

Now, one may ask why the Association has entered the device field. There are several reasons. First, no agency outside of the federal government was conducting any type of evaluation of complex devices in relation to safety of the patient, the dentist, and auxiliary personnel. The dentist at present has no information to use in advising his patients on devices for use at home. The success of the Association's programs in materials indicated that research in improvement and development of new equipment could be hastened by the new program.

Another factor which should not be dismissed lightly is the sale of many quack devices in the medical field to the elderly of the country. The Food and Drug Administration currently has authority to consider the safety of devices. These are defined as: "Instruments, apparatus, and contrivances, including their components, parts, and accessories, intended (1) for use in the diagnosis, care, mitigation, treatment, or prevention of disease in man or other animals; or (2) to affect the structure or any function of the body of man or other animals."

Even restorative materials used in dentistry are included in this definition of devices. If new legislation similar to that which has been introduced in the past two sessions of Congress is enacted, the Food and Drug Administration will be given additional authority to consider the safety and efficacy of devices and to regulate certain marketing practices. The extent to which FDA regulations are applied to dental devices, including materials, may depend in part upon the effectiveness of an existing professional program.

One of the main reasons the evaluation program for materials of the Association has been successful over the last 35 years has been the increasing cooperation of the manufacturers in standardization and improvement of their materials. The Association especially desires this cooperation and assistance from all in the field of therapeutic agents, dental materials, and devices in the years ahead.

VIII. Appendix. NBS Dental Research Section Personnel

Personnel of the Dental Research Section of the National Bureau of Standards

The Dental Research Section of the National Bureau of Standards has served not only as a research laboratory but also as a school for dental researchers. Alumni of the Section are widely scattered in research facilities and educational institutions throughout the United States and in other countries. In the following tables on personnel of the Dental Research Section an attempt has been made to include everyone who has worked in the Section for six months or longer. Because the tables cover a relatively long period of time and since some of the personnel records are incomplete or unavailable, there are undoubtedly omissions and inaccuracies.

During the past 50 years about 175 people have been members of the staff of the NBS Dental Research Section, table 1. American Dental Association research associates numbered 62; there were 64 military or Veterans Administration personnel; 31 were Civil Service employees; and 25 others were research associates of Weinstein Research Laboratories, guest workers from various laboratories, or summer students. A summary is given in table 2. Several members were in more than one category and because of this the total is more than 175.

Seventeen members of the staff have been in the Section ten to 40 years, while 23 others were in the Section from five to ten years. Nearly 90 staff members were military personnel, Veterans Administration employees, and other guest workers, who were stationed in the Section for periods from a few months to as long as six years. Forty-one of these were dentists and 22 were chemists. Eleven of the guest workers were from outside the United States.

An indication of the variety of backgrounds is shown in table 3 which lists personnel by profession.

Although the present activities of many of our former personnel are not known, at least ninety of those listed in table 1 are still in the field of dentistry. Thirty-five remain in the Dental Research Section; thirty-seven are in the Federal dental services or in dental schools, and seventeen are in dental practice, in the American Dental Association research facility in Chicago or in other dental activity.

Dr. Wilmer Souder, the founder of our group, has been retired for some time but is hale and hardy, living in Landisville, Pennsylvania. Dr. George C. Paffenbarger who first came to the Dental Research Section over 40 years ago is still working in the Section on a part-time basis, although theoretically retired. Dr. Irl C. Schoonover, one of our four Section Chiefs, became Deputy Director of the National Bureau of Standards, the second in command, before retiring from Government service in early 1969. Mr. William T. Sweeney, another former Section Chief and a Government service retiree in 1968, is now working as an associate professor at the University of Alabama. Dr. John W. Stanford has become Director of the Division of Biophysics of the American Dental Association. Dr. Harvey W. Lyon is the Director of the Division of Clinical Studies for the ADA. Dr. A. F. Forziati is Acting Assistant Director of Physical Sciences, Division of Water Quality Research, Federal Water Pollution Control Administration. Dr. Robert J. Nelsen is the Executive Secretary of the American College of Dentists. Mr. Denton L. Smith is Director of Research for The J. M. Ney Company. This position was previously held by Mr. Richard L. Coleman, now retired, one of the early research associates in the Dental Research Section.

TABLE 1. *Personnel of the Dental Research Section, NBS, 1919-1969*

Name	Affiliation	Profession	Tenure	Present location or employment
ADLER, Mr. Alfred G.	Army	Metallurgist	1954-1956	New York.
AREVJEV, Mr. Vsevolod	Army		1958-1959	
ARGENTAR, Mr. Harold	Army-ADA	Chemist	1962-present	NBS Dental Research.
AUSTIN, Mr. Clarence	ADA	Metallurgist	1960-1961	Redstone Arsenal, Ala.
AVNIMELECH, Dr. Yoram	ADA	Chemist	1965-1967	Israel Institute of Technology, Haifa.
BALEKJIAN, Dr. Aran	ADA	Chemist	1964-1965	Naval Medical Research Institute.
BARBER, Dr. Ronald	Navy	Dentist	1934-1936	Retired, Boston, Mass.
BARONE, Dr. Joseph J.	Army	Dentist	1957-1960	Army, Fort Sill, Okla.
BARTON, Dr. John A.	Air Force	Dentist	1965-present	NBS Dental Research.
BEALL, Mr. John R.	ADA	Mechanical engineer	1934-1947	Army Med. R&D Command, Washington, D.C.
BEEBE, Dr. Douglas M.	Army	Dentist	1953-1954	Deceased.
BERGER, Dr. Howard S.	ADA	Dentist	1928-1929	Private practice, Falls Church, Va.
BOOTH, Miss Esther	ADA	Typist	1965-1969	Washington, D.C.
BOWEN, Mrs. Joy S.	ADA	Chemist	1968-present	NBS Dental Research.
BOWEN, Dr. Rafael L.	ADA	Dentist	1956-present	NBS Dental Research.
BRAUER, Dr. Frank J.	Navy	Dentist	1955-1957	Private practice Wautoma, Wisconsin.
BRAUER, Dr. Gerhard M.	NBS	Chemist	1950-present	NBS Dental Research.
BROWN, Mr. James J.	NBS	Student trainee	1958-1959	Washington, D.C.
BROWN, Dr. Walter E.	ADA	Chemist	1962-present	NBS Dental Research.
BURNS, Miss Claire L.	NBS	Chemist	1951-present	NBS Dental Research.
BURNS, Mr. Francis R.	NBS	Chemist	1954-1956	Chicago, Illinois.
BUSH, Mrs. Jesse W.	NBS	Secretary	1948-1953	Washington, D.C.
CARLSON, Mr. Elmer T.	ADA	Chemist	1968-present	NBS Dental Research.
CARLSON, Mr. John C.	Navy	Technician	1958	
CASSEL, Dr. James M.	NBS	Chemist	1969-present	NBS Dental Research.
CAUL, Mr. Harold J.	ADA	Chemical engineer	1937-present	NBS Dental Research.
CHANDLER, Dr. Harry	ADA	Dentist	1968-present	NBS Dental Research.
CHIVIAN, Dr. Simon	Army	Dentist	1961-1963	Walter Reed Hospital.
COLEMAN, Mr. Richard L.	Weinstein Research Laboratory	Engineer	1922-1928	Retired, West Hartford Connecticut.
COPELAND, Dr. Henry I.	Air Force	Dentist	1953-1956	Andrews AFB.
CRIST, Dr. Ray F.	Summer student	Stud. techn.	1962-1963	Navy, Garden Grove, California.
DAVENPORT, Mrs. Ruth M.	NBS	Technician	1950-present	NBS Dental Research.
DEMAREE, Dr. Neil C.	Navy	Dentist	1959-1961	Navy, Camp Pendleton, California.
DENTON, Miss Glenna M.	NBS	Secretary	1966-present	NBS Dental Research.
DICKENS, Dr. Brian	NBS	Chemist	1966-present	NBS Dental Research.
DICKSON, Mr. George	NBS	Physicist	1940-present	NBS Dental Research.
DIORIO, Mr. Alfred F.	ADA	Chemist	1956-1959	Georgetown Univ. Hosp.
DRIESSENS, Dr. Ferdinand C. N.	Guest worker	Chemist	1968-1969	Katholieke University, Nijmegen, Netherlands.
DUFFEY, Mr. Depue H.	ADA	Chemist	1961-1963	Georgetown Univ., Med.
DURANY, Mr. George	Army-ADA	Chemist	1962-1966	ADA, Chicago, Illinois.
EDEN, Dr. George T.	Navy	Dentist	1964-1965	Navy, Univ. of Michigan.
EICK, Mr. John D.	ADA	Mathematician	1963-1966	State Univ. of New York at Buffalo.
EL SADR, Mrs. Betty Lee	ADA	Secretary	1963-1965	Arlington, Virginia.
EPSTEIN, Mr. Earl F.	ADA	Chemist	1963-1964	Univ. of Wisconsin.
FANNING, Mrs. Rachel J.	ADA	Chemist	1953-1955	University Park, Md.
FARRIS, Dr. Lovell L.	Summer student.	Student technician.	1965, 1966	Private practice, Eatontown, New Jersey.
FEE, Mrs. Jean G.	NBS	Chemist	1951-1954	Philadelphia, Penna.
FERGUSON, Dr. George W.	Navy	Dentist	1946-1949	State Univ. of New York at Buffalo.
FISCHER, Dr. Theodore E.	Army & Air Force	Dentist	1947-1951	Univ. of Alabama.
FORSYTH, Mr. John W.	NBS	Technician	1953-1955	Howard University, Washington, D.C.

TABLE 1. *Personnel of the Dental Research Section, NBS, 1919-1969—Continued*

Name	Affiliation	Profession	Tenure	Present location or employment
FORZIATI, Dr. Alfonse F.	ADA	Chemist	1950-1962	Dept. of the Interior, Washington, D.C.
GARDNER, Mr. Alvin F.	Guest worker	Chemist	1958-1959	
GARDNER, Dr. Thomas V.	Army	Dentist	1962-1965	Army, Fort Sill, Okla.
GLASSON, Dr. Gilbert F.	Air Force & ADA	Dentist	1947-1952	Private practice, Waterloo, Iowa.
GREGORY, Mr. Thomas M.	ADA	Chemist	1963-present	NBS Dental Research.
GRUNEWALD, Dr. Alvin H.	Navy	Dentist	1947-1949	Northwestern University.
HANSEL, Mr. Grant, Jr.	Army		1956-1957	
HANSEN, Mr. William C.	NBS	Physicist	1951-1956	Washington, D.C.
HARTLEY, Dr. Jack L.	Air Force	Dentist	1951-1955	Consultant, San Antonio.
HARVEY, Mr. Jack L.	Army	Chemist	1949	NBS (Tire systems).
HAWKINS, Mr. Norman D., III	NBS	Physicist	1932	Deceased.
HEGDAHL, Mr. Trond M.	Guest worker	Dentist	1965	University of Bergen Oslo, Norway.
HICHO, Mr. George E.	Army	Metallurgist	1962-1963	NBS (Engineering metallurgy).
HIDNERT, Dr. Peter	NBS & ADA	Physicist	1957-1960	Deceased.
HOBSON, Dr. Robert W.	Army	Dentist	1952-1953	Army, Fitzsimons Gen. Hosp., Denver, Colorado.
HOWE, Mr. Willard B.	Army	Chemist	1957-1959	
HUDSON, Dr. Donald C.	Air Force	Dentist	1950-1956	Univ. of Texas, Houston.
HUFF, Mr. Richard L.	Army	Chemist	1957-1959	
HUGET, Dr. Eugene F.	Army	Dentist	1965-1968	Walter Reed Hospital, Washington, D.C.
ISAACS, Mr. Aaron	NBS	Chemist	1930-1935	Deceased.
JØRGENSEN, Prof. Knud Dreyer	Guest worker	Dentist	1957-1958	Royal Dental College, Copenhagen, Denmark.
KING, Dr. Richard	Summer student	Student technician	1958, 1959	Private practice, California.
KINGSBURY, Mrs. Pamela	ADA	Technician	1967-present	NBS Dental Research.
KROGH-POULSON, Dr. Willy G.	Guest worker	Dentist	1947	Royal Dental College, Copenhagen, Denmark.
KUMPULA, Mr. John W.	NBS	Mech. Engr. technician	1952-present	NBS Dental Research.
KUMPULA, Mrs. Marion P.	ADA	Secretary	1952-present	NBS Dental Research.
LAURILA, Dr. Riita	ADA	Chemist	1958-1960	Paris, France.
LAWSON, Mr. Melvin E.	ADA	Technician	1950-1957	Washington, D.C.
LEDLEY, Dr. Robert S.	Army	Dentist	1951-1952	Hyattsville, Maryland.
LEHMANN, Mr. Frank H.	Army	Chemist	1959-1960	New York, N.Y.
LEIBFRITZ, Mr. Walter A.	Army	Metallurgist	1953-1954	Chicago, Illinois.
LEUSSING, Dr. Daniel L.	ADA	Chemist	1962	Ohio State University.
LOEBENSTEIN, Dr. William V.	NBS	Chemist	1964-present	NBS Dental Research.
LONGTON, Dr. Robert W.	Navy	Dentist	1961-1963	Navy, Evanston, Illinois.
LYON, Dr. Harvey W.	Navy	Dentist	1949-1951	ADA, Chicago, Illinois.
MABIE, Mr. Curtis P.	ADA	Petrographer	1968-present	NBS Dental Research.
MACASAET, Dr. Avelino A.	Guest worker	Dentist	1960-1962	Univ. of the Philippines, Manila, Philippines.
MALMSTEDT, Mrs. Margaret	ADA	Secretary	1968-present	NBS Dental Research.
MANCEWICZ, Miss Sandra A. (Mrs. John Hefferen).	ADA	Chemist	1958-1965	Evanston, Illinois.
MANUSZEWSKI, Mr. Richard C.	ADA	Metallurgist	1966-present	NBS Dental Research.
MARGETIS, Dr. Peter M.	Army	Dentist	1953-1956	Deceased.
McCONNELL, Mr. Robert M.	Army	Technician	1954-1956	ADA, Chicago, Illinois.
McDOWELL, Dr. Hershel	ADA	Chemist	1963-present	NBS Dental Research.
McLAUGHLIN, Mr. Richard D.	Summer student	Student technician	1966, 1967, 1968	Georgetown University, Washington, D.C.
MERCHANT, Dr. Hubert W.	Army	Dentist	1956-1957	Emory Univ., Atlanta.
MILLER, Dr. William A. C.	Air Force	Dentist	1955-1958	State University of N.Y. at Buffalo.
MITCHELL, Dr. James A.	Navy	Dentist	1951-1954	Private Practice, Opelousas, Louisiana.
MOORE, Mr. Clarence	Army	Chemist	1959-1961	
MOORE, Mr. Robert E.	Army	Chemist	1953-1955	Cape Kennedy Florida.
MORENO, Dr. Edgard C.	ADA	Chemist	1963-present	NBS Dental Research.

TABLE 1. *Personnel of the Dental Research Section, NBS, 1919-1969—Continued*

Name	Affiliation	Profession	Tenure	Present location or employment
MORRIS, Mr. Richard W	Army	Chemist	1960-1962	
MORRIS, Mr. Stephen	Army		1961-1962	
MOSHONAS, Mr. Manual G	Army	Chemist	1956-1957	Florida.
MOWERY, Dr. William E	Veterans Administration	Dentist	1950-1952	Veterans Administration, Dayton, Ohio.
MULLINEAUX, Mrs. Anna G	ADA	Dental Asst.	1958-present	NBS Dental Research.
MULZET, Dr. Alfred P	NBS	Mech. Engr	1966-1968	IBM, New York.
NELSEN, Dr. Robert J	ADA	Dentist	1950-1955	American College of Dentists, St. Louis, Mo.
NELSON, Mrs. Barbara	ADA	Technician	1957-1958	
OFSTEAD, Mr. Eilert A	ADA	Technician	1957-1958	
OGLESBY, Mr. Philip L	NBS	Physicist	1957-present	NBS Dental Research.
OHASHI, Dr. Masayoshi	Guest worker	Physical Science	1962-1965	Nihon University, Tokyo, Japan.
OLIVER, Mr. Jerry A	Army	Chemist	1964	
OPPENHEIM, Mr. William L	Summer student	Student Technician	1963, 1964, 1965, 1967.	Georgetown University, Washington, D.C.
OVERBERGER, Dr. James E	Army	Dentist	1954-1956	Univ. of West Virginia.
PAFFENBARGER, Dr. George C	ADA	Dentist	1929-present	Retired, NBS Dental Research.
PALCIC, Miss Julia C	ADA	Chemist	1967-present	NBS Dental Research.
PARETZKIN, Mr. Boris	ADA	Chemist	1958-1961	NBS (Inorganic Mat.).
PATEL, Dr. Prafull R	ADA	Chemist	1965-present	NBS Dental Research.
PEIPERL, Mrs. Martha D	ADA	Chemist	1957-1958; 1962-1963.	Silver Spring, Maryland.
PERLOFF, Dr. Alvin	Army	Chemist	1954-1956	NBS (Crystallography).
PERKINS, Dr. Robert R	Navy	Dentist	1957-1959	Navy, Norfolk, Va.
PETERSON, Dr. Gert Forum	Guest worker	Dentist	1961-1962	Copenhagen, Denmark.
PFEIFFER, Dr. Kenneth R	Veterans Administration	Dentist	1950	Deceased.
PIERMARINI, Mr. Gaspar J	Army	Chemist	1957-1958	NBS (Crystallography).
PINCOCK, Mr. Douglas G	Summer student	Student technician	1966-1967	Temple University, Philadelphia, Pa.
POPPE, Mr. W. A	Weinstein Res. Lab.	Engineer	1925-1928	Washington, D.C.
POSNER, Dr. Aaron S	ADA	Chemist	1950-1961	Hospital for Special Surgery, New York.
ROBERTS, Mrs. Cora L	NBS	Secretary	1961-1966	Walter Reed Hospital.
RODRIGUEZ, Dr. Mario S	Guest worker	Dentist	1959-1963	Loyola University, New Orleans, La.
RUPP, Dr. Nelson W	Navy & ADA	Dentist	1953-1955, 1969-present.	NBS Dental Research.
RYGE, Dr. Gunnar	Guest worker	Dentist	1949	U.S.P.H.S., San Francisco, Calif.
SACCHI, Dr. Hector	Guest worker	Dentist	1954-1955	Montevideo, Uruguay.
SANGERMANO, Mr. Lawrence D	Army	Chemist	1961-1962	General Electric Co.
SCHOONOVER, Dr. Irl C	NBS	Chemist	1935-1953	Retired, NBS.
SCHOUBOE, Mr. Paul J	ADA, NBS	Chemist	1954-1955	Jacksonville, Florida.
SERIO, Dr. Andrew F	Army	Dentist	1950-1952	Private practice, Huntsville, Ala.
SHEEHAN, Mr. William D	Army	Chem. engr	1949-1951	
SIMON, Mr. Lester	Army	Chemist	1959-1961	New York, N.Y.
SLADE, Dr. Philip E	Army	Chemist	1956-1958	Chemstrand, Pensacola, Florida.
SMITH, Mr. Denton L	ADA	Metallurgist	1947-1957	J. M. Ney & Co., Bloomfield, Conn.
SMITH, Mr. W. Harold	ADA	Chemist	1957-1958	Deceased.
SNOVER, Miss Dorothy	Weinstein Res. Lab.	Chemist	1925-1926	
SOUDER, Dr. Wilmer	NBS	Physicist	1919-1945	Retired, Landisville, Pa.
STANFORD, Dr. John W	ADA	Chemist	1952-1965	ADA, Chicago, Illinois
STEPHENSON, Mr. S. R.	Army	Chemist	1950	
STEINBERG, Mr. Harold L	Army	Chemist	1958-1959	NBS (Radioactivity)
STRASSBURGER, Mr. John	NBS	Chemist	1957-1959	Carrier, Inc. Syracuse, N.Y.
SULLIVAN, Miss Sandra	ADA	Secretary	1957-1959	

TABLE 1. *Personnel of the Dental Research Section, NBS, 1919-1969—Continued*

Name	Affiliation	Profession	Tenure	Present location or employment
SUSA, Mr. Martin E.....	Army.....	Chemist.....	1959-1960.....	
SUTTER, Dr. John R.....	NBS, ADA.....	Chemist.....	1966-1967.....	Howard University Washington, D.C.
SWANEY, Mr. Aubrey C.....	ADA.....	Chemist.....	1946-1950.....	Detroit, Michigan.
SWANGER, Mr. William H.....	Weinstein Res. Lab.	Chemist.....	1924-1928.....	Deceased.
SWEENEY, Mr. W. Timothy.....	Summer student	Student Technician	1965-1966.....	Medical College of Virginia.
SWEENEY, Mr. William T.....	NBS, ADA, NBS	Physicist.....	1922-1941, 1949-1969.	Retired, University of Alabama.
TAYLOR, Dr. Duane F.....	NBS.....	Metallurgist.....	1954-1961.....	Univ. of North Carolina Chapel Hill, N.C.
TAYLOR, Dr. Norris O.....	ADA.....	Chemist.....	1928-1931.....	Deceased.
TERMINI, Mr. Dominic J.....	NBS.....	Chemist.....	1965-present.....	NBS Dental Research.
TURNER, Mr. John F.....	ADA.....	Technician.....	1964-1965.....	
VIOHL, Dr. Jochen.....	Guest worker.....	Dentist.....	1965-1966.....	Free University of Berlin, Germany.
WALDRON, Dr. John T.....	Summer student.....	Student Technician	1959, 1960.....	Private practice, Pittsburgh, Penna.
WALLACE, Mrs. Betty M.....	ADA.....	Chemist.....	1963-present.....	NBS Dental Research.
WATERSTRAT, Mr. Richard M.....	ADA.....	Metallurgist.....	1961-present.....	NBS Dental Research.
WEBB, Miss Georgia I.....	NBS.....	Secretary.....	1953-1960.....	State University, Ames, Iowa.
WEIGEL, Mr. Keith V.....	ADA.....	Chemist.....	1957-1959.....	Washington, D.C.
WEINER, Mrs. Helen.....	ADA.....	Typist.....	1959-1963.....	Washington, D.C.
WEISS, Mr. Jonas.....	Army.....	Chemist.....	1957-1958.....	New Brunswick, N.J.
WHITE, Dr. Eli E.....	Summer student.....	Student Technician	1955, 1956, 1957.	Private practice, Merritt Island, Fla.
WIEDEMAN, Mr. William.....	Army.....	Chemist.....	1962-1963.....	Buffalo, New York.
WILLIAMS, Mrs. Billie S.....	ADA.....	Secretary.....	1966-1968.....	Washington, D.C.
WOELFEL, Dr. Julian B.....	ADA.....	Dentist.....	1957, 1958.....	Ohio State University.
WOLCOTT, Dr. Robert B.....	Navy.....	Dentist.....	1949-1951.....	UCLA.
WORTHINGTON, Dr. Chas. R.....	Guest worker.....	Chemist.....	1957-1958.....	
YOST, Mr. Ernest L.....	Army.....	Physicist.....	1952.....	Pittsburgh, Pa.
YUDOWITCH, Dr. Kenneth L.....	ADA.....		1957-1958.....	
ZELENKA, Mr. Donald.....	Army.....	Metallurgist.....	1960-1962.....	Flushing, Michigan.

TABLE 2. *Affiliation*

American Dental Association.....	62
NBS (Civil Service).....	31
U.S. Army.....	42
U.S. Navy.....	13
U.S. Air Force.....	7
Veterans Administration.....	2
Weinstein Research Laboratory, guest workers, summer students.....	25
Total.....	182

TABLE 3. *Profession*

Chemists.....	65
Dentists.....	47
Technicians (including summer students).....	19
Clerical (administrative).....	11
Physicists.....	8
Metallurgists.....	9
Engineers.....	7
Mathematician.....	1
Mineralogist.....	1
Other.....	6
Total.....	174