1956-2 Dr. Paffenbarger

NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

July 1 to December 31, 1956

Dental Research Laboratory

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

U. S. DEPARTMENT OF COMMERCE
Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS
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THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its headquarters in Washington, D. C., and its major field laboratories in Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant reports and publications, appears on the inside back cover of this report.

WASHINGTON, D. C.

Electricity and Electronics. Resistance and Reactance. Electron Tubes. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

Heat and Power. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology and Lubrication. Engine Fuels.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. AEC Radiation Instruments.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Gas Chemistry. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Organic Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metals Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Heating and Air Conditioning. Floor, Roof, and Wall Coverings. Codes and Specifications.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analogue Systems. Application Engineering.

- Office of Basic Instrumentation
- Office of Weights and Measures

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering.

Radio Standards. Radio Frequencies. Microwave Frequencies. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.

NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

July 1 to December 31, 1956

Dental Research Laboratory

The dental research program at the National Bureau of Standards is carried on in cooperation with the Council on Dental Research of the American Dental Association, the Army Dental Corps, the Air Force Dental Service, the Navy Dental Corps, and the Veterans Administration.

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

A wide variety of research on materials and equipment used by dentists in civil and Federal services has been continued at the National Bureau of Standards during the half year ending December 31, 1956.

Lists of the papers published, reports issued and summaries of work in progress during the period are given below. Copies of the reports are appended.

2. REPORTS ISSUED

NBS Report 4940	Relative Reactivities of Polymerization Inhibitors.
NBS Report 4958	Some Physical Properties of Synthetic Rubber-based Dental Impression Materials.
NBS Report 5105	Some Observations on the Dimensional Accuracy of Dentures as Measured with NBS Comparator.
NBS Report 5106	Determination of Some Compressive Properties of Human Enamel and Dentin.

3. PAPERS PUBLISHED

American Dental Association Specifications for Dental Materials, 1956 Edition. George C. Paffenbarger and W. T. Sweeney. American Dental Association, Chicago, Illinois, July 1956.

Determination of Monomer Content of Polymethyl Methacrylate. Harold J. Caul, Leo A. Wall and Nicolo Acquista. JADA 53:56 July 1956.

Relationship Between Residual Monomer and Some Properties of Self-curing Dental Resins. Harold J. Caul, W. T. Sweeney and George C. Paffenbarger. JADA 53:60 July 1956.

Dental Materials and Instruments - 1951-1955. George C. Paffenbarger. Internat. Dent. J. 6:229 Sept. 1956.

Preparation of Pure Hydroxyapatite Crystals. Alvin Perloff and Aaron S. Posner. Science 48:383 Sept. 28, 1956.

Alloys of Gallium with Powdered Metals as Possible Replacement for Dental Amalgam. Denton L. Smith and Harold J. Caul. JADA 53:315 Sept. 1956.

Accelerating Effect of Amines on Polymerization of Methyl Methacrylate. G. M. Brauer, Ruth M. Davenport and William C. Hansen. Modern Plastics 34:153 Nov. 1956.

In Vitro Production of Experimental Enamel Caries. A. F. Forziati, F. L. Losee, W. W. Pigman, W. H. Jennings and M. E. Lawson, Jr. JADA 53:655 Dec. 1956.

Some Physical Properties of Gallium-Copper-Tin Alloys. Denton L. Smith, Harold J. Caul and William T. Sweeney. JADA 53:677 Dec. 1956.

4. WORK IN PROGRESS

4.1 Human Tooth Enamel and Dentin

(a) Fluorescence Studies.

The intensity of the fluorescence of powdered enamel and dentin, treated with ethylenediamine to remove organic material, increased slightly at first, and then decreased rapidly to the constant low level characteristic of the mineral residue. A similar enhancement, followed by gradual diminution, of the fluorescence intensity was observed at the leading edge of the carious process in ground sections of teeth. This observation suggests that dental caries affects the organic matrix first. This interpretation is being investigated further.

The histological investigation of the dentino-enamel junction by fluorophotographic methods has been continued.

A preliminary study to determine if interference microscopy is suitable for use in the determination of the microstructure of teeth was started. Difficulty in obtaining satisfactory images must be overcome to make this method useful.

(b) Crystallographic Studies.

The studies of non-stoichiometric apatites have been continued. X-ray diffraction data collected on single crystals of pure hydroxyapatite and pure lead apatite will be used to determine the arrangement in space of the atoms of the apatites by a three-dimensional, least squares analysis of the atomic parameters and temperature coefficients on an IBM electronic comparator.

Based on the non-stoichiometric apatite study, a cooperative program with Dr. R. C. Likins of the National Institute of Dental Research, National Institutes of Health, was carried out on the reduction of whole tooth solubility by chemical treatment. Whole rat teeth and powdered non-stoichiometric apatite were shaken in weak calcium acetate solutions. It was possible to reduce the solubility of the specimens in weak lactic acid by 60% as compared to the same samples treated in a solution of ammonium acetate alone.

It is felt that by filling the Ca defects a less soluble, more perfect apatite is formed in synthetic and biological apatites.

The hydrothermal studies on defect apatites corroborated earlier heat loss curves published by Dallemagne. This also confirms the view that his so-called "alpha tri-calcium phosphate" is just a defect apatite with a molar Ca/P of 9/6. This work is continuing.

4.2 Metals

(a) Amalgam.

Sn-Hg-Ag Structure Studies.

X-ray diffraction studies of a series of binary Sn-Hg alloys have been made for correlation with the earlier diffusion data. The results of this work indicate that the divergence of the diffusion data from that predicted from the existing diagrams is more probably due to an error in currently accepted limits of solid solubility of mercury in tin than to the appearance of the δ-phase postulated by Gayler. Confirmation should be possible by either vapor pressure or low temperature x-ray diffraction measurements. Vapor pressure test equipment is being constructed.

Amalgam Setting Time.

Work has been completed on the effect of variations in test procedure upon the determined value of setting time. The test procedure as outlined was found to be insensitive to any likely chance variations in technic. The current work on this project is directed toward changes in setting time that have been observed to occur with age. A series of nine popular commercial alloys tested to date all show a tendency to set more slowly with age. Apparently this effect is caused by a surface reaction as it is reduced by annealing in a hydrogen atmosphere. This phenomenon appears to have been involved in the unsatisfactory properties of some dental amalgam delivered to the Armed Forces in recent years. This work is being continued to define the exact mechanism involved and develop methods to prevent deterioration.

(b) Gold Foil.

A study of physical properties of dental gold foil was initiated in cooperation with the American Academy of Gold Foil Operators. A committee with Dr. Bruce Smith, Seattle, Washington, as Chairman, will prepare specimens under various dental technics for physical tests in molds designed by the National Bureau of Standards. Mechanical properties of these will be determined in the laboratory. Also the effect of surface conditions and

annealing on the cold welding of the foil, will be included in the study to ascertain the mechanism controlling the "cohesive" and "non-cohesive" properties of foil in welding into a tooth restoration.

4.3 Resins

(a) Denture Reliners.

A study of denture reliners of the type sold to the public has included ten brands. The following properties were determined, time of setting, distortion of denture base resin, crazing of denture base resin, effect of reliner on strength of base resin, evaporation of solvent, color stability and adhesion to base resin.

The tests completed indicate four types (1) the resinous type, (2) a cream type, (3) a wax, and (4) a highly volatile ester type. Adhesion to base resin varied from zero to 1500 psi after two weeks storage in water at 37°C. Chemical investigations show a wide variation in resistance to organic solvents. The reliners having greatest adhesion had the greatest adverse effects on the properties of the denture base resin, such as, crazing, strength and stiffness.

(b) Epoxy resins.

Phosphoric-acid-hardened epoxy polymers were found to be adversely affected by the presence of water during hardening so this reaction would not be clinically useful. It was found that by the addition of acrylic or methacrylic acid to the oxirane groups of the liquid epoxy resin, an intermediate is formed which appears to be an epoxy-acrylate or epoxy-methacrylate ester. This liquid can then be polymerized at room temperature by the peroxide-amine catalyst-accelerator system. Qualitative tests of synthesized batches with fillers have been made. The room temperature polymerization, the effect of water and acetone, and the degree of adhesion to smooth, "wet" dentin surfaces have been studied. These results are promising enough to warrant further study along these lines.

(c) Polymerization Reactions.

The study of the relative reactivities of polymerization inhibitors was completed. In a vacuum the rate of disappearance of diphenylpicrylhydrazyl (DPPH) in the presence of efficient inhibitors such as iodine or m- or p- nitroaniline and azo-bis-isobutyronitrile is decreased considerably as compared to the rate of disappearance in air. The kinetics of disappearance rate of DPPH becomes complex which may possibly be due to the

formation of intermediate complexes which interfere with the colorimetric determination of DPPH.

A detailed report on the relative reactivities of polymerization inhibitors is appended.

The ratio of the moles of DPPH used up per mole of benzoyl peroxide in the dimethylaniline accelerated decomposition of benzoyl peroxide in benzene was investigated in detail. The reaction does not show a clear cut stoichiometry. Approximately 2 moles of DPPH are used up per mole of peroxide initially present over a considerable DPPH concentration range.

4.4 Elastic Impression Materials

(a) Alginate Materials.

Physical properties of irreversible alginate impression materials were studied. Compressive strength was found to increase with increasing powder-liquid ratio and with age and exposure of specimens to normal room environment and to vary widely from one material to another. A stiffness test was devised in which deflection of a thin triangular membrane of alginate material was induced by the weight of hydrocal dental stone poured into the impression. Deflection of the membrane was found related to compressive strength, that is, the material having lower compressive strength showed more deflection.

A working-time test was devised in which degree of penetration of a standard cone with a 50 gram load was related to reproducibility of detail and flow. Working times for all materials were found to be reasonably close. Setting time was determined at 22°C, 60% relative humidity and 37°C and 100% relative humidity and found to vary widely with temperature for some materials and negligibly for others.

(b) Synthetic Rubber Base Materials.

A detailed report on the properties of synthetic rubber base impression materials is appended. Data contained in this report is being utilized in the development of a proposed specification for rubber base impression materials.

4.5 Panoramic X-ray Machine

The panoramic x-ray machine has been tested clinically at Lackland Air Force Base. The very favorable results obtained demonstrate the desirability of making x-ray machines of this type available at various service installations.

4.6 Color Standards

In the investigation of silicate cement colors, the color and change of color with time of thirty different commercial shades were measured with a photoelectric tristimulus color difference meter, the color differences with various powder-liquid ratios were also observed.

Several samples of each shade were pressed into uniform discs and stored in distilled water for over 60 days. Color changes during this period for most specimens were approximately 4 to 6 NBS units of color difference. Color differences between shades were shown by plotting the final equilibrium color on the ICI chromaticity diagram. Low powder-liquid ratios resulted in differences of 1/2 to 1 NBS units from specimens of standard consistency.

4.7 Zinc Oxide Materials

The physical properties of products obtained on reacting zinc oxide with o-ethoxybenzoic acid (EBA) and EBA-eugenol mixture were studied. Mixtures of ZnO and EBA result in products which appear promising as impression pastes or temporary cements. Addition of eugenol to ZnO-EBA mixes produces a decrease in setting time, water solubility and adhesion and an increase in crushing strength. Maximum crushing strength of 10,600 psi is obtained with 75% EBA, 25% eugenol. Addition of powdered quartz increases the crushing strength slightly. Other inert fillers or partial substitution of EBA by 2,4 dimethoxycinnamic acid for EBA does not improve the physical properties.

ZnO-quartz-EBA-eugenol mixtures of standard consistency use a higher powder-liquid ratio, much shorter setting time, much higher crushing strength and higher density and water solubility than ZnO-eugenol mixes.

4.8 Rotating Cutting Instruments

Development of equipment for determining the torque-speed characteristics of dental handpieces has continued. Improvements in the torque-measuring instrument have increased its capacity as required for belt-driven handpieces. Tests of a speed-measuring system employ a frequency meter and a photo electric pickup actuated by light reflected from a disk rotated by the handpiece indicated that the system is not as stable as desired. If this system cannot be improved, the use of a magnetic pickup will be investigated.

4.9 Gas Chromatography

A chromatograph (manufactured by Consolidated Electrodynamics Corporation) for analysis of organic materials by the gas chromatographic method has been obtained. This method which has just recently come into general use offers the advantages of rapid analysis of small samples. The equipment has been calibrated using known samples of water, acetone, methacrylates, styrenes and mixtures of these materials. A study of the pyrolysis products of polymers has been started. The characteristic peaks of methylmethacrylate and styrene have been obtained in trial runs on Plexiglass and the denture resin, Jectron, respectively.

4.10 Evaluation of Materials

Materials evaluated for the Federal dental services and the American Dental Association by specification and special test methods included amalgam, denture base resin, inlay casting gold, inlay casting investment and inlay casting wax.

For the Director
by
W. T. Sweeney

W. T. Sweeney, Chief
Dental Research Section

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

RELATIVE REACTIVITIES OF POLYMERIZATION INHIBITORS

by

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This work is a part of the dental research program conducted at the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association, the Army Dental Corps, the Air Force Dental Service, the Navy Dental Corps and the Veterans Administration.

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NATIONAL BUREAU OF STANDARDS

RELATIVE REACTIVITIES OF POLYMERIZATION INHIBITORS

Abstract

The relative reactivity of typical inhibitors was investigated. The procedure is based on the competitive reaction of these inhibitors or their decomposition products and diphenylpicrylhydrazyl (DPPH) for cyanopropyl radicals. The rate of formation of cyanopropyl radicals from azo-bis-isobutyronitrile can be followed colorimetrically by determining the rate of disappearance of DPPH. The apparent zero order DPPH disappearance rate will (1) decrease (2) remain unchanged (3) increase depending on the preferential reactivity of any added inhibitor or DPPH for cyanopropyl radicals.

Inhibitors containing active hydrogen react directly with DPPH. Quinones, nitroaromatic compounds, sulfur, and many other inhibitors appear to be ineffective in the competitive reaction with DPPH for cyanopropyl radicals. Iodine and m and p-nitroaniline are effective free radical scavengers.

The rate of disappearance of DPPH is decreased considerably in the absence of air. This retardation may be caused by a change in stoichiometry of the reaction between DPPH and cyanopropyl radicals.

The kinetics of the rate of disappearance of DPPH in the presence of efficient inhibitors and the absence of air become complex.

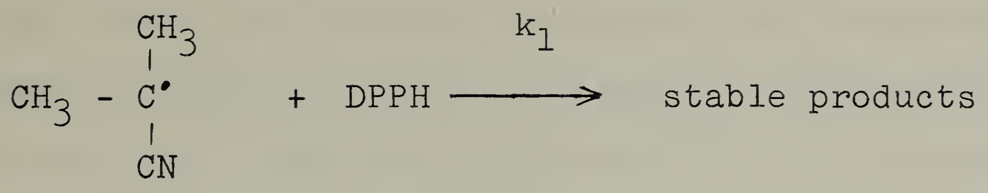
1. INTRODUCTION

The stable-free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) is a very active interceptor of radical chains [1-16] and hence, an effective inhibitor for addition polymerization Since few studies have dealt with the relative efficiency of typical inhibitors [17-21], it appeared of interest to compare the reactivity towards cyanopropyl radicals of a number of commonly used inhibitors with that of DPPH.

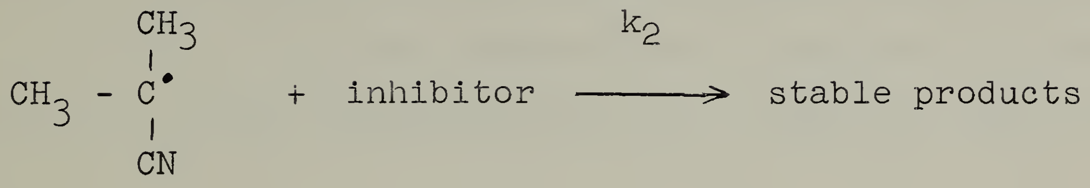
The free radicals were generated by the thermal decomposition of 2,2-azo-bis-isobutyronitrile (AIBN).

$$\text{AIBN} \xrightarrow{k_I} 2\ (CH_3)_2\ C^{\bullet}CN + N_2 \qquad (1)$$

This initiator was chosen since it decomposes unimolecularly and the reaction is not complicated by radical-induced decomposition. The rate of free radical formation is nearly independent of the initial AIBN concentration and the solvent used. Furthermore, the reaction of isopropyl radicals with inhibitors is of special interest since these radicals are structurally somewhat related to chain radicals involved in the methyl methacrylate polymerization. Measurements of the relative reactivities with free radicals were based on the competition of inhibitor and DPPH for cyanopropyl radicals.



$$\mathrm{CH_3-\underset{CN}{\underset{|}{\overset{CH_3}{\overset{|}{C^{\bullet}}}}}} + \mathrm{DPPH} \xrightarrow{k_1} \text{stable products} \qquad (2)$$



$$\mathrm{CH_3-\underset{CN}{\underset{|}{\overset{CH_3}{\overset{|}{C^{\bullet}}}}}} + \text{inhibitor} \xrightarrow{k_2} \text{stable products} \qquad (3)$$

$$\mathrm{DPPH} + \text{inhibitor} \xrightarrow{k_3} \text{stable products} \qquad (4)$$

The magnitude of the rate constants, k_1 and k_2, depends on the ease with which DPPH and the respective inhibitors act as scavengers for the cyanopropyl radicals.

The rate of disappearance of DPPH can be determined colorimetrically [2, 8, 14, 15]. If the inhibitor reacts preferentially with cyanopropyl radicals, that is k_2 is large compared to k_1, the rate of disappearance of DPPH will decrease. If k_1 is large, addition of inhibitor will not alter the disappearance rate. If the reaction between DPPH and inhibitor [4] is predominant, the apparent DPPH disappearance rate will increase. In this case it is not possible to determine the reactivity of the inhibitor towards the free radicals.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Azo-bis- isobutyronitrile after two recrystallizations from benzene had a melting point of 104°C.

The method of Goldschmitt and Renn [22] was used to synthesize 2,2-diphenyl-1-picryl hydrazyl. A later batch was synthesized by a modified procedure [23]. Its melting point was 136°C. A benzene solution showed maximum absorption at 5240 Å. Benzene solutions obeyed Beer's law over the DPPH concentration range investigated (1.777×10^{-6} to 3.554×10^{-4} M/ℓ).

Tetraphenylhydrazin was prepared according to the procedure given by Gattermann [24] (M.P. = 142°C).

The 2,6-ditertiarybutyl-4-methylphenol was obtained from the Shell Chemical Co.

Monoclinic sulfur was obtained by melting sulfur at 130°C, cooling slowly to 110°C and removing the liquid portion.

Diisopropylthiourea, 1,3-diethylthiourea and ethylenethiourea were obtained from Sharples Chemical Division of the Pennsylvania Manufacturing Co.

All other inhibitors were Fisher Scientific or Eastman reagent grade.

Nitrobenzene, methyl methacrylate and styrene were fractionated before use.

Benzene was dried over calcium chloride.

2.2 Procedures

2.2.1 In Air

Benzene solutions containing a predetermined amount of AIBN, DPPH and inhibitor were prepared. Two minutes after

addition of DPPH to the solution containing the other reactants, the DPPH concentration was determined by optical density measurements of a portion of the solution. The remaining solution was kept in a water bath at 45.00 ± 0.01°C. At various time intervals, until the DPPH concentration had reached half its original value, the optical density of samples of the solution was measured by means of a Beckman DU spectrophotometer. Most experiments were made in duplicate. Measurements of the decomposition of DPPH in the presence of AIBN and the absence of other inhibitors were made with each series of runs.

The AIBN concentration was kept in large excess to that of DPPH and inhibitor so that it might be regarded as constant during the experiment. In most runs the solutions contained 4.268×10^{-3} M/ℓ AIBN, 1.777×10^{-4} M/ℓ DPPH and 0.07 g/ℓ or 0.07 mℓ/ℓ inhibitor. Preliminary experiments showed that accurate measurements of the decomposition rate could be conducted within reasonable time at 45°C. A solution of DPPH in benzene showed less than 1% decomposition after 20 hours at this temperature.

The DPPH decomposition proceeds through an intermediate compound. The final products and the intermediate show considerable absorption at 5200 Å. Therefore, the optical density measurements were conducted at 6700 Å. At this wave length the hydrazyl still absorbs considerably. Any absorption due to the reaction products is negligible as evidenced by measure-

ments of the optical density of the solutions after 24 hours reaction time.

The absorption of inhibitor-AIBN solution at 6700 Å was also determined. Only negligible optical density values were obtained with the inhibitors reported in this study. The rate of disappearance of DPPH in solutions containing inhibitor only was also investigated for a series of inhibitors. Those inhibitors which fail to alter appreciably the system when AIBN is present or which compete effectively with DPPH for cyanopropyl radicals usually produce negligible discoloration of the DPPH solution.

2.2.2 In Vacuum

Benzene solutions containing AIBN were pipetted into flask A, Figure 1. Small glass boats containing weighed amounts of inhibitor and DPPH were placed into the side arm which was then connected to a vacuum pump. The absorption cell B was connected to the flask through the glass joint C. All joints and stopcocks were previously lubricated with high vacuum silicone grease. The flask was placed into a trichloroethylene-dry ice bath for 15 minutes before the vacuum pump was turned on. It was evacuated for at least 20 minutes, stopcock D was then closed and the benzene solution was allowed to warm up to room temperature. The flask was again immersed in a dry-ice bath. After 15 minutes the stopcock D was opened and the evacuation was

repeated for 20 minutes. The stopcock D was then closed and the vessel was immersed in hot water. After the benzene solution had melted, the flask was tilted carefully so that the boat with the inhibitor fell into the solution, and the contents were shaken until the inhibitor had completely dissolved. The flask was tilted again allowing the DPPH containing boat to enter the solution and was shaken vigorously. The container was then tilted allowing the solution to fill most of the absorption cell. Stopcock E was closed and stopcock D opened. The absorption cell was then removed and placed in a Beckman spectrophotometer which was equipped with a dual thermospacer set supplied by the manufacturer and an insulated Plexiglass housing of 16.5 cm. length, 11.5 cm. height and 10.0 cm. width. Water from a thermostated bath was circulated through coils in the thermospacer set and through copper coils in the housing. The temperature in the absorption cell compartment was maintained at 45.0 ± 0.2°C.

This procedure was slightly modified in measurements of the inhibiting efficiency of iodine to avoid any loss due to sublimation. Since iodine does not react with AIBN the initial solution contained both AIBN and this inhibitor.

Flushing oxygen-free nitrogen through the reaction vessel before evacuation did not prove to be desirable since non-reproducible DPPH disappearance rates were obtained. The cause for this erratic behavior is not known. All runs in vacuum

were made in duplicate or until reproducible results were obtained.

3. RESULTS AND DISCUSSION

3.1 In Air

A plot of the residual DPPH concentration versus time gives a straight line in the presence of most inhibitors indicating that the DPPH disappears at a zero order rate (Figure 2). This zero order kinetics applies for the range of DPPH concentrations investigated (0.89×10^{-4} to 3.55×10^{-4} M/ℓ) which is shown in Table 1. Measurements of the DPPH disappearance rate at varying initial AIBN concentrations confirm Bawn's [2] results that AIBN dissociates by true first-order kinetics. Neglecting those cyanopropyl radicals which recombine or disproportionate before escaping the solvent cage, the rate of disappearance of DPPH in the absence of other inhibitors is:

$$- d\,(\mathrm{DPPH})/\,dt = 2\,k_I\,(\mathrm{AIBN}) \tag{5}$$

Using the average value of the rate of disappearance of DPPH of 15 "blank" runs the value of k_I at 45.0°C was found to be 5.09×10^{-3} hrs^{-1} with a standard deviation of 0.14 hrs^{-1}. This compares with a value of 4.05×10^{-3} hrs^{-1} reported by Bawn [2] at a temperature of 45.2°C. This difference in the rate constant may be due to the fact that the previous investigators followed the reaction until the complete disappearance of the DPPH, whereas the present results are based on measurements extending over the 100 to 50% residual DPPH range only.

~~the 100 to 50% residual DPPH range only.~~

The effect of addition of inhibitors on the apparent DPPH disappearance is given in Tables 2-5. The apparent half time decomposition of the DPPH was determined from the straight lines of the DPPH concentration versus time curves. The half time disappearance of DPPH in the presence of AIBN alone amounts to 123 minutes (coefficient of variation 3.5 min.). Values of $\frac{\Delta \text{DPPH}}{\Delta t}$ were calculated from the half time decomposition. Tables 2 and 3 list those inhibitors which react directly with DPPH, that is, $k_3 \gg k_2$. In the presence of inhibitors reacting rapidly with DPPH the linear relationship between residual DPPH concentration and reaction time does not hold exactly. $\frac{\Delta \text{DPPH}}{\Delta t}$ values were obtained from the straight line representing most closely the experimental data and are only approximate for these inhibitors. Deviations from the linear behavior should be expected since the rate of disappearance under these conditions is:

$$- d(\text{DPPH})/dt = 2\, k_I\, (\text{AIBN}) + k_3\, (\text{DPPH})^x\, (\text{inhibitor})^y \quad (6)$$

The exponents x and y were determined for the reaction between phenol and DPPH. Using an excess of phenol (approximately 8 moles per mole of DPPH) DPPH disappears by second order kinetics as indicated by the linear relationship of time versus the reciprocal DPPH concentration (Figure 3). From the slope of the plot of the logarithm of the initial rate of disappearance of DPPH versus the logarithm of the phenol concentration a value of $y = 1$ is obtained, Hence,

$$- d\,(\text{DPPH})/dt = k_3\, (\text{DPPH})^2\, (\text{phenol}) \quad (7)$$

Third order kinetics have been observed for the dehydrogenation reaction of 1,2 and 1,4-dihydronaphthalene, 9,10-dihydroanthracene and hydroquinone with DPPH [25]. The same order kinetics probably apply to inhibitors which react directly with DPPH.

Calculation of k_3 for the reaction of 1.488×10^{-3} M/ℓ phenol with 1.777×10^{-4} M/ℓ DPPH gives a value of 3.50×10^{4} min^{-1} $(\text{M}/\ell)^{-2}$. The difference in the DPPH disappearance rates of solutions containing inhibitor, AIBN and DPPH and those containing AIBN and DPPH only can also be used to determine k_3. However, this difference is usually too small to obtain an accurate value for k_3.

The strong hydrogen acceptor properties of DPPH are indicated by the instantaneous reaction with aromatic inhibitors such as catechol, hydroquinone or pyrogallol containing two or more phenolic groups.

DPPH also abstracts hydrogen somewhat slower from 2,4-dinitrophenylhydrazine, 2,6-ditertiarybutyl-4-methylphenol, phenol, and substituted nitroaromatic compounds such as o-nitrobenzoic acid, picric acid and o-bromonitrobenzene. Substituted thioureas such as ethylene-, 1,3-diethyl- and diisopropylthiourea show a similar behavior. An exception is 1,3-dibutylthiourea which due to steric effects of the larger substituents does not decrease the apparent DPPH decomposition

rate. Maleic anhydride which is an inhibitor for some vinyl polymerizations also reacts slowly with DPPH.

Typical inhibitors which do not effect the hydrazyl disappearance are shown in Table 4. In the competitive reaction with DPPH for cyanopropyl radicals these inhibitors are apparently ineffective, that is, $k_1 > k_2$, $k_1 \gg k_3$[1]. The half time (123 min.) and $\Delta DPPH/\Delta t$ values (0.723×10^{-6} M/ℓ min.$^{-1}$) for the DPPH disappearance are not altered within the limits of experimental errors. This group includes chloranil and p-quinone. Other quinones of lower redox potential were not investigated since according to Aparicio and Waters [21] their reactivity towards cyanopropyl radicals decreases in the approximate order of their potentials with quinones of redox potential below + 0.45 volts undergoing no apparent reaction. Nitroaromatic compounds and sulfur which are considered good polymerization retarders [26] do not change the half time disappearance of DPPH. Similar results are obtained with triphenylmethyl chloride, trans stilbene, methyl methacrylate, and styrene.

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[1] It is conceivable, however, that the cyanopropyl radical reacts with certain inhibitors, especially those containing carbon to carbon double bonds with the formation of unstable compounds which in turn react with DPPH. Hence, the apparent rate of disappearance of DPPH may not be altered.

In the presence of a small number of inhibitors an increase in the half time disappearance of DPPH is obtained (Table 5). These inhibitors react directly with cyanopropyl radicals and k_2 is appreciable compared to k_1. The rate of disappearance of DPPH and inhibitor is governed by the following equation:

$$- (dDPPH/dt + dIn/dt) = 2\ k_I\ (AIBN) \qquad (8)$$

Most inhibitors in this group do not react appreciably with DPPH; i.e. k_3 is very small. Values of $-\Delta In/\Delta t$ and the ratio of $\Delta In/\Delta t$ to $\Delta DPPH/\Delta t$ were calculated and are given in Table 5. Calculations are based on the assumption that the AIBN concentration remains constant. (Actually about 5% AIBN has been consumed when 50% of the DPPH has decomposed).

Inhibitors which produce a slight decrease in the apparent DPPH decomposition rate include tetraphenylhydrazine (which in solution decomposes into diphenyl nitrogen) and o-nitroaniline. The isomeric m-and p-nitroanilines as well as 2,4-dinitroaniline slow down the DPPH disappearance considerably. By far the most effective inhibitor is iodine. In the presence of 0.007% iodine the apparent half time decomposition increases to 205 min. and the ratio $\frac{\Delta In}{\Delta t} \Big/ \frac{\Delta DPPH}{\Delta t}$ is 0.666. This effect is not surprising considering Bartlett and Kwart's [1] observation of the strong inhibiting effect of iodine in the peroxide-induced polymerization of vinyl acetate. These authors attribute the inhibiting effect to $I_3^{\bullet}$ radicals possessing a high degree of

reactivity towards other free radicals. These $I_3^{\bullet}$ radicals are in equilibrium with diatomic iodine:

$$3I_2 \rightleftharpoons 2\ I_3^{\bullet} \qquad (9)$$

Hammond, Sen, and Boozer [15] have reported that the rate of AIBN decomposition is not affected by the presence of iodine.

Aniline, methylaniline and diphenylamine also slow down the DPPH disappearance. Reaction kinetics in the presence of these compounds appear to be more complex than with other compounds investigated. In Figure 4 the DPPH disappearance curves for aniline derivatives are given. The curves are corrected for the considerable effect of the materials on the DPPH decomposition at 45°C. It is conceivable that these inhibitors attack the unstable dimethylketenecyanoisopropylimino intermediate which according to Erben and Bywater [27] is formed during the decomposition of AIBN. This reaction would cause an appreciable deviation from the first order kinetics. In the presence of dimethylaniline the apparent DPPH decomposition rate is much faster. It appears that the presence of an NH group is necessary for the reduced DPPH disappearance.

3.2 In A Vacuum

Results of studies of inhibitor efficiencies in a vacuum are given in Figure 5. In the presence of AIBN alone (Figure 5, Curve A) the rate of disappearance of DPPH is greatly reduced

but still follows zero order kinetics. The half time disappearance is increased from 123 to 332 min. It has been shown previously that the rate of decomposition of AIBN and the final reaction products are not altered appreciably in the presence of air [28, 29]. This retardation may therefore be caused by a change in stoichiometry of the reaction between DPPH and cyanopropyl radicals.

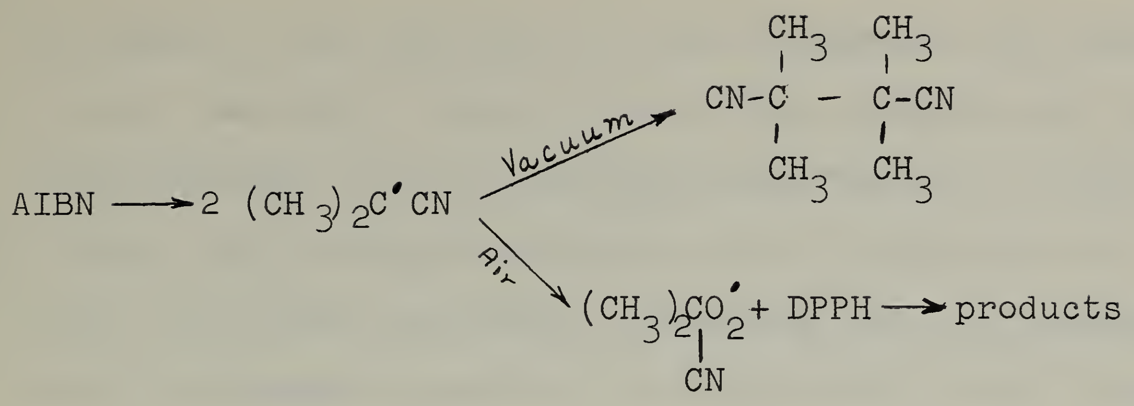
The concentration of DPPH is extremely small and presence of traces of oxygen can readily change the course of this reaction as evidenced by the marked increase in the DPPH disappearance rate. Bawn and Mellish did not find any change in the rate of disappearance of DPPH in the presence of nitrogen and oxygen [2]. The present investigation suggests the possibility that in their measurements in a nitrogen atmosphere air was not completely removed.

It has been suggested [15] that in the absence of oxygen a partial regeneration of DPPH may take place:

$$(CH_3)_2C^{\bullet}CN + DPPH \longrightarrow CH_2 = C(CH_3)CN + H\text{-}DPPH \qquad (10)$$

$$H\text{-}DPPH + (CH_3)_2C^{\bullet}CN \longrightarrow (CH_3)_2CHCN + DPPH \qquad (11)$$

Bevington [28] showed that tetramethylsuccinodinitrile is formed during the decomposition of AIBN in benzene in the absence of air even in the presence of fairly high concentrations of hydrazyl. In air cyanopropyl radicals react to form a peroxide radical which subsequently reacts with DPPH.



$$AIBN \longrightarrow 2\,(CH_3)_2\dot{C}CN \xrightarrow{\text{Vacuum}} CN-\underset{CH_3}{\overset{CH_3}{C}} - \underset{CH_3}{\overset{CH_3}{C}}-CN \qquad (12)$$

$$2\,(CH_3)_2\dot{C}CN \xrightarrow{\text{Air}} (CH_3)_2\underset{CN}{C}O_2^{\bullet} + DPPH \longrightarrow \text{products} \qquad (13)$$

Reaction (13) competes with the direct interaction of cyanopropyl radicals.

Since DPPH does not react with those radicals that recombine with their original partners a low apparent rate of DPPH disappearance in vacuum should be expected.

The DPPH disappearance in the presence of m and p-nitroaniline as well as iodine is decreased considerably and is smaller than the AIBN-DPPH "blank" (Figure 5). With the nitroanilines the kinetics are complicated. The DPPH initially decomposes very rapidly, then follows zero order kinetics over a short range, and again shows an increased rate. With iodine approximately zero order kinetics to 55% residual DPPH are observed. These kinetics may be indicative of the formation of intermediate complexes which interfere with the colorimetric determination of DPPH.

4 SUMMARY

1. The relative reactivity of typical inhibitors with respect to 2,2-diphenyl-1-picryl hydrazyl (DPPH) were investigated

by means of the reaction of these compounds with cyanopropyl radicals. These radicals were generated by the decomposition of 2,2'-azo-bis-isobutyronitrile (AIBN).

2. Iodine and m and p-nitroaniline were found to be the most efficient inhibitors. Compounds such as quinones and nitrobenzene appear to be ineffective in the competitive reaction with DPPH for cyanopropyl radicals. Inhibitors containing active hydrogen react directly with DPPH.
3. The apparent decomposition rate of DPPH is decreased considerably when the AIBN decomposition is conducted in a vacuum. This retardation may be caused by a change in the stoichiometry of the reaction between DPPH and cyanopropyl radicals. The kinetics of the rate of disappearance of DPPH in the presence of efficient inhibitors and the absence of air becomes complex.

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Table 1

Rate of Decomposition of DPPH

AIBN Conc: 4.27×10^{-3} M/l T = 45°C

DPPH Conc. M/l	Half-time DPPH min.	$-\frac{\Delta DPPH}{\Delta t}$ (M/l)min^{-1}
0.89×10^{-4}	67	6.7×10^{-7}
1.78	123	7.2
3.55	251	7.1

Table 2

Inhibitor reacts directly with DPPH

$k_3 \gg k_1$ $k_3 \gg k_2$

T = 45°C DPPH conc: 1.78×10^{-4} M/l

AIBN conc: 4.27×10^{-3} M/l Inhibitor conc: 0.007%

Inhibitor	Half-time DPPH
pyrocatechol	instantaneous[a]
t-butylcatechol	instantaneous
hydroquinone	instantaneous
pyrogallol	instantaneous
p-phenylenediamine	instantaneous
phenothiazine	instantaneous
benzidine	- - - - - - [b]

[a]: half-time less than 1 minute

[b]: colored products interfere with the measurement of the DPPH concentration.

Table 3

Inhibitor reacts directly with DPPH

$k_3 > k_1$ $k_3 > k_2$

Inhibitor	Half-time DPPH min.	$-\frac{\Delta \mathrm{DPPH}}{\Delta t}$ (M/l) min^{-1}	
2,4-dinitrophenylhydrazine	14	64	x10^{-7}
gum guriac	27	33	
resorcinol	32	28	
2,6-ditertiarybutyl-4-methylphenol	45	20	
ethylenethiourea	90	9.87	
diisopropylthiourea	91	9.76	
1,3-diethylthiourea	92	9.66	
phenol	97	9.15	
picric acid	104	8.54	
o-nitrobenzoic acid	106	8.38	
maleic anhydride	108	8.23	
o-bromonitrobenzene	114	7.79	
triphenylmethane	115	7.73	

Table 4

Inhibitors Less Efficient than DPPH

(Cyanopropyl radicals react preferentially with DPPH)

$k_1 > k_2$	$k_1 \gg k_3$
Half-time (DPPH) = 123 ± 5 min.	
p-quinone	methyl methacrylate (0.01%)
chloranil	*l*-ascorbic acid
nitrobenzene	dimethyl-1-naphthylamine
trinitrobenzene	sulfur
triphenylmethyl chloride	1,3-dibutylthiourea
trans stilbene (0.5%)	diethyldithiocarbamic acid, sodium salt
styrene (0.01%)	

Table 5

Cyanopropyl Radical reacts with DPPH and Inhibitor

$k_1 > k_3$ $k_2 > k_3$

Inhibitor	Half-time DPPH min.	$-\frac{\Delta DPPH}{\Delta t}$ $(M/l)min^{-1}$	$-\frac{\Delta In}{\Delta t}$ $(M/l)min^{-1}$	$\frac{\Delta In}{\Delta t} / \frac{\Delta DPPH}{\Delta t}$
tetraphenylhydrazine	136	6.54×10^{-7}	0.69×10^{-7}	0.106
o-nitroaniline	129	6.89	0.34	0.049
m-nitroaniline	153	5.81	1.42	0.244
p-nitroaniline	152	5.85	1.38	0.236
2,4-dinitroaniline	152	5.85	1.38	0.236
iodine	205	4.34	2.89	0.666

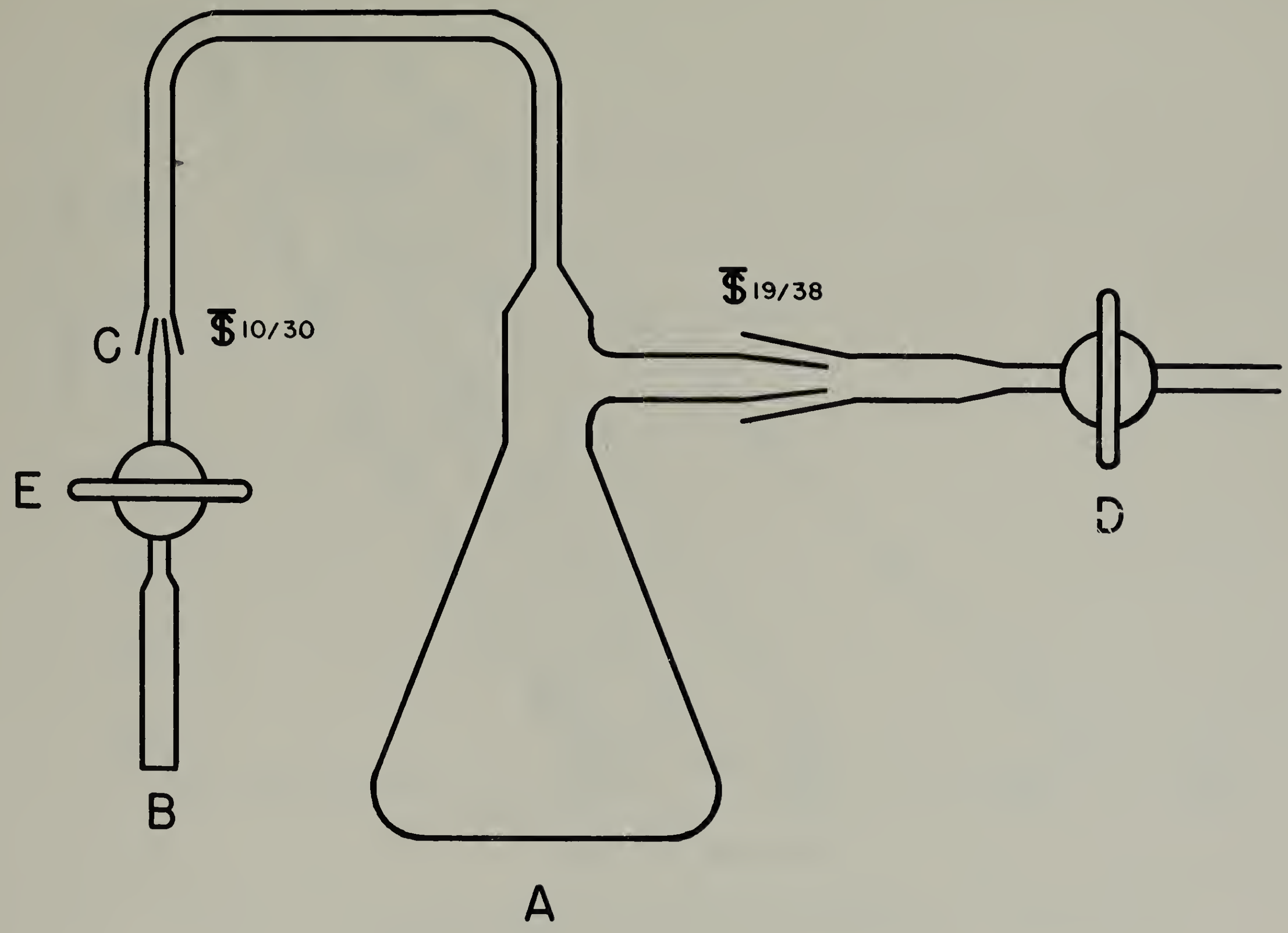

Figure 1. Apparatus for measuring disappearance of DPPH in a vacuum.

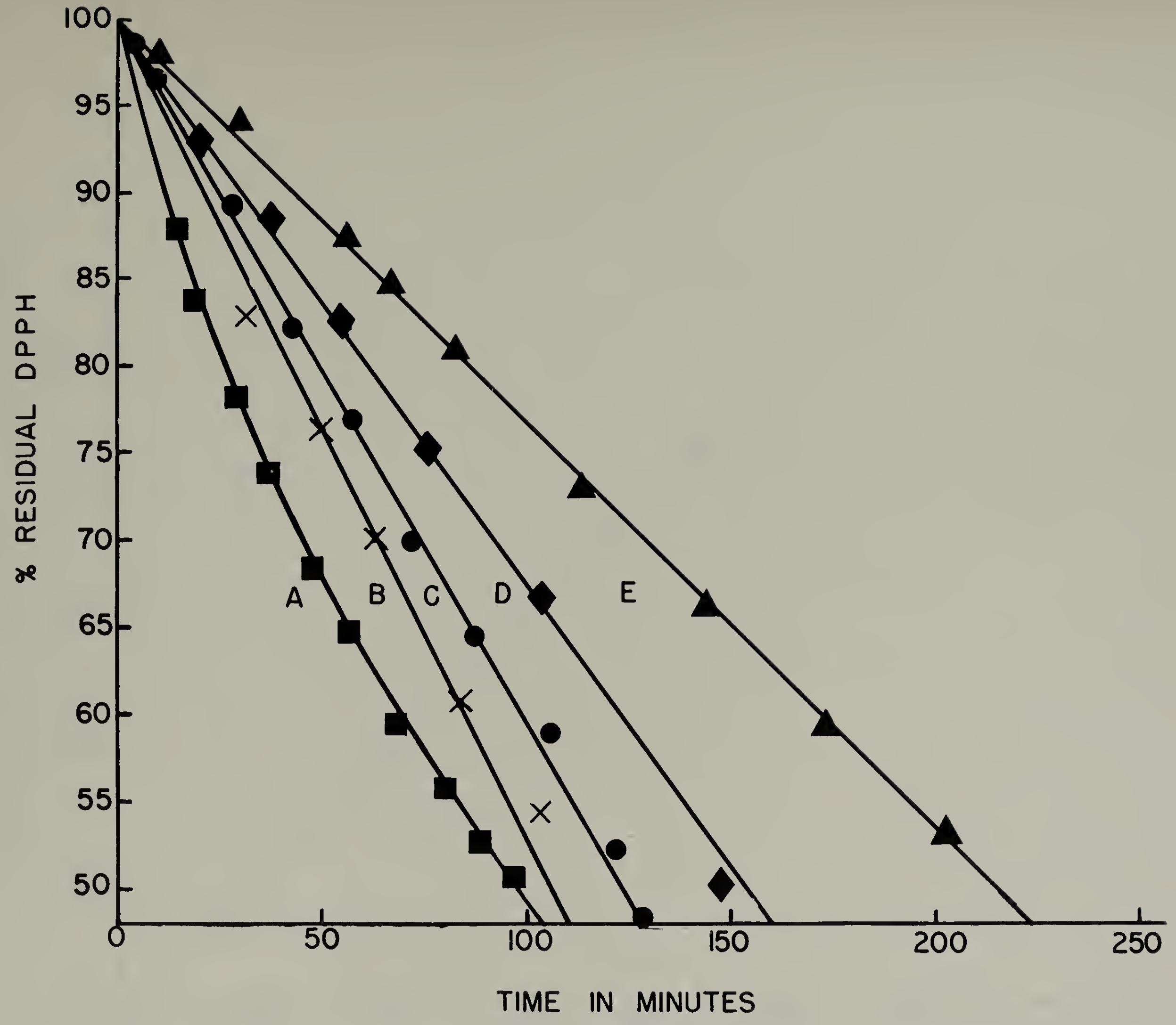

Figure 2. Decomposition of DPPH in the presence of AIBN and inhibitors.
DPPH conc: 1.78×10^{-4} M/l.
Inhibitor conc: 0.007%.
AIBN conc: 4.27×10^{-3} M/l.

Added inhibitor:
A. Phenol.
B. *o*-Nitrobenzoic acid.
C. None.
D. *p*-Nitroaniline.
E. Iodine.

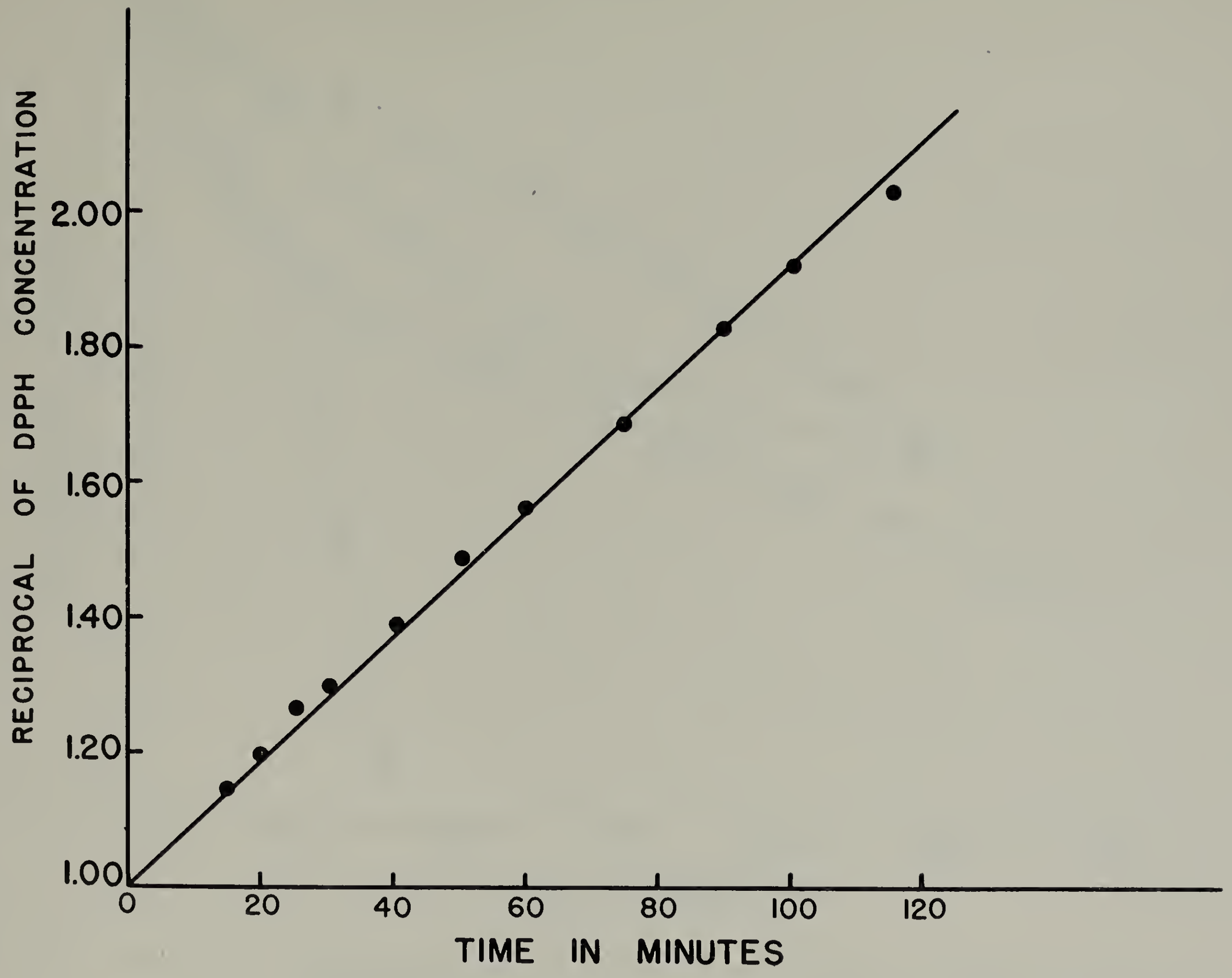

Figure 3. Disappearance of DPPH in the presence of phenol.
DPPH conc: 1.78×10^{-4} M/l.
Phenol conc: 1.49×10^{-3} M/l.

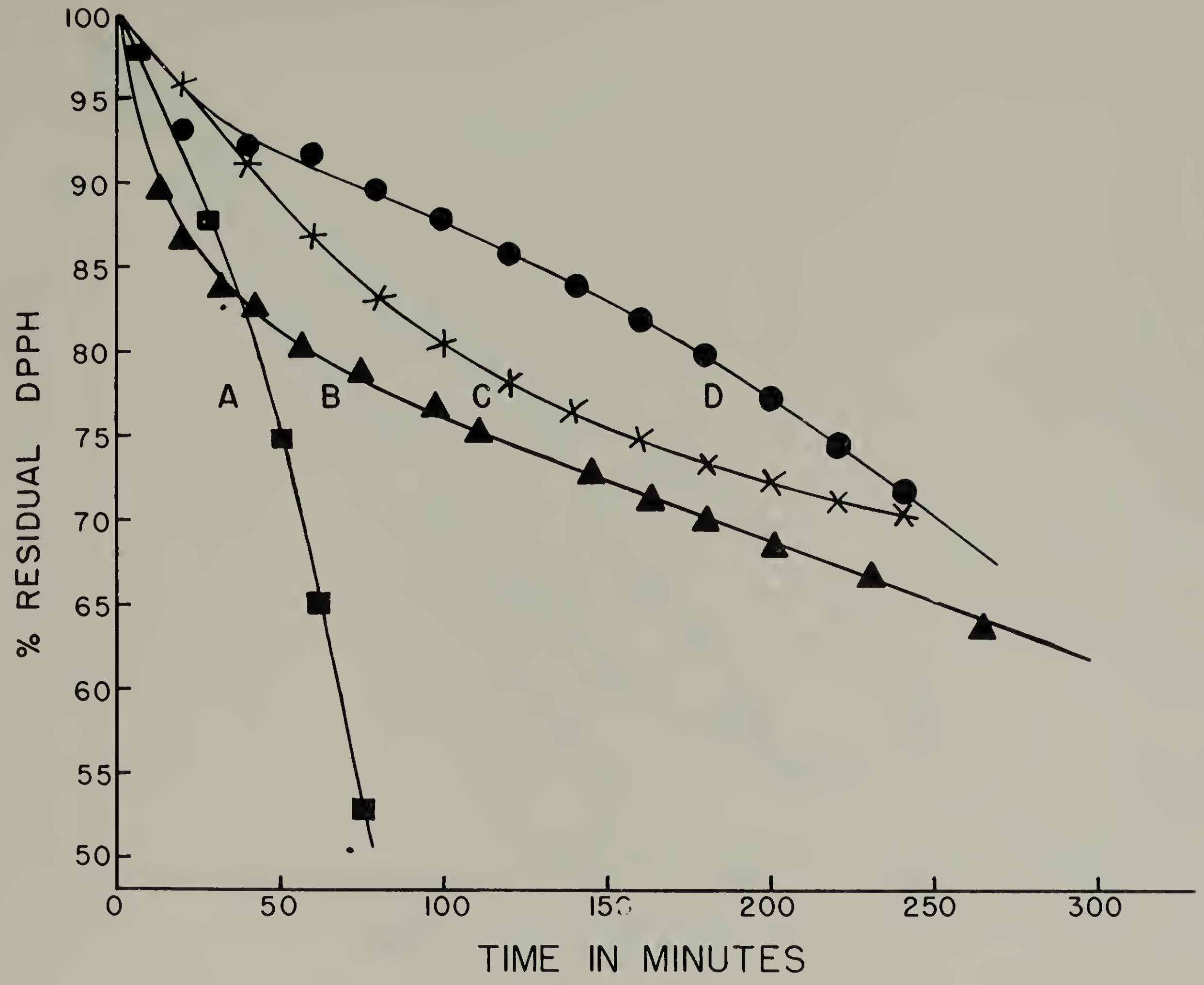

Figure 4. Decomposition of DPPH in the presence of AIBN and aniline derivatives.

A. Dimethylaniline.
B. Diphenylamine.
C. Aniline.
D. Methylaniline.

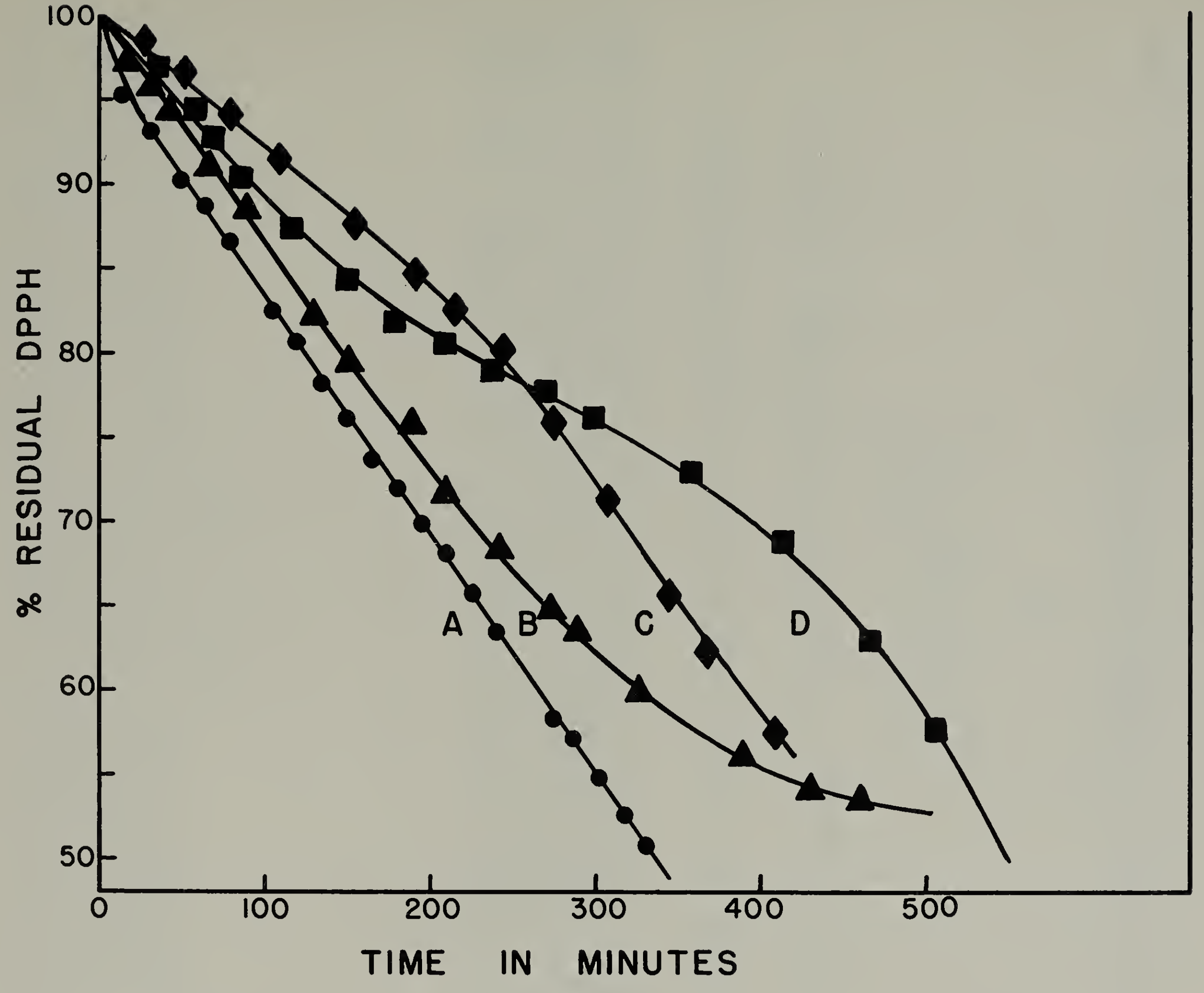

Figure 5. Disappearance of DPPH in a Vacuum.

Added inhibiter.
  A. None.
  B. Iodine.
  C. m-Nitroaniline.
  D. p-Nitroaniline.

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

SOME PHYSICAL PROPERTIES OF SYNTHETIC RUBBER-BASED DENTAL IMPRESSION MATERIALS

by

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NBS

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

SOME PHYSICAL PROPERTIES OF SYNTHETIC RUBBER-BASED DENTAL IMPRESSION MATERIALS

Abstract

The physical properties of rubber base impression materials (ten brands of the Thiokol type and one brand of the silicone type) were investigated. Setting time ranged from 9 to 30 minutes at 22°C and from 4 to 9 minutes at 37°C. Temperature rise above 22°C during cure of 1.5 cc of material ranged from 3.0°C to 5.2°C. At one hour all materials complied with the requirement for strain in compression, but only seven materials complied with the requirement for set after compression of ADA Specification No. 11. Some materials reached the required one hour values for strain and set in 5 or 10 minutes at 37°C. Flow under a load of 80 gm/cm^2 for one hour ranged from 0.2 to 5.9%. The Thiokol materials shrank 0.2% or less, linearly, in 24 hours. The silicone material shrank approximately 0.5% in 24 hours. The Thiokol materials were compatible with six gypsum materials tested. The silicone material was compatible with only one of these. All materials displayed surface depression after standing for a few hours.

1. INTRODUCTION

In recent years new elastic materials for dental impressions have appeared on the market. They are basically synthetic rubbers, either of the Thiokol type or silicone type. In both types the base material is supplied in a collapsible metal tube, with the accelerator for the Thiokol also being supplied in a tube and the accelerator for the silicone being supplied in a polyethylene dropping bottle. The material is prepared by spatulating the component parts together for 30 seconds to 2 minutes depending upon the manufacturer's directions.

An analysis of one brand of Thiokol base material has been reported by S. L. Pearson [1] to show the following composition

	%
BASE	
Polysulfide rubber	79.72
Zinc oxide	4.89
Calcium sulfate	15.39
ACCELERATOR	
Lead peroxide	77.65
Sulfur	3.52
Castor oil	16.84
Other	1.99

The chemical reaction that occurs when the Thiokol base material and accelerator are mixed has been extensively studied [2, 3, 4, 5]. A metallic peroxide in the accelerator reacts with the polysulfide rubber to form an intermediate compound, and water. The sulfur in the accelerator then reacts with the intermediate compound to form the end product and the

metal's sulfide as shown below

$$2HS - (RSS)_{23}R - SH + PbO_2 \longrightarrow [-S(RSS)_{23}\ RS\ -]_2Pb + 2H_2O$$

$$[-S(RSS)_{23}\ RS]_2\ Pb + S \longrightarrow -S(RSS)_{23}RSSR(SSR)_{23}S- +PbS$$

$$\text{Where}\quad R = C_2H_4-\ O\ CH_2-O-C_2H_4$$

An analysis of the silicone material is not yet available in the literature. The silicone material before vulcanization may be a linear polymer of the form

$$\left[-OSi(CH_3)_2-\right]_x$$

although phenyl and other groups may be present in preference to the methyl groups above. Vulcanization is promoted by free radicals formed from benzoyl peroxide or some similar catalyst [6]. A text on the technology of silicones by R. R. McGregor [6] gives information on the theory and application of these materials.

2. MATERIALS INVESTIGATED

At the time this work was begun, ten brands of the Thiokol type were available. Somewhat later, one brand of the silicone type became available. All of these materials were included in the study and are listed by brand name, batch number when available and manufacturer in Table 1.

3. EXPERIMENTAL PROCEDURE AND RESULTS

3.1 General Procedure

Unless otherwise specified the materials were mixed according to the manufacturer's directions and tested at a room temp-

erature of 22 ± 1°C (71.6 ± 1.8°F) and a relative humidity of 53 ± 7%. When tests were run under simulated mouth conditions, the specimens were tested while immersed in water at 37 ± 1°C (98.6 ± 1.8°F). Except where noted all tests were done in triplicate and the data and curves given are the averages of the data taken on three specimens.

3.2 Setting Time

Setting time was determined by the use of a penetrometer with 1 mm diameter flat ended needle under a 100 gm load. Specimens of uniform thickness were made by placing the impression material in holes 5 mm in diameter in a 5 cm by 6 cm brass plate 8.1 ± 0.1 mm thick. Only one penetration was made in each hole. The depth of the penetration was determined to within 0.001 in. by means of a dial gage.

Tests were made at both room temperature and mouth temperature. All tests were made under water to minimize the adhesion of the uncured and partially cured material to the penetrometer needle. The material was placed under water two minutes after the beginning of the mix. At 30 second intervals the needle was placed on the surface of the material and released. At the end of 10 seconds a reading of the dial gage in thousandths of an inch was recorded. When the depth of penetration was essentially constant for three or more readings the measurements were discontinued. Figure 1 shows representative curves for the depth of penetration versus time from the start of mix for two different brands of the Thiokol type of material at both

37°C (98.6°F) and 22°C (71.6°F). The first two curves show the abrupt change in the rate of cure exhibited by some materials and the more gradual change characteristic of other materials. The second two curves show that lower temperatures result in a more gradual change in curing rate for both brands of the Thiokol material even though one remains noticeably more abrupt. A gradual change in the rate of cure makes the determination of a definite setting time for a material difficult.

To arrive at a definite setting time which would not include the long period of very slow curing at the top of the curves and to minimize the effect of slight variations in the surface level of the specimen, 0.010 in. was arbitrarily added to the final penetration value. The time at which the penetration was 0.010 in. greater than the final penetration was called the setting time. Average setting times determined by this method are shown in Table 2. Variations in setting time between different brands at the same temperature and in the same brand at different temperatures are evidenced. At 22°C the values for material 3 had a range of 11.5 minutes. The maximum range for the other materials was 4 minutes. At 37°C the maximum range was 2 minutes.

3.3 Temperature Rise on Setting

Using a recording potentiometer with a four junction iron-constantan thermopile, the temperature rise above 22°C during the curing of 1.5 cc of one specimen from each material with the exception of material 11

was determined. The temperature rise of material 11 was determined using a portable potentiometer with a single iron-constantan thermocouple. It was found that the peak of the temperature rise occurred before the materials reached their clinical set. For all of the materials the temperature rise was between 3.0°C (5.4°F) and 5.2°C (9.4°F) (Table 2).

3.4 Strain and Set

Strain and set were determined by the procedure described in American Dental Association Specification No. 11 for Hydrocolloidal Impression Materials, Agar Type. According to this specification procedure the specimens are subjected to stresses of 100 gm/cm^2, 1000 gm/cm^2, 0 gm/cm^2 and 100 gm/cm^2 in that order, with each load on the specimen for approximately one minute. The strain is calculated from the difference in the length of the specimen under the initial 100 gm/cm^2 stress and the 1000 gm/cm^2 stress. The set is calculated from the difference in the length of the specimen under the inital and final 100 gm/cm^2 stresses. The readings are made 30 seconds after the application of the load. The materials were also tested at ages other than one hour. The results are shown in Figures 2 and 3. All materials complied with ADA Specification No. 11 for strain. That is, the strain was not less than 4.0% nor more than 20.0% at 1 hour. The range in strain for material 7 at 15 minutes was 11.0%. The maximum range for the remainder of the specimens was 5.5%. Seven materials complied with the requirement of ADA Specification No. 11

which permits a maximum set of 3% at approximately 1 hour. The range in set for material 7 at approximately 15 minutes was 16.3%, for material 1 at approximately 30 minutes it was 3.0%. The maximum range for the remainder of the specimens was 2.0%.

Three representative materials of the Thiokol type and the one silicone type were also tested for set at room temperature by the method set forth in Federal Specification U-I-498, Impression Material, Hydrocolloidal, Alginate Type, Dental. In this test, set is calculated from the difference between the original and final lengths after releasing an applied strain of 12% from the specimen. The strain is applied 1 hour after the mix is started and is maintained for 1 minute. The final length is determined 1 minute after the release of the strain. The results of these tests are compared with the results for the same materials obtained by the method described in ADA Specification No. 11 (Figure 4). As can be seen, the agreement between the two methods regarding the absolute values of the set is not particularly close. The values, however, remain in the same relative order for the four materials. The maximum range in set for these four materials was 0.3% by the Federal Specification and 0.7% by ADA Specification No. 11.

Another series of tests was run to obtain set and strain data on the materials under simulated clinical conditions (Figures 5 and 6). At the end of one minute from the beginning of the mix the specimens were placed in a 37°C water bath for different lengths of time, removed and immediately tested in

air as in the previous ADA specification test. The one exception was material 7 which was placed in the water bath after 2 minutes because of its longer mixing time. Readings were made at 5, 10 and 15 minutes after start of mix. No readings were made at 5 minutes on materials 3, 7 and 11 because they were not sufficiently cured at that time. All specimens read had strain values which were between 4.0% and 20.0% at 5, 10 and 15 minutes after the start of the mix. One specimen had a set value less than 3% at approximately 5 minutes after start of mix, five specimens at approximately 10 minutes after the start of the mix and eight specimens at approximately 15 minutes after the start of the mix.

The range in strain of material 1 at 5 minutes was 4.3%, of material 11, 4.5% at 10 minutes and 5.7% at 15 minutes. The maximum range in strain of the remainder of the materials was 2.9%. The range in set of material 1 at 5 minutes was 2.1%, of material 10 at 5 minutes was 2.7%. The maximum range in set of the remainder of the materials was 1.2%.

3.5 Flow

Flow of the materials under a light load at 22°C was investigated. As in the tests for strain and set, the specimens were cylinders 0.5 in. in diameter and 0.75 in. long. They were aged in air for one hour, prior to testing. A 100 gm load which exerted a stress of approximately 80 gm/cm^2 was placed on the specimen and a dial gage reading in thousandths

of an inch was taken at the end of 30 seconds. 1 hour later another dial gage reading was made and the reduction in length of the specimen was considered as flow. Flow values were between 0.9 and 5.9% for the Thiokols and averaged 0.2% for the silicone material (Figure 7). The range in flow was 1.4% for material 1 and 0.7% for materials 4 and 6. The maximum range for the remainder of the materials was 0.3%.

3.6 Dimensional Stability

Some investigators [1, 7, 8] have determined dimensional accuracy by taking impressions of dies, making restorations and trying the finished restorations back on the original dies to check the fit. In the tests for dimensional stability described here, specimens of each impression material approximately 2.25 in. by 0.75 in. by 0.125 in. were made. Small pieces of polished metal on which cross lines had been ruled with a diamond were imbedded in the surface. The specimens were placed on a glass surface which had been thoroughly dusted with talc, as had the contacting surface of the specimens, permitting the specimens to change dimensions freely on the glass surface. The distance between the ruled lines was measured at various times from 15 minutes to 24 hours after the specimens were made. To eliminate error due to repositioning the specimens, each was left on the table of the measuring microscope until all the measurements upon it were completed.

In the earlier part of the measurements, some materials showed an immediate decrease in linear dimension, others showed an increase and still others showed no immediate change. All specimens did show a definite decrease in length over a 24 hour period.

Figure 8 shows the trend of the dimensional stability. The mean deviation in dimensional change was 0.01% or less for readings taken at 6 hours or less. At 24 hours the mean deviation was 0.02%. Material 5 had mean deviations of 0.02% at 4 hours and 0.03% at 6 hours and 24 hours. Material 6 had a mean deviation of 0.01% at 24 hours. Material 11 had mean deviation of 0.02% at 45 minutes, 1 hour and 2 hours.

3.7 Effect of Synthetic Rubber Base Impression Materials on Impression Compound

In the course of this work it was noted that the accelerators for both the Thiokol and silicone materials had a softening effect on dental impression compound. The base materials had no effect. The Thiokol material when cured had a softening effect on dental impression compound when the two were in contact for several weeks. Further investigation indicated that this last effect was probably due to the castor oil in the accelerator for the Thiokol material.

3.8 Compatibility of Synthetic Rubber Base Impression Materials with Gypsum Materials

To determine the compatibility of these impression materials with gypsum materials, rather large mixes of three representative Thiokol materials (numbers 2, 4, 8) and the one silicone material were formed into sheets approximately 4" x 4" x 1/4". When these had aged for several hours, two "improved" stones, one regular stone, one casting investment, one model plaster and one soluble impression plaster were mixed and applied to the surfaces of the impression materials. After two hours the gypsum materials were removed and the contacting surfaces examined.

In all cases the gypsum materials which had been in contact with the Thiokol materials exhibited a smooth reproduction of the Thiokol surface.

Of the materials in contact with the silicone material, only the soluble impression plaster exhibited a smooth reproduction. The other materials had pitted and roughened surfaces, and some left a film on the silicone material.

Figure 9 shows the surfaces of a gypsum product which was cast against a Thiokol material on the left and the silicone material on the right. As can be seen easily, the compatibilities are substantially different. Magnification in the figure is 15x.

3.9 Surface Effects and Detail

All materials displayed depressions on the surface after standing undisturbed for several hours. The cause of these depressions is as yet unknown. The location of these depressions was always over an internal void near the surface.

Figure 10 shows three materials (3, 6, 11) at ages of 1 hour and 24 hours. The depressions were strongly evident at 24 hours. Magnification in the figure is 15x.

The reproduction of the detail of a line 0.0015 in. wide scribed on a steel block was excellent. The maintenance of the detail was also excellent with the exception of the formation of the surface depressions mentioned above.

4. DISCUSSION

The rubber base dental impression materials have physical properties which compare very favorably with those of the hydrocolloids.

The setting times at 37°C for the rubber base materials are not as short, in some cases, as the gelling time for the hydrocolloids, but they are not excessively long. The setting time of Thiokol rubbers in general is a function of the humidity and temperature under which the material is mixed, in that the higher the humidity or the temperature, the higher is the rate of cure. The effect of humidity on the setting time of the Thiokol material as used in dentistry has not been studied as yet. Some effect is to be expected but it is of unknown

magnitude. This dependency may be critical, particularly in tropic zones. Because of the difficulty encountered in determining the setting time by means of the penetrometer test, and because the setting time so determined is dependent upon the type of penetrometer used, it seems advisable that a more satisfactory test should be devised.

The temperature rise on setting for the rubber base materials is not clinically significant since it amounts to approximately 3-5°C (5-9°F) for 1.5 cc of material.

As previously noted the silicone and six of the Thiokol materials complied with the requirement of ADA Specification No. 11 for set and all materials complied with the requirement for strain. Hydrocolloids do not have extreme changes in physical properties between the time they have gelled and the time at which they are tested according to the specifications. The rubber based materials do undergo extreme changes in physical properties during the time interval preceding the 1 hour test prescribed by the ADA specification as can be seen in Figures 2 and 3. However, in practice, the curing of the material occurs at 37°C. It seems advisable to test the rubber base materials at earlier times than 1 hour and at a temperature of 37°C rather than room temperature. Fairhurst et al [9] have investigated the strain and set at room temperature at 5, 6, 8 and 10 minutes after start of mix. The decrease in the set at five minutes to the lower value of set at ten

minutes (Figures 5 and 6) indicates that if the material is kept in the mouth until ten minutes after mixing set and strain should be within clinically acceptable limits.

The flow of the specimens under a stress of 80 gm/cm^2 did not appear to be excessive in most of the specimens. However, the high values obtained for some materials may be indicative of a tendency for impressions made from these materials to flow and distort over a long period of time.

A definite advantage the Thiokol materials and to a lesser extent the silicone product have over the hydrocolloids is their dimensional stability. Phillips [10] has stated that in no instance can accurate dies routinely be produced from reversible hydrocolloid impressions which were stored for as long as 30 minutes, regardless of the media employed. The Thiokol materials can be stored in air for as long as 24 hours with a decrease in linear dimension of approximately 0.2%. The one silicone material tested has an equivalent decrease in dimension in from 4-6 hours. The advantages of relatively good dimensional stability are nullified to some extent by the appearance of surface irregularities after a few hours.

The chief disadvantage of the synthetic rubber base materials is the difficulty of mixing homogeneously, relatively large quantities for full mouth and other large impressions. The silicone has the further disadvantages of high shrinkage after set and incompatibility with certain gypsum products.

5. SUMMARY

1. In most of the properties tested there was considerable variation between different brands of the material.
2. It seems advisable that a more satisfactory test should be devised for setting time.
3. The temperature rise during curing is negligible in all brands tested.
4. All of the materials tested had strain values which complied with ADA Specification No. 11 for Hydrocolloidal Impression Material, Agar Type, and seven of the materials had set values which complied with this specification.
5. It appears that impressions should be left in the mouth until ten minutes or longer after mixing to minimize permanent deformation upon removal.
6. All materials displayed flow under a light load, with some showing a relatively large amount.
7. The dimensional change of most of the Thiokol materials during a 24 hour period following the initial set is probably not large enough to be clinically significant.
8. The silicone material was incompatible with certain gypsum products.
9. All materials displayed depressions in the surface after a few hours.

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Table 1

Brand Name	Batch Number	Manufacturer
Coe-Flex	SS2	Coe Laboratories, Inc. Chicago, Illinois
Dura Flex	None	Reliance Dental Mfg. Co. Chicago, Illinois
Form-Flex	5205	The William Getz Corp. Chicago, Illinois
Neo-Plex	26455	Surgident, Ltd. West Los Angeles, California
Paragel	105 6102	Dental Perfection Co. Glendale, California
Permlastic	LL986MM128 583	Kerr Manufacturing Co. Detroit, Michigan
Plastodent	A11725	Plastodent, Inc. New York, New York
R-28	5278	The William Getz Corp. Chicago, Illinois
Sili-Gel	100	Dental Perfection Co. Glendale, California
Sta-tic	None	Stalite, Inc. New York, New York
Sta-tic "X"	None	Stalite, Inc. New York, New York

Table 2

TEMPERATURE RISE AND SETTING TIME OF SYNTHETIC RUBBER BASE IMPRESSION MATERIAL

Material	Temperature Rise* above 22°C (71.6°F)		Setting Time in Minutes	
	°C	°F	22°C (71.6°F)	37°C (98.6°F)
4	3.0	5.4	9	4.0
6	3.7	6.7	11	4.5
1	4.1	7.4	14	4.5
9	5.2	9.4	11	5.0
8	4.8	8.6	15	6.5
2	4.8	8.6	16	7.0
10	4.8	8.6	16	7.5
5	4.3	7.7	18	7.5
3	5.2	9.4	30	8.0
11	3.3	5.9	15	9.0
7	3.9	7.0	24	9.0

* Specimen volume was 1.5 cc.

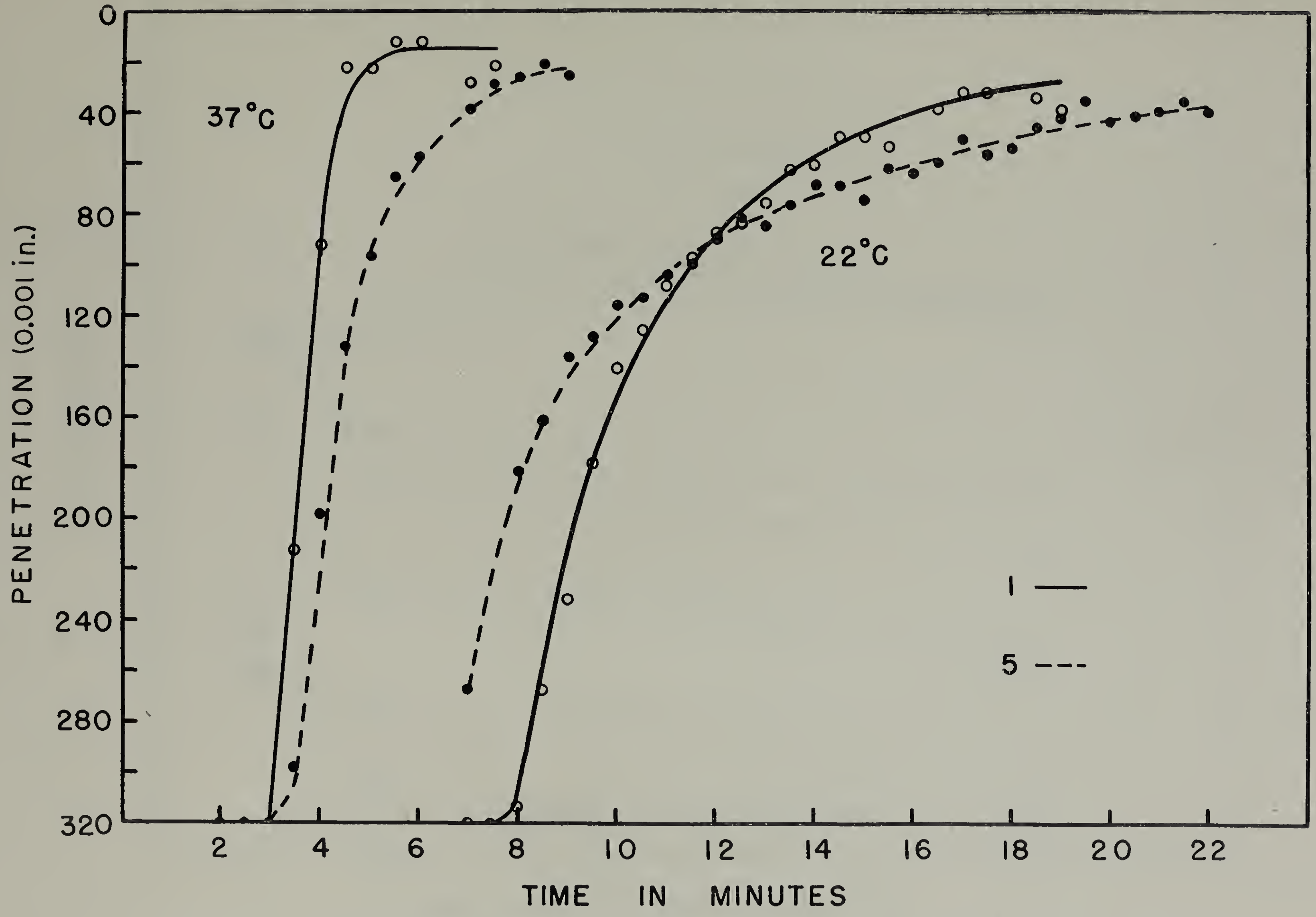

Figure 1. Representative curves for the depth of penetration versus time for two different Thiokol materials at 22°C and 37°C.

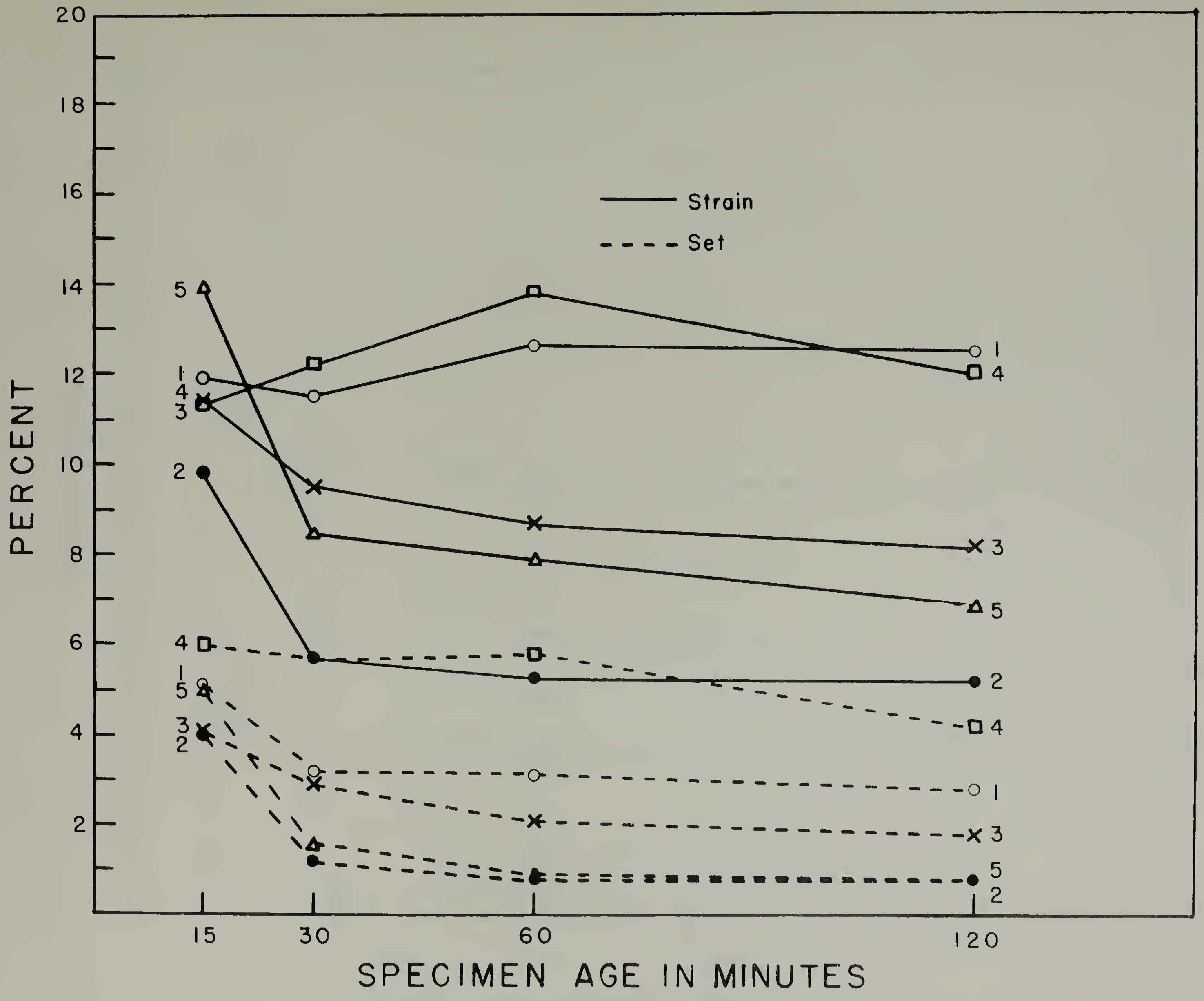

Figure 2. Percent strain and set at 22°C for materials 1 through 5 using the procedure of A.D.A. Specification No. 11.

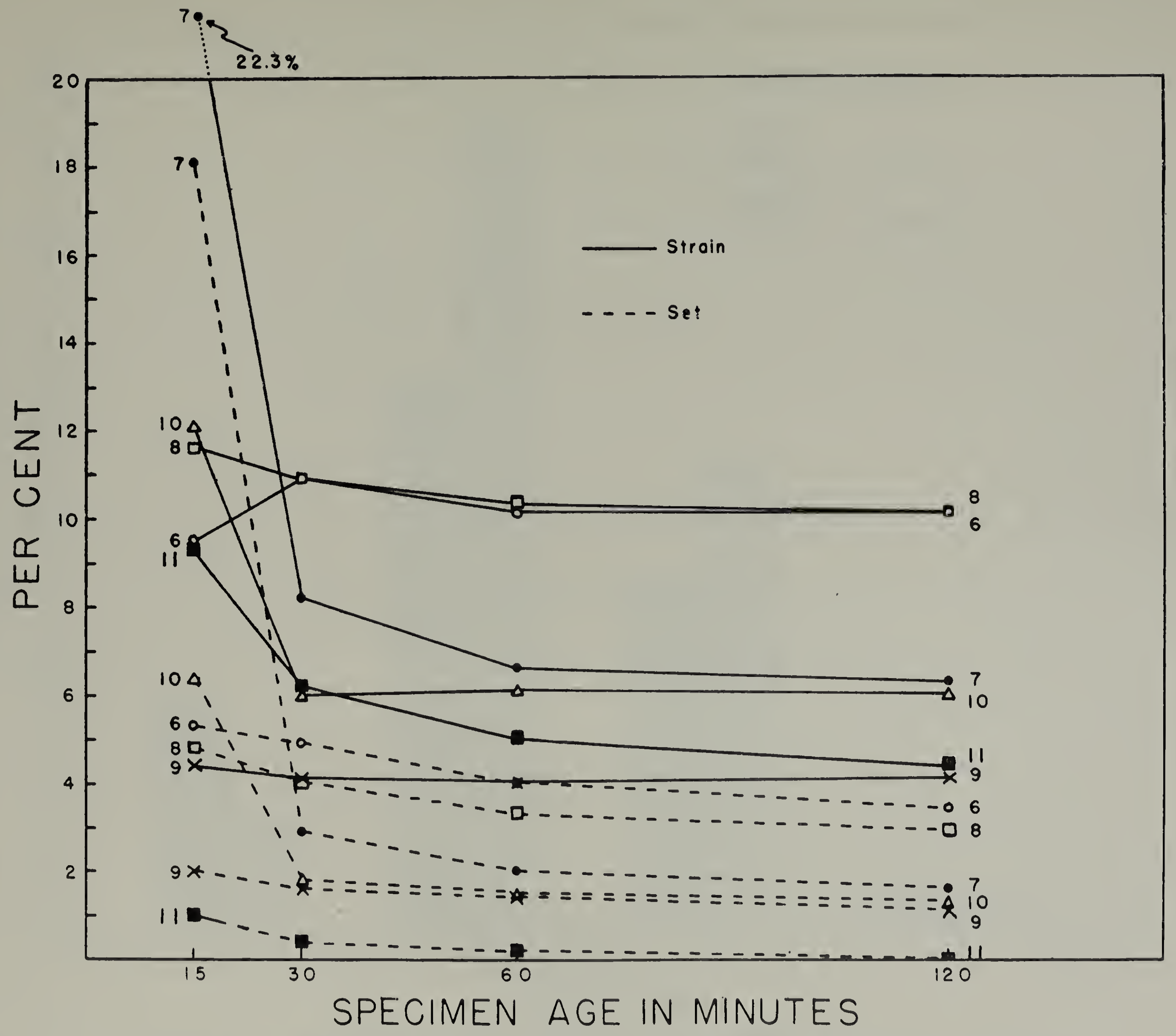

Figure 3. Percent strain and set at 22°C for materials 6 through 11 using the procedure of A.D.A. Specification No. 11. The value for material 10 at 2 hours is the average of two specimens.

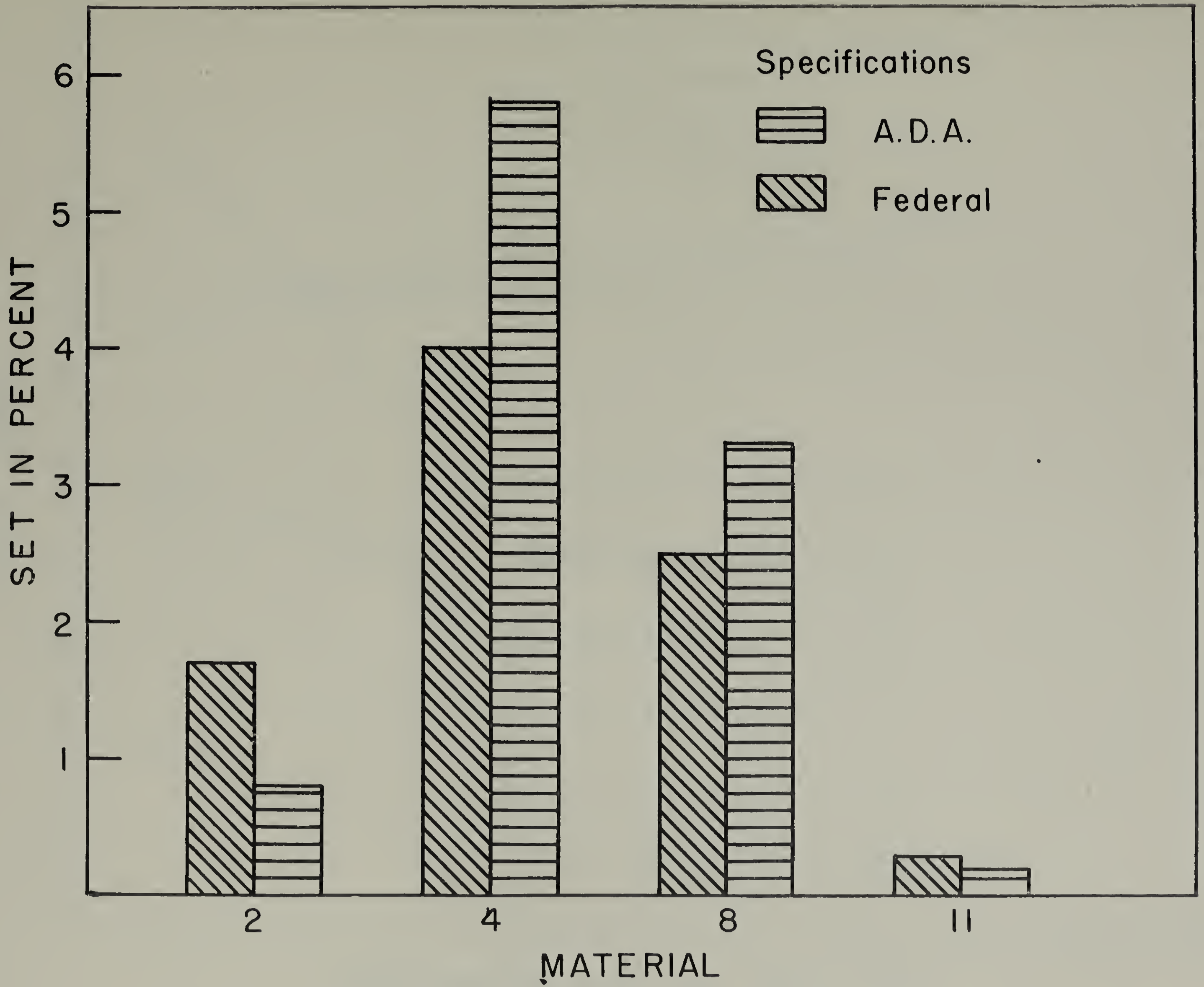

Figure 4. Comparison of percent set as determined by A.D.A. Specification No. 11 and Federal Specification No. U-I-498 at 22°C. The value for material 4 as tested by the Federal Specification is the average of two readings.

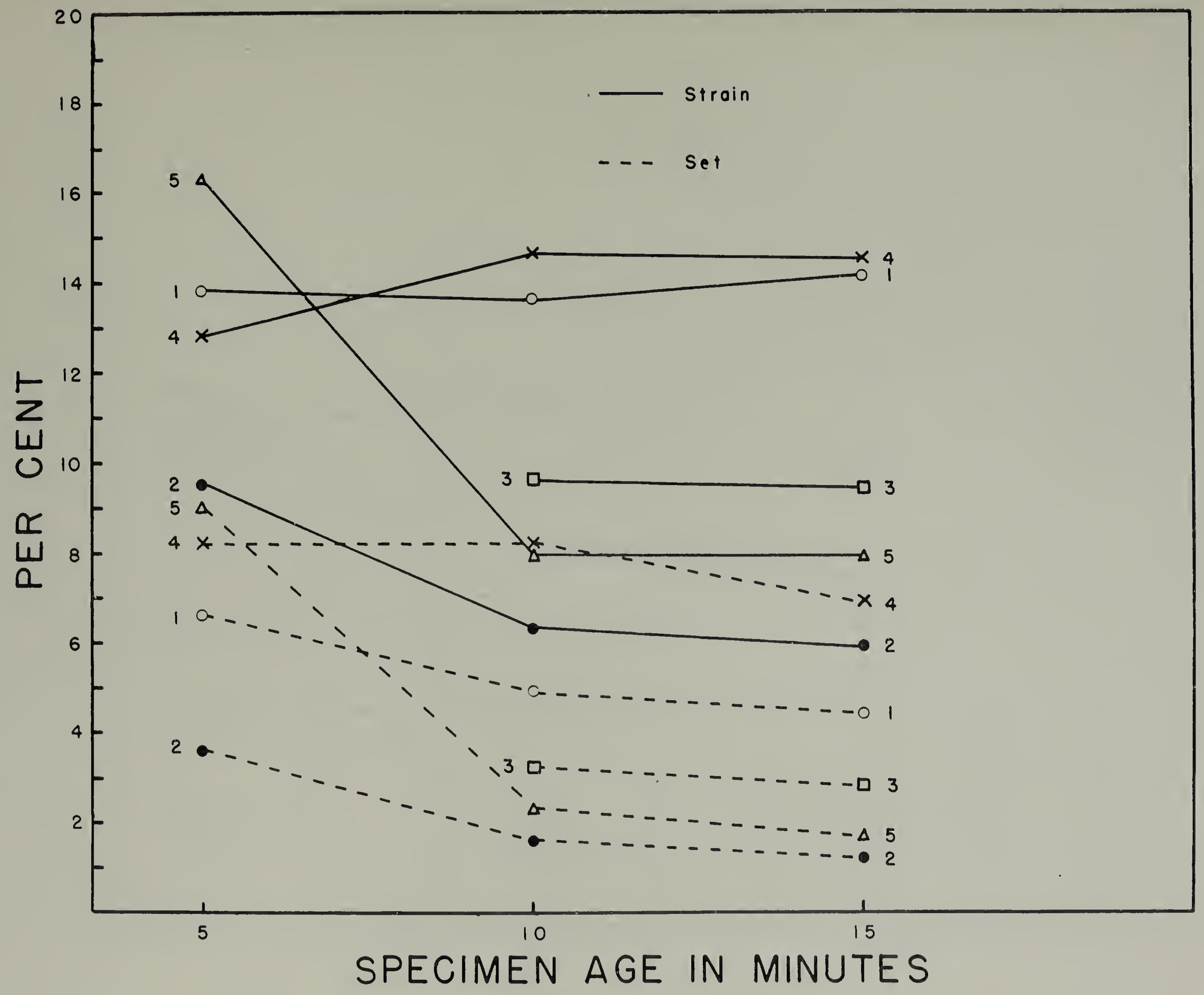

Figure 5. Percent strain and set at 37°C for materials 1 through 5 using the procedure of A.D.A. Specification No. 11.

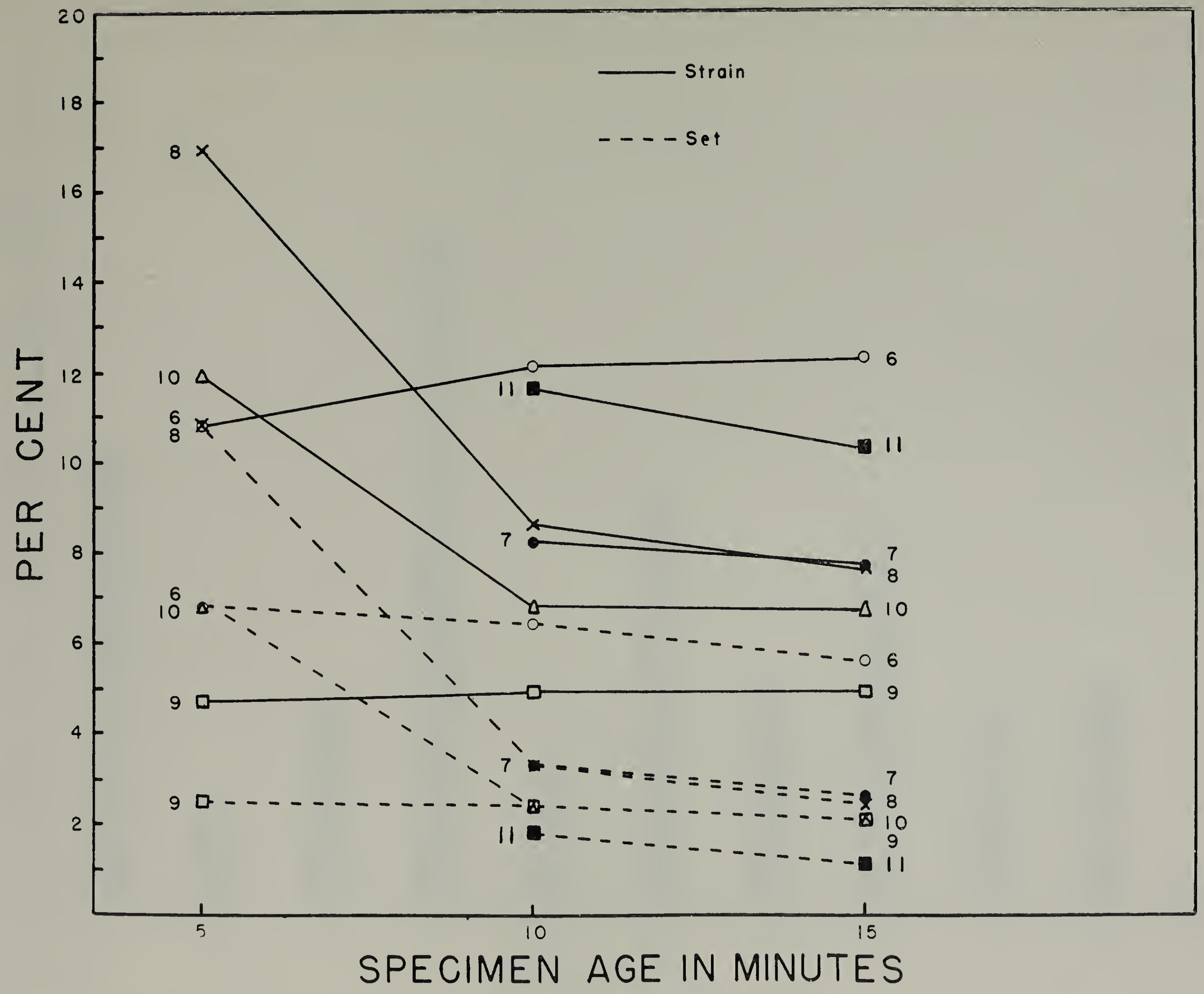

Figure 6. Percent strain and set at 37°C for materials 6 through 11 using the procedure of A.D.A. Specification No. 11.

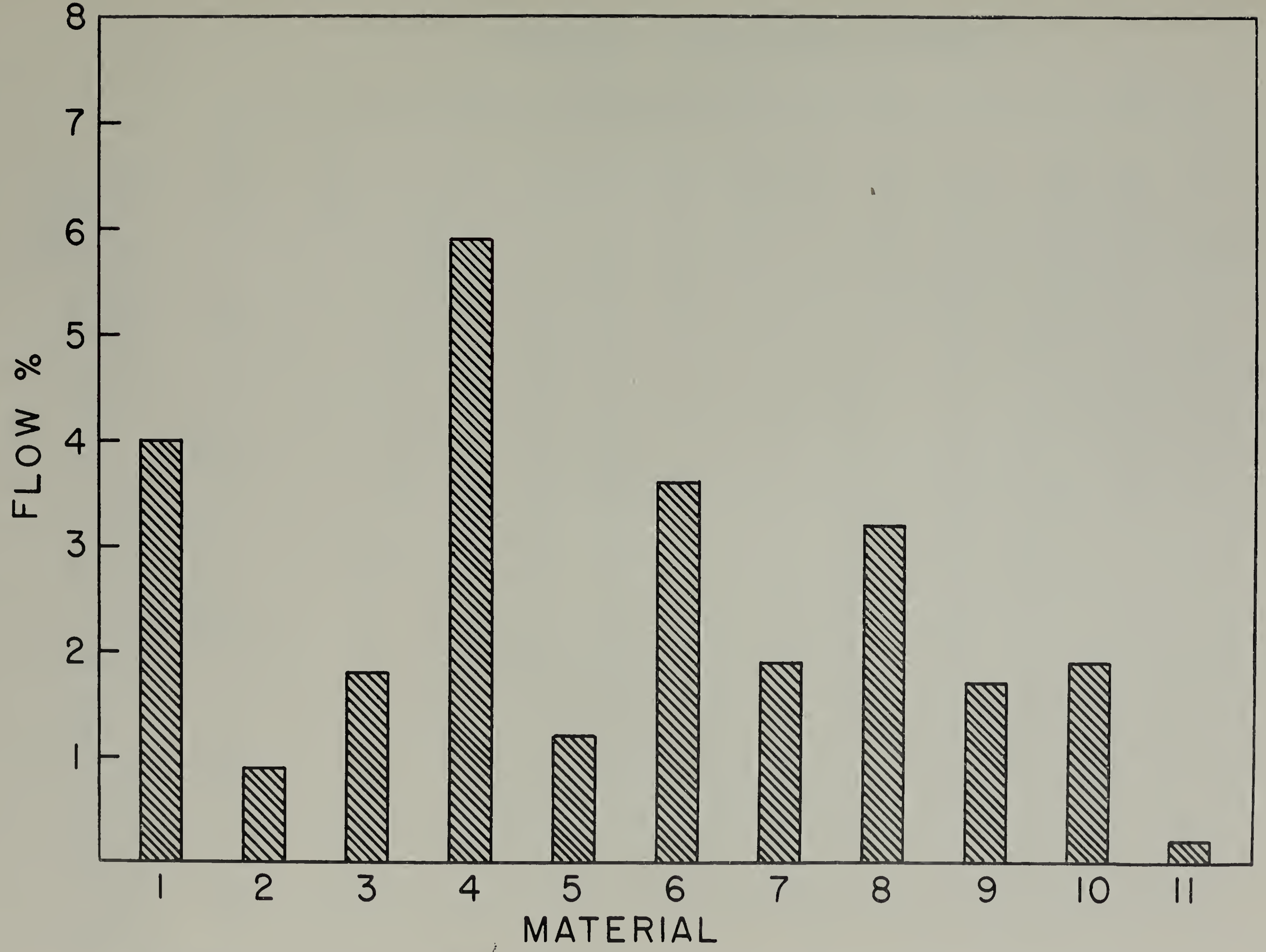

Figure 7. Percent flow at 22°C under a stress of 80 g/cm^2 for one hour.

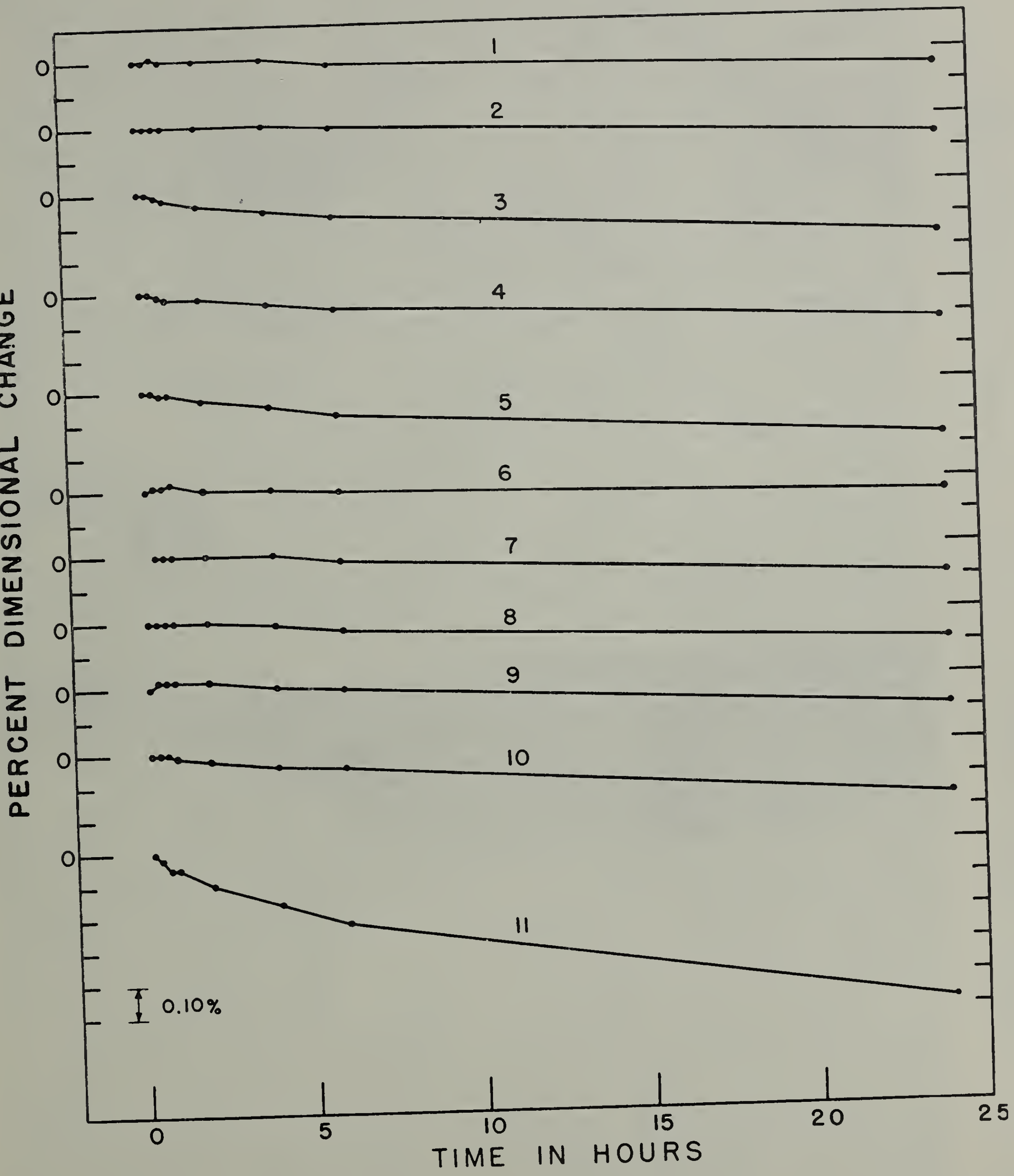

Figure 8. Percent dimensional change versus time. Only two specimens were measured at the following readings; material 2 at 4 and 6 hours, material 3 at all readings, material 4 at 4 hours, material 7 at 4 hours, and material 10 at 2 and 6 hours.

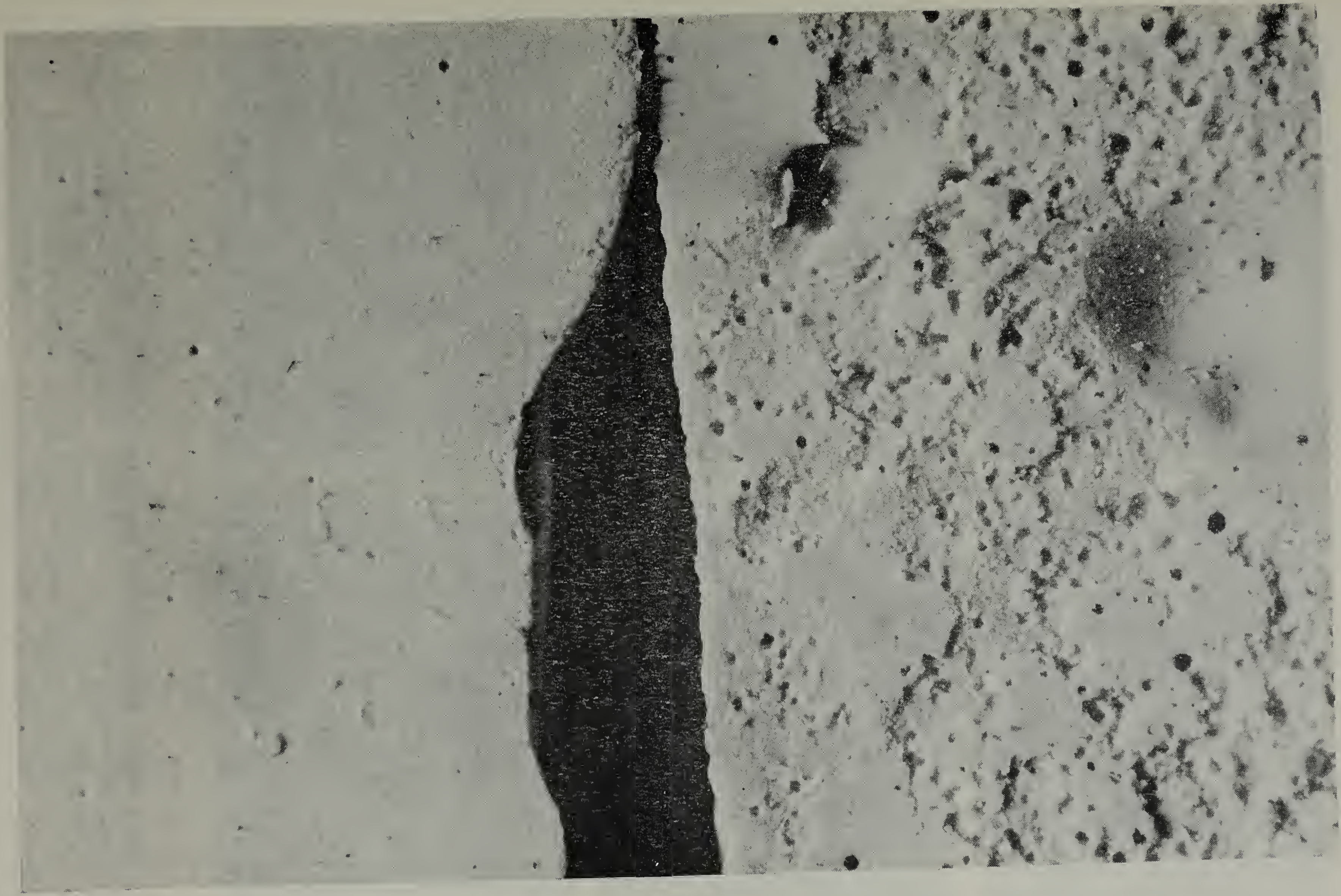

Figure 9. A gypsum product poured against a Thiokol material, left, and the silicone material, right. The gypsum product was in contact for two hours before removal.

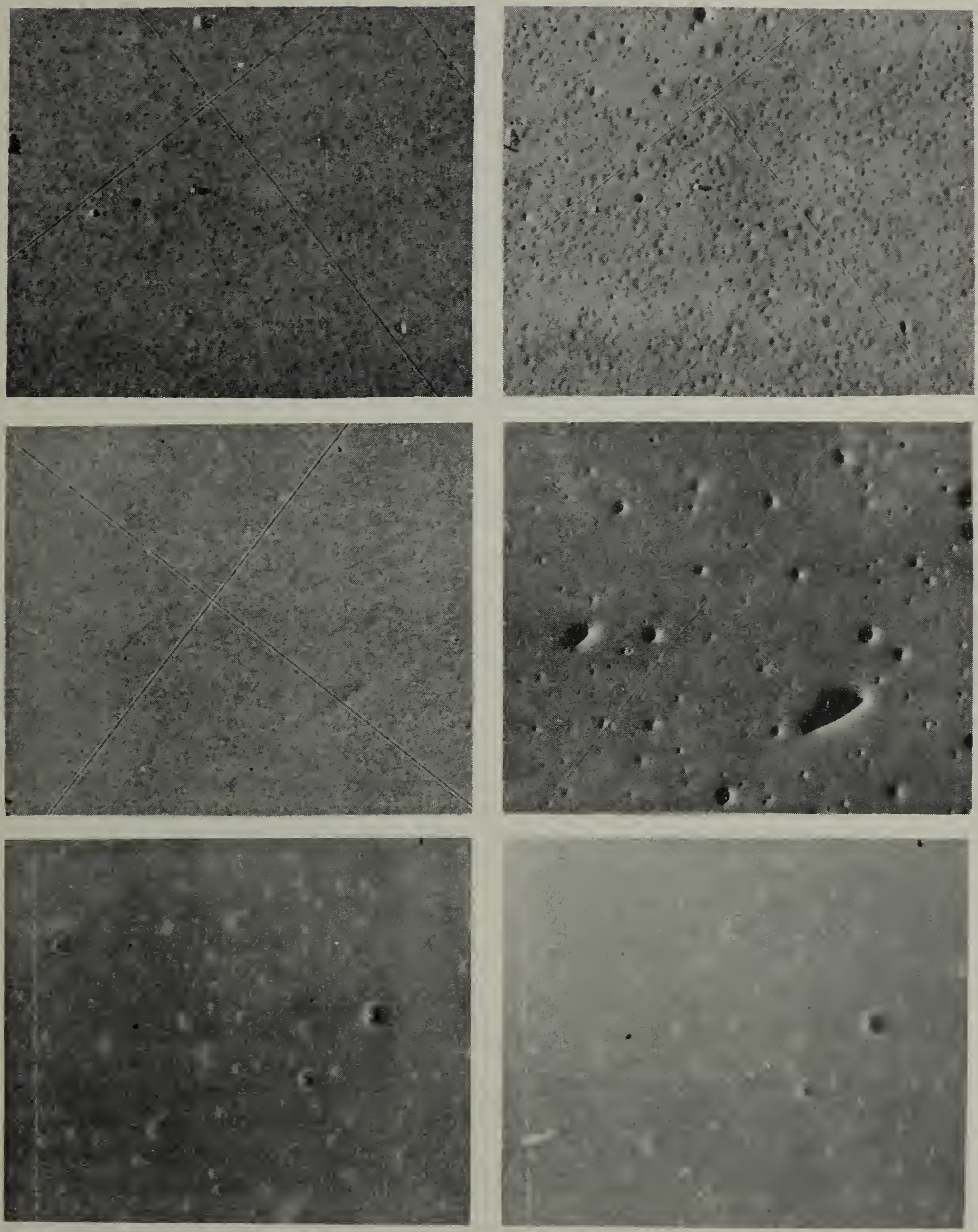

Figure 10. Age effects on the surface of rubber base impression materials. The left column is the appearance of the surface one hour after start of mix, the right column the appearance 24 hours after start of mix. The top row is material 3, the middle row is material 6, and the bottom row is material 11.

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Progress Report

DETERMINATION OF SOME COMPRESSIVE PROPERTIES OF HUMAN ENAMEL AND DENTIN

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DETERMINATION OF SOME COMPRESSIVE PROPERTIES OF HUMAN ENAMEL AND DENTIN

Abstract

A method of preparation of cylindrical specimens of hard tooth tissues by a grinding process has been developed. The results obtained show that the compressive properties of the tested enamel specimens fall into three categories depending on their original location: cusp, side and occlusal surface of the tooth. Values for enamel ranged from 4.0×10^6 to 8.2×10^6 psi for modulus of elasticity, from 15,000 to 34,000 psi for elastic limit and from 18,000 to 40,000 psi for compressive strength. Average values for dentin were 4.1×10^6 psi for modulus of elasticity; 25,000 psi for elastic limit; and 50,400 psi for compressive strength.

1. INTRODUCTION

A large amount of information on the physical properties of the restorative materials used in dentistry has been compiled during the past years. However, relatively few data have been published on the physical properties of the hard tooth tissue, the foundation for the restorative materials.

Knowledge of the physical properties of the hard tooth tissue is equally as important as knowledge of the restorative materials, since the success or failure of a restoration depends upon the properties of both the material and the tooth.

The objective of this research was to supply information on some mechanical properties of enamel and dentin. The properties determined, compressive strength, elastic limit, and modulus of elasticity, are defined as follows [1]:

1. Compressive strength is defined as the maximum compressive stress which a material is capable of developing, based on original area of cross-section. Standard tests for compressive strength specify test conditions such as size and shape of specimens in order that the stress at the critical cross-section will be, as nearly as practicable, uniaxially compressive. In an investigation of hard tooth tissue the quantity of material available is so limited that specimens cannot always be made to standard dimensions and the results obtained are not necessarily the same as would have been obtained under ideal conditions.

2. The elastic limit is defined as the greatest stress that a material is capable of developing without any permanent strain remaining upon complete release of the stress. Ordinarily, elastic limit and proportional limit of materials are considered to be approximately equal, and the elastic limit is determined as the highest stress on the straight-line portion

of the stress-strain diagram.

3. Modulus of elasticity is defined as the ratio of stress to the corresponding strain below the proportional limit. It is equal to the slope of the straight-line portion of the stress-strain diagram and is a measure of the stiffness of a material. The term modulus of elasticity alone generally refers to tensile modulus of elasticity. Moduli of elasticity in tension and compression are usually approximately equal for a given material.

An investigation of physical properties of tooth tissue was reported in 1895 by G. V. Black [2] who determined the crushing strength of 0.080 inch cubes of dentin. At that time he also reported an indication of the crushing strength of enamel. An average value for dentin was reported as 37,200 psi. With enamel specimens, whose dimensions were 0.080 inch x 0.080 inch x 0.040 inch, no matter how they were cut (as to direction of the enamel rods) or how the stress was applied, enamel rods would begin to split off with very light stress compared to dentin. The whole block collapsed at from 30 to 75 pounds load. (Approximately 4,700 to 11,700 psi).

Souder and Paffenbarger in 1942 [3] estimated the ultimate strength of sound enamel to be over 100,000 psi on the basis of its hardness compared to dentin. In 1952 Peyton, Mahler, and Hershenou [4] reported physical properties of cylinders of dentin prepared by a hollow drill coring method.

After the coring of the cylinders from the teeth, the ends of the specimens were finished to insure parallelism and flatness. Tuckerman Optical Strain Gages were used to determine the proportional or elastic limits of the dentin. The average values reported for dentin from this study were as follows:

1. Modulus of Elasticity 1.67×10^6 psi
2. Proportional limit 23,400 psi
3. Compressive strength 36,100 psi

No values were reported on enamel.

2. EXPERIMENTAL PROCEDURE AND RESULTS

Cylindrical specimens as large as possible were prepared of enamel, dentin, and combinations of enamel and dentin including the dentino-enamel junction. The first method used in the preparation of specimens was a coring method similar to that reported by Peyton [4]. Hollow drills made of several different metals such as copper, bronze, and stainless steel were used. Different abrasives used varied from aluminum oxide to diamond dust. Also, diamond particles were embedded on a phosphor-bronze tool. Due to the shattering of the enamel it was impossible to obtain specimens with these tools. In an attempt to prepare specimens from dentin, only truncated cones could be produced by this method. The second method used consisted of grinding blocks of tooth tissue into cylinders. Freshly extracted teeth were mounted in rings with gypsum and slices were made into the tooth using the machine shown in

Figure 1. Slices were made approximately 0.1 inch apart. After these slices were made the teeth were remounted and slices were made at approximately 90 degrees to the previous ones. The resulting blocks were removed from the tooth and identified as to original location. These blocks were chucked in small collets in the milling machine shown in Figure 2. Different types and sizes of cutting wheels were used and it was found that the diamond cutting stone worked most efficiently. The tooth specimen and the diamond cutting stone were rotated in opposite directions. Light cuts were first made across the end of the block in order to true that end so that it would be perpendicular to the sides of the finished cylinder. Cuts were then made the length of the block until a cylindrical specimen was obtained as shown in Figure 3. At this point the tooth specimen was removed from the collet and turned end for end so that the excess could be removed and the ends made plane and parallel. All cutting and grinding operations were done with a steady dripping of water on the field of cutting, and the cylinders were stored in distilled water until tested. A typical specimen of hard tooth tissue is shown in Figure 4.

A Tinius Olsen testing machine operating over a range of 0 to 1000 lb. load was used as the loading device for applying stresses on the specimens. The platens were constructed of hardened tool steel (Figure 5). Two guide pins were fixed in the upper platen to align with holes in the

lower platen so that during loading the platens would not get out of line.

Because of the small size of the specimens of tooth tissue it was necessary in measuring the deformation to fasten the Tuckerman Strain Gages on the platens across the specimen length. A specimen in place between the platens is shown in Figure 5. The strain gages thus measured the deformation in both the specimen and that portion of the steel platens which lay within the gage length. The assumption that all the deformation measured took place over the length of the specimen would be a source of experimental error.

To determine the possible extent of this error, tests were conducted on materials for which the moduli of elasticity are well known. Small cylinders of carbon steel, AISI-1070; aluminum alloy, 2024-T4; and magnesium alloy, AZ31A, were prepared in a manner similar to that used in preparing those of tooth tissue, and tested in compression. Longer specimens of these three materials were also tested in tension. The results of the two types of tests did not agree. However, there are certain corrections which can be applied to this type of determination. The total deformation measured in conducting the compressive test involves four separate items which are designated as follows:

Item 1. Actual deformation or shortening of the specimen.

Item 2. Gap effect or apparent shortening due to imperfect fit of ends of specimens with platens. Included here would

also be the effect of friction between platens and ends of specimens restricting lateral expansion of the specimens near the ends.

Item 3. Elastic shortening of the platens over the gage length involved.

Item 4. Deformation of the platen surfaces or foundation effects.

There is no known equation for the correction of item 2 since it involves probability of how the platens contact the ends of the specimens.

The deformation correction, U, for item 3, the elastic shortening of the platens, is given by Hooke's law [5]:

$$U = \frac{P(L_g - L_s)}{E_p \times A_p} \qquad \text{(a)}$$

Where: P = load in pounds.

L_g = gage length of strain gage in inches.

L_s = length of specimen in inches.

E_p = modulus of elasticity of the steel platen.

A_p = cross-sectional area of platen.

The deformation correction, V, for item 4, the foundation effect for each platen, is given by the following equation [6]:

$$V = \frac{mP(1 - \nu_p^2)}{E_p \sqrt{A_s}} = \frac{P}{E_p \times d_s} \qquad \text{(b)}$$

Where: m = a function of the shape of section, 0.96 for circular cross-section.

ν_p = Poissons ratio of the platen, 0.28 for steel

A_s = Cross-sectional area of specimen,

$\frac{\pi d_s^2}{4}$, where d_s = diameter of specimen.

Then the corrected deformation, Δ, from (a) and (b) is given by:

$$\Delta = Z - (U+2V) = Z - \frac{P}{E_p}\left[\left(\frac{L_g - L_s}{A_p}\right) + \frac{2}{d_s}\right] \qquad (c)$$

Where Z = observed deformation, inches.

Then the strain, ε, = $\frac{\Delta}{L_s}$, and the modulus of elasticity of the specimen in compression is given by:

$$E_s = \frac{P}{A_s \varepsilon} \qquad (d)$$

Equation (d) was evaluated for the three known materials after corrections in deformations (equation c) were made. The results are shown compared to the observed moduli in compression and tension in Table 1. Also accepted or "True Moduli" in tension are shown for comparison.

Examination of Table 1 showed that the corrected values of moduli in compression still differed from the measured or accepted values in tension. Therefore, other factors are involved which cannot be corrected for by known equations. To compensate for these errors the accepted values of modulus of elasticity in tension were plotted as "True Moduli" versus

the corrected compression values and are shown in Figure 6. Also the modulus of elasticity of dental amalgam determined by Smith and Caul [7] using a direct measurement of deformation was plotted versus the modulus determined in compression using the same method employed in this research. The four plotted points in Figure 6 lie very nearly on a straight line. Tables 2, 3 and 4 of the results which are discussed in the following section include three average values for the modulus of elasticity. They are column 1, the observed experimental value; column 2, the corrected experimental value; and column 3, the average corrected value taken from the curve in Figure 6.

3. DISCUSSION OF RESULTS

The data for enamel, (Table 2), indicate that the values are related to the original location of the specimens in the teeth. The highest strength, modulus of elasticity and proportional limit were obtained for specimens of cusp enamel. This can possibly be explained by the presence of gnarled enamel rods in that area. The lowest values for these three properties determined on enamel were for specimens from the occlusal surface. Areas of possible decalcification may account for these lower values. Also during loading of this type of enamel specimen it was noted that at fracture the cylinder, instead of shattering, split lengthwise in tiny slivers. This type of failure would be expected if the general direction of the rods were lengthwise and if the pri-

mary failure were in the bonding material.

The values determined for specimens of enamel taken from the sides of the teeth fall between the above-mentioned determinations. In this location, the direction of enamel rods would tend to be perpendicular to the long axis of the specimen and this may account for the values obtained. Figure 7 shows a representative stress-strain curve for each area of the tooth enamel tested.

The data determined for dentin are shown in Table 3. No attempt was made to determine tubule direction in these specimens. The average value (50,400 psi) determined for compressive strength is higher than that reported by Peyton [3] (36,100 psi) whereas the values for the elastic limit and modulus of elasticity with the exception of the value for the modulus taken from Figure 6 are comparable. Figure 8 shows a representative stress-strain curve for dentin.

The data for the three properties on combinations of enamel and dentin are shown in Table 4. The values appear upon inspection to form two divisions depending upon the location of the dentino-enamel junction in the specimen. The higher values for the three properties were obtained on specimens in which the dentino-enamel junction peaked in approximately the center. The lower values obtained were on samples in which the dentino-enamel junction ran diagonally through the cylinder. However, the properties do vary from specimen

to specimen such that the differences may not be of significance. The average values for the three properties appear to fall between those determined for enamel and dentin separately. Figure 9 shows a representative stress-strain curve for dentin and enamel combinations.

4. SUMMARY

1. A method for preparation of small cylinders of hard tooth tissues was presented.
2. A calibration curve which may serve in evaluating determinations of moduli of elasticity in compression on small specimens of material was presented.
3. The average values determined in compression for the three properties are as follows:

Material	Modulus of Elasticity			Elastic Limit	Compressive Strength
	Observed	Corrected by Equations	From Curve Figure 6		
	$\times 10^6$ psi	$\times 10^6$ psi	$\times 10^6$ psi	psi	psi
Enamel					
Cusp	5.4	6.9	8.2	34,200	40,200
Side	3.8	4.4	6.3	21,200	28,200
Occlusal Surface	1.2	1.3	4.0	15,400	18,200
Dentin	1.5	1.6	4.1	25,100	50,400
Dentin and Enamel	2.4	2.7	5.0	23,900	34,200

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TABLE 1

CALIBRATION DATA FOR DETERMINATION OF MODULUS OF ELASTICITY

Material	Observed E Compression	Corrected E Compression	Observed E Tension	Accepted* E Tension
	x10^6 psi	x10^6 psi	x10^6 psi	x10^6 psi
Magnesium alloy, AZ31A	4.2	4.8	6.5	6.5
Aluminum alloy, 2024-T4	7.2	9.6	10.5	10.6
Carbon Steel, AISI-1070	14.0	32.5	28.0	29.0

* Source: Metals Handbook, The American Society for Metals, 1948.

TABLE 2

PROPERTIES OF ENAMEL

Original Location of Specimens in Tooth	Dimensions of Specimens		Property Determined				
			Modulus of Elasticity			Elastic Limit	Compressive Strength
	Diameter	Length	(1) Observed	(2) Corrected[a]	(3) Average of Column 2 Corrected[b]		
	in.	in.	$x10^6$ psi	$x10^6$ psi	$x10^6$ psi	psi	psi
Tips of Cusps	0.038	0.079	6.1	7.4		38,900	42,500
	0.040	0.065	5.3	6.7		32,000	37,600
	0.038	0.050	5.7	7.8		35,000	39,800
	0.033	0.057	4.6	5.8		31,000	41,100
Average			5.4	6.9	8.2	34,200	40,200
Side	0.038	0.071	3.8	4.3		15,000	26,600
	0.040	0.064	4.0	4.8		25,600	26,400
	0.042	0.057	4.0	4.8		24,000	31,900
	0.040	0.061	3.2	3.8		20,000	28,000
Average			3.8	4.4	6.3	21,000	28,200

Table 2 (Continued)

Original Location of Specimens in Tooth	Dimensions of Specimens		Property Determined				
			Modulus of Elasticity				
	Diameter	Length	(1) Observed	(2) Corrected[a]	(3) Average of Column 2 Corrected[b]	Elastic Limit	Compressive Strength
	in.	in.	x10^6 psi	x10^6 psi	x10^6 psi	psi	psi
Occlusal Surface	0.062	0.065	1.4	1.6		10,000	11,200
	0.039	0.041	1.6	1.8		20,000	23,300
	0.040	0.028	0.4	0.4		16,000	20,800
	0.040	0.044	0.9	0.9		17,600	18,000
	0.039	0.059	0.8	0.8		20,000	22,500
	0.058	0.054	2.1	2.5		17,000	20,800
Average	...	...	1.2	1.3	4.0	16,800	19,400

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

TABLE 3

PROPERTIES OF DENTIN

Dimensions of Specimens		Property Determined				
		Modulus of Elasticity			Elastic Limit	Compressive Strength
Diameter	Length	(1) Observed	(2) Corrected[a]	(3) Average of Column 2 Corrected[b]		
in.	in.	$x10^6$ psi	$x10^6$ psi	$x10^6$ psi	psi	psi
0.056	0.091	1.8	2.0		20,400	45,000
0.042	0.068	1.4	1.5		26,000	47,800
0.047	0.068	1.6	1.8		27,500	47,500
0.052	0.052	1.2	1.3		26,000	52,400
0.039	0.055	1.3	1.4		24,000	56,000
0.057	0.047	1.4	1.5		28,000	54,900
0.052	0.071	1.6	1.8		24,500	50,000
0.054	0.087	1.8	1.9		24,000	49,600
Average		1.5	1.6	4.1	25,100	50,400

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

TABLE 4

PROPERTIES OF COMBINATIONS OF ENAMEL AND DENTIN

Dimensions of Specimens		Property Determined				
		Modulus of Elasticity			Elastic Limit	Compressive Strength
		(1)	(2)	(3)		
Diameter	Length	Observed	Corrected[a]	Average of Column 2 Corrected[b]		
in.	in.	x10^6 psi	x10^6 psi	x10^6 psi	psi	psi
0.052	0.088	3.3	3.7		26,600	38,600
0.038	0.102	2.5	2.7		23,000	32,700
0.057	0.082	2.7	3.1		25,000	35,300
0.048	0.101	2.7	2.9		28,000	38,300
0.045	0.074	1.8	1.9		18,600	25,300
0.040	0.100	1.6	1.7		22,000	35,200
Average		2.4	2.7	5.0	23,900	34,200

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

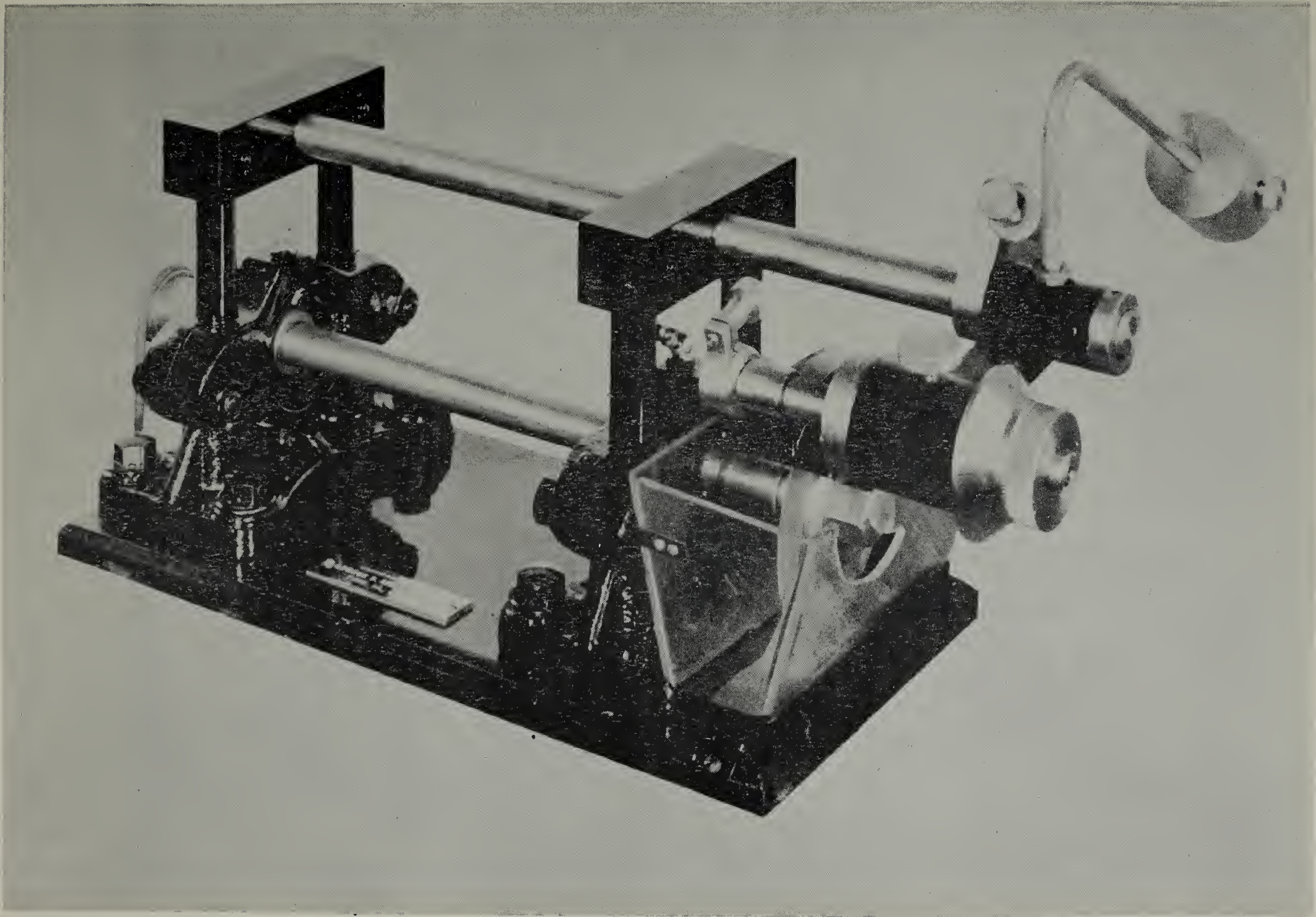

Figure 1. Tooth cutting machine.

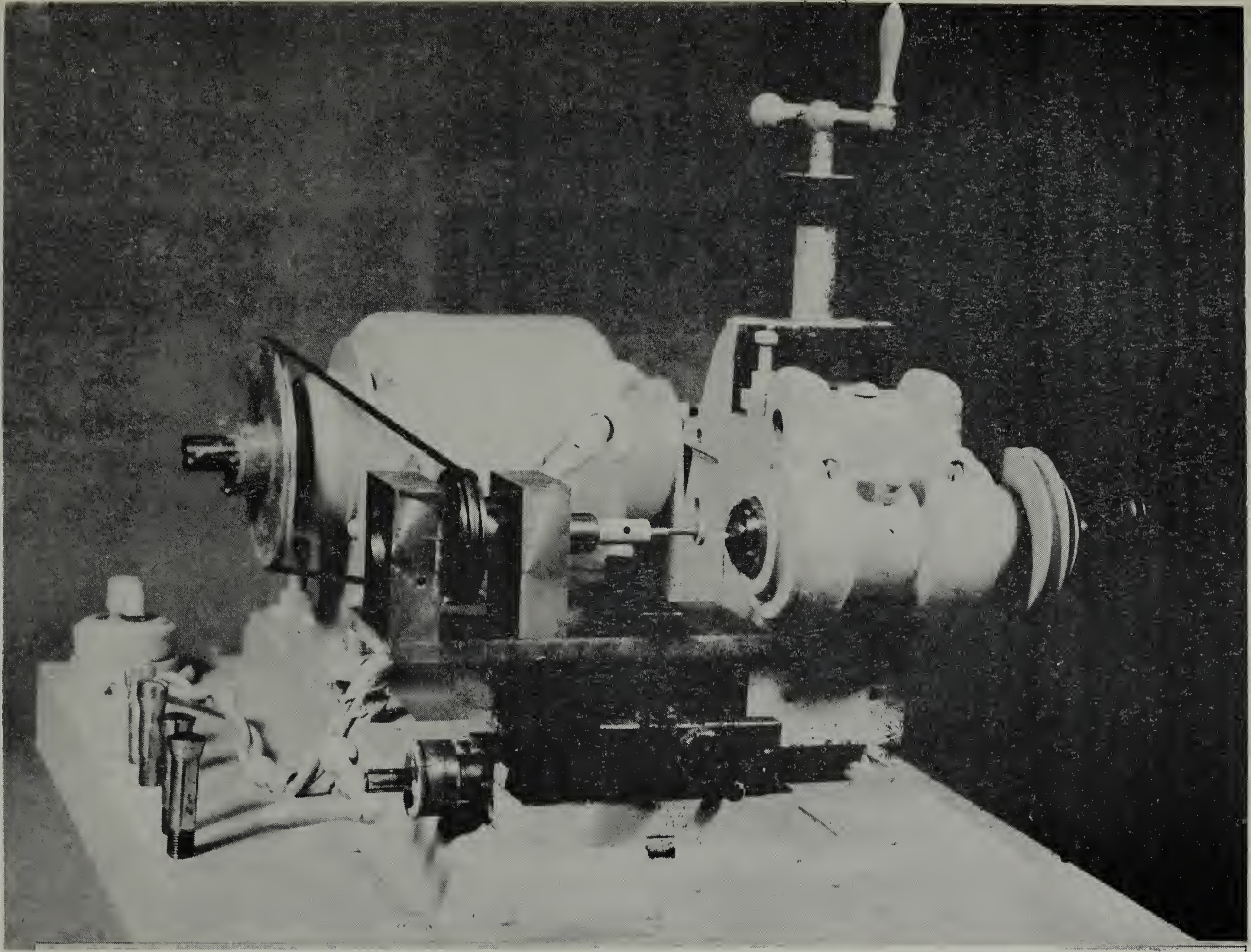

Figure 2. Milling machine used for making cylindrical specimens of enamel and dentin.

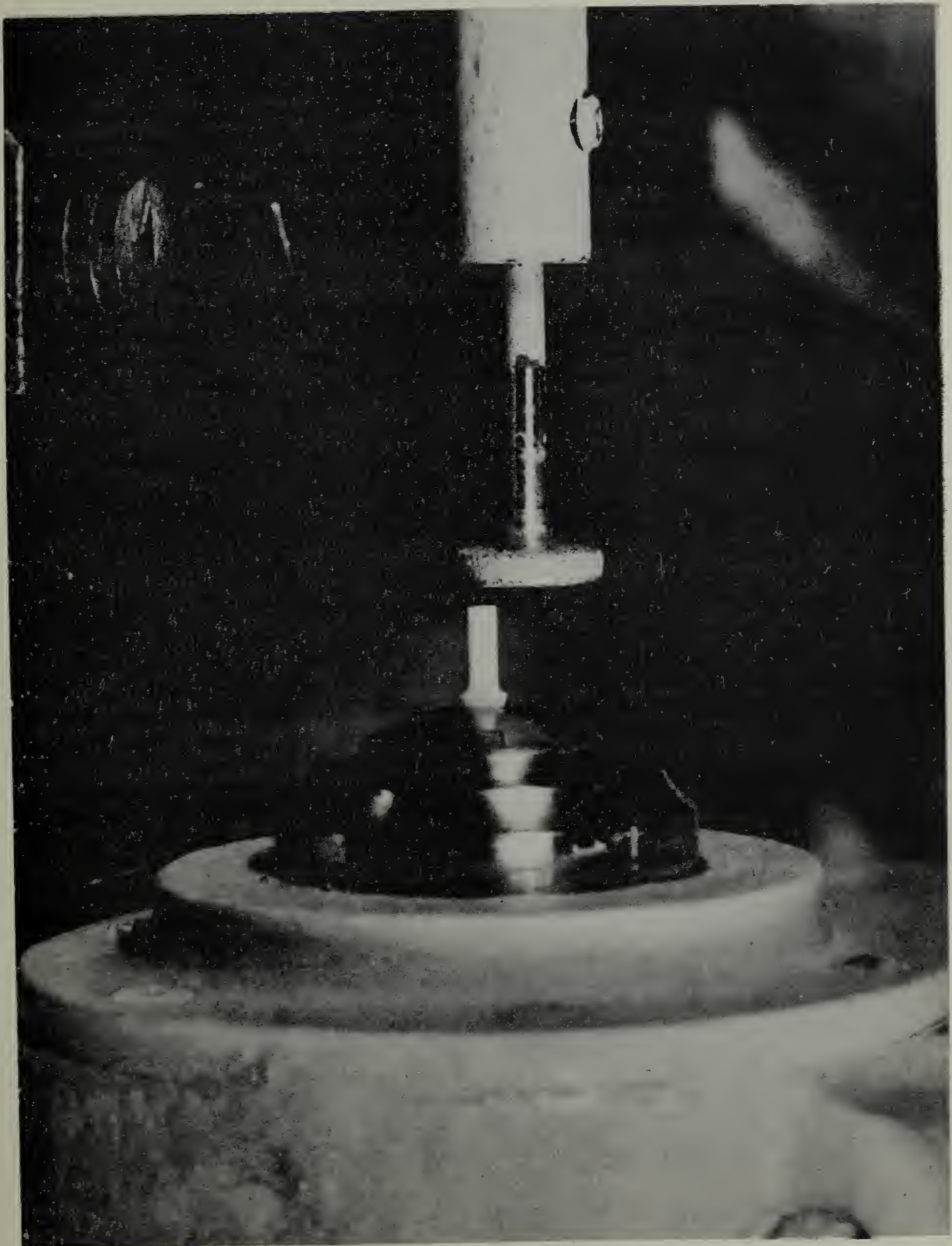

Figure 3. Close up of diamond wheel and tooth tissue in milling machine.

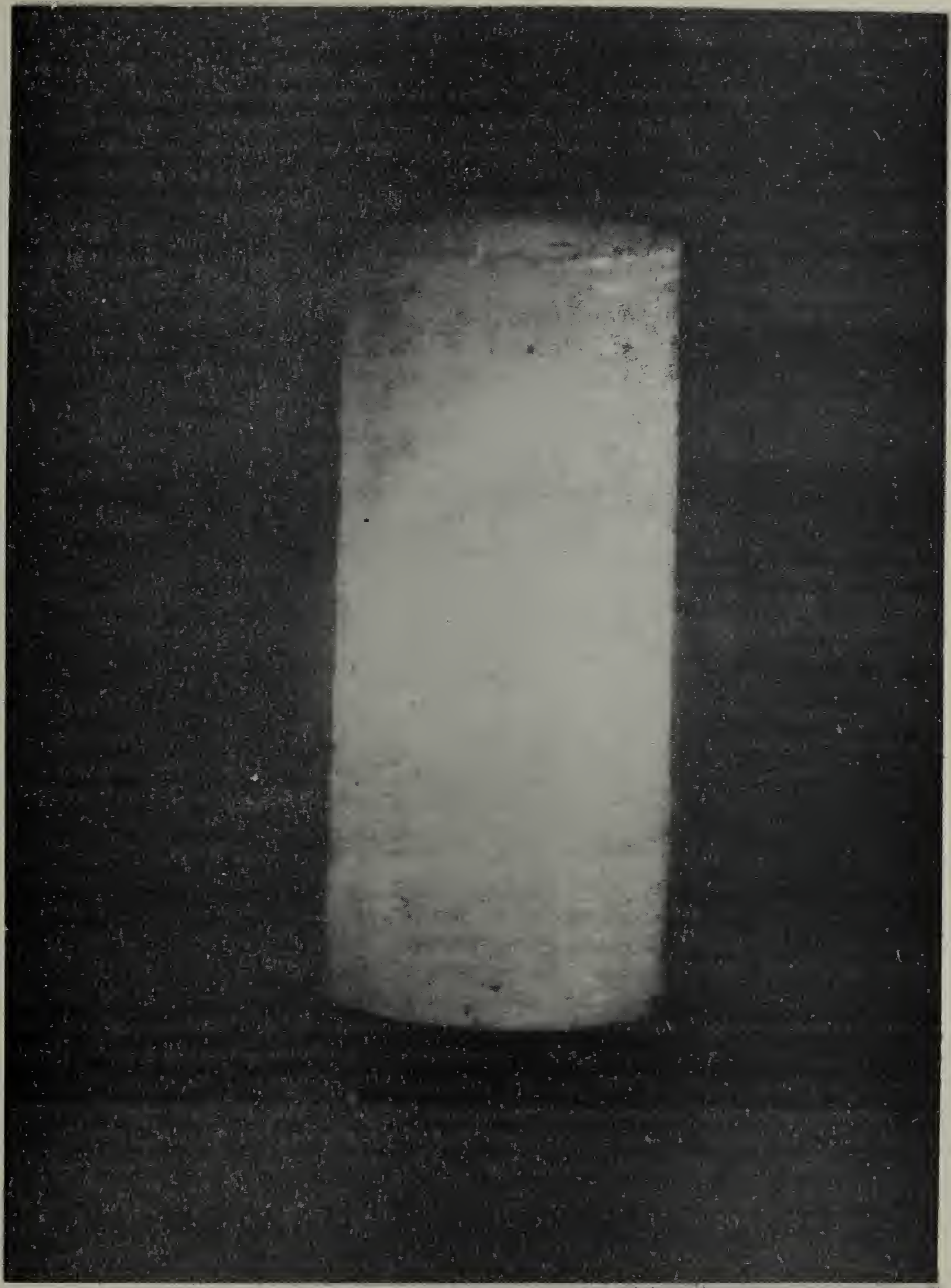

Figure 4. Specimen of hard tooth tissue.
Magnification 35X

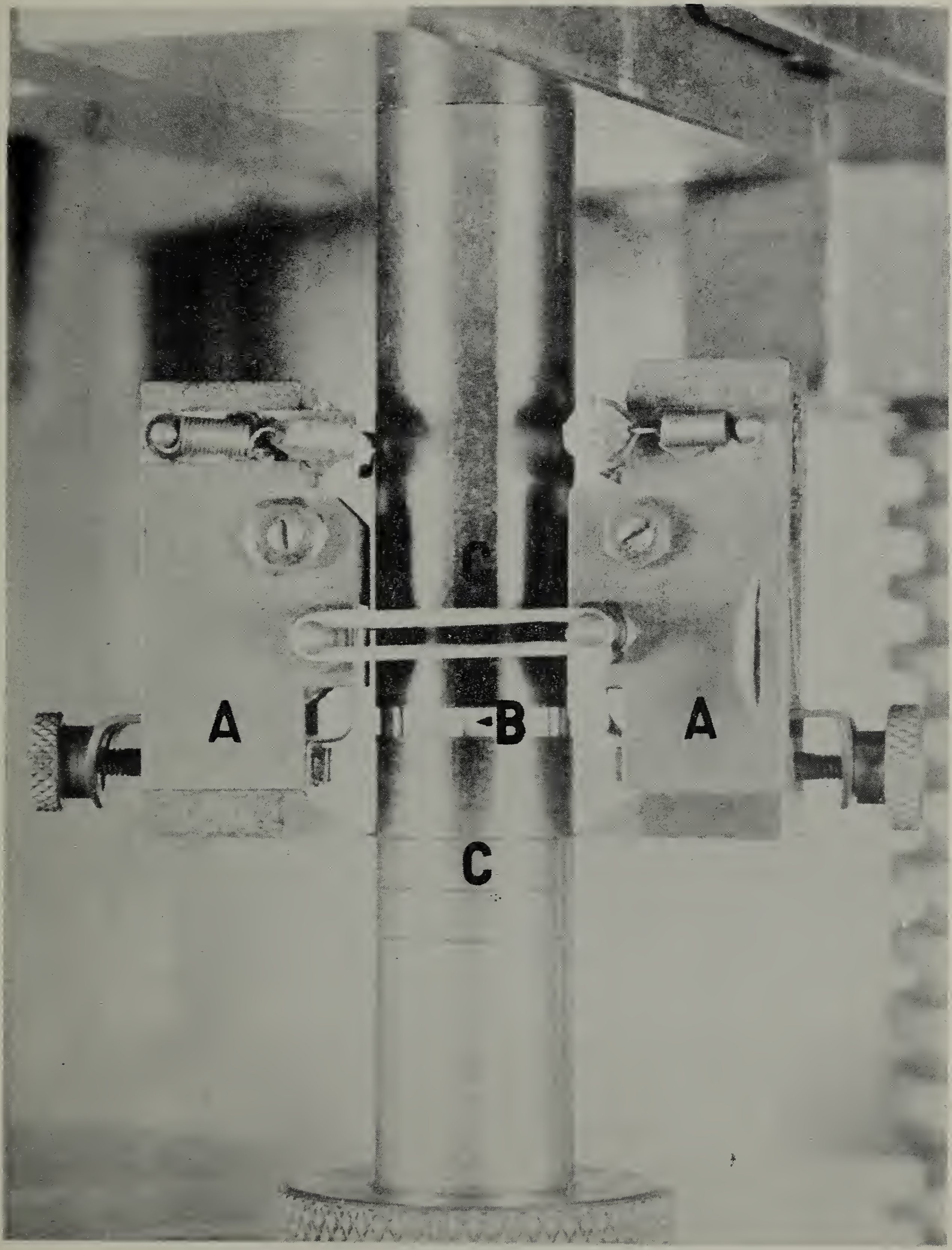

Figure 5. Specimen in position for determination of compressive properties.

A. Tuckerman strain gages
B. Specimen of hard tooth tissue
C. Platens

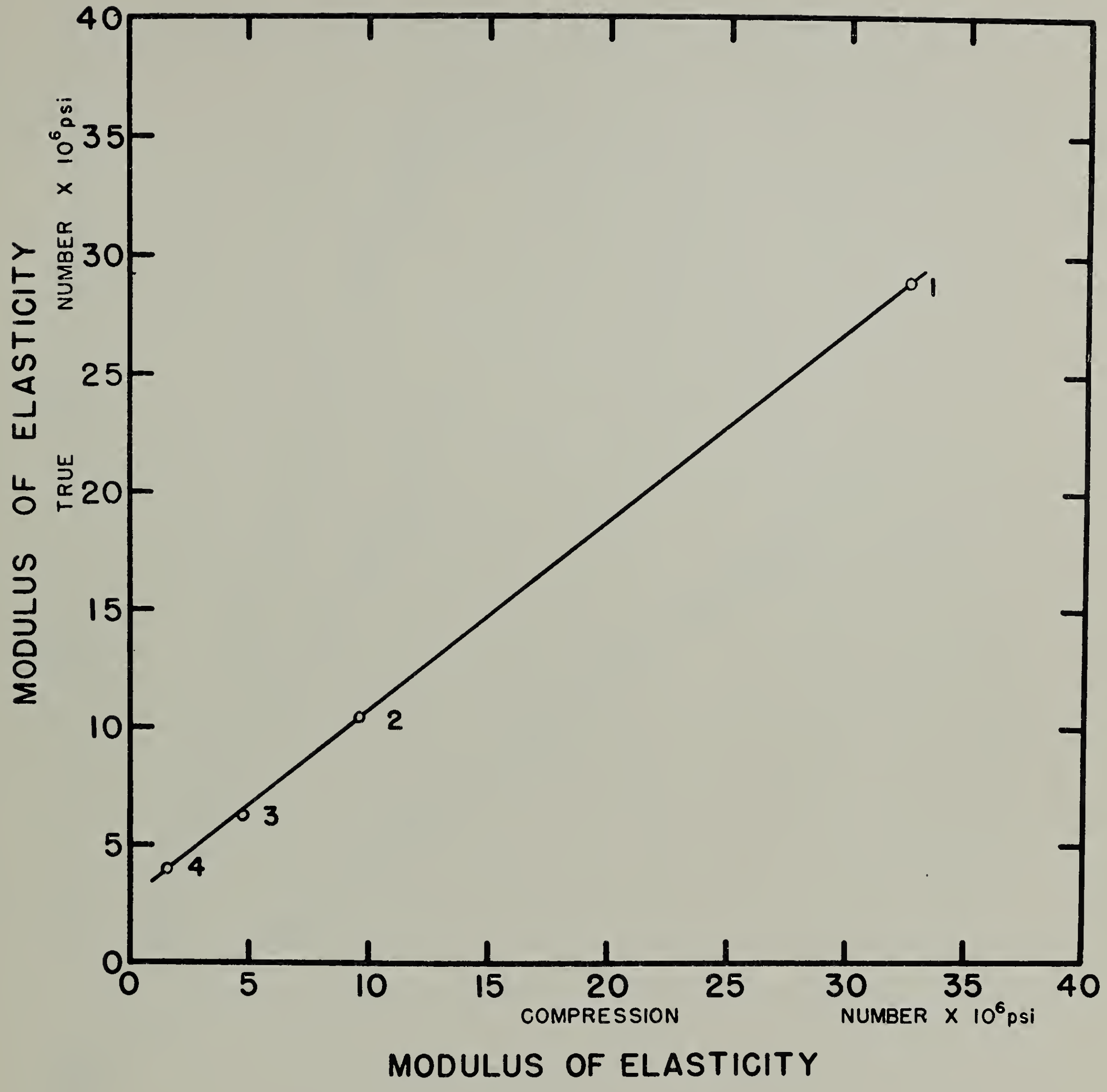

Figure 6. Calibration curve for modulus of elasticity determinations.

1. Steel
2. Aluminum
3. Magnesium
4. Dental Amalgam

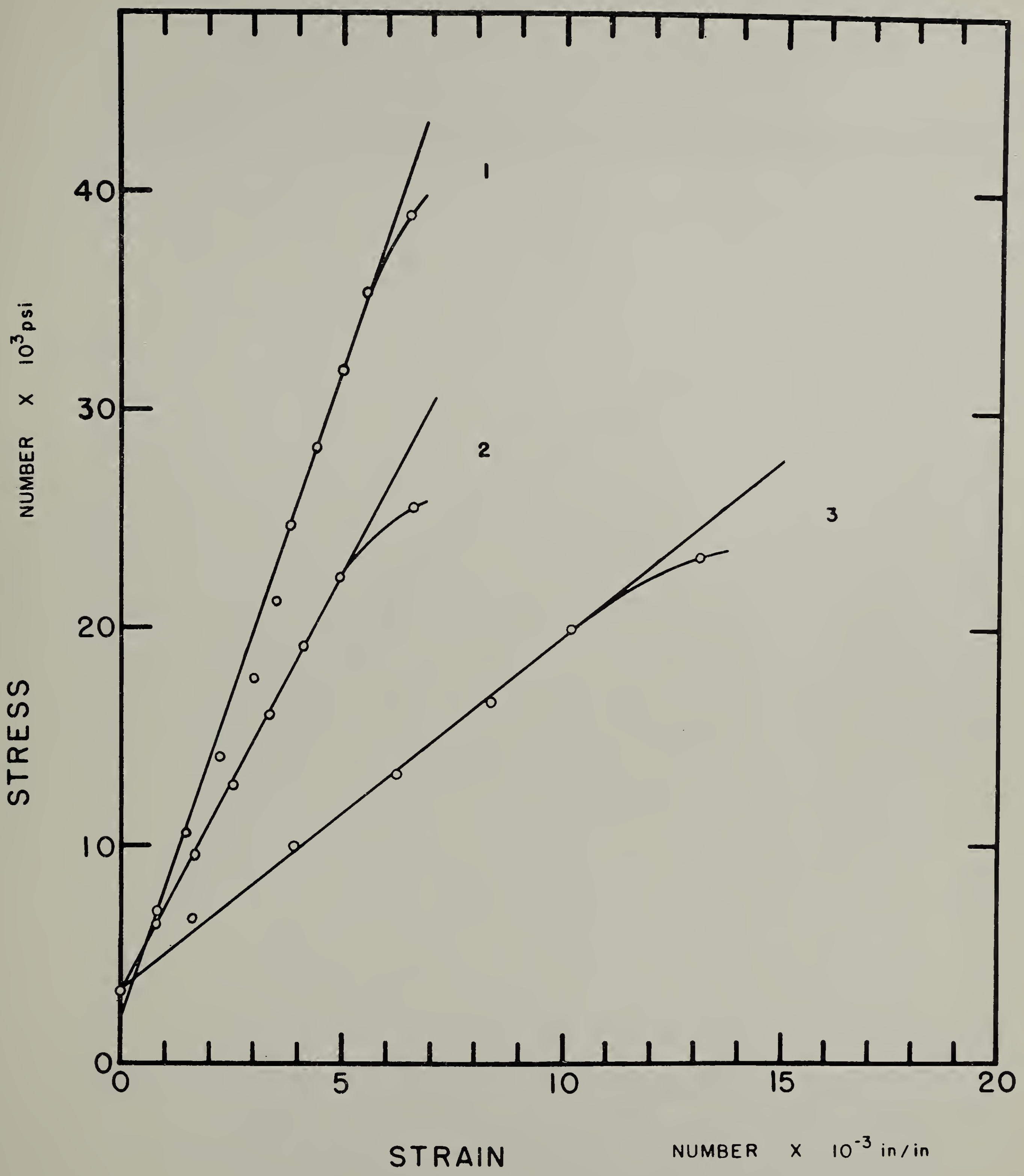

Figure 7. Representative stress-strain diagram for enamel.
1. Cusp
2. Side of tooth
3. Occlusal surface

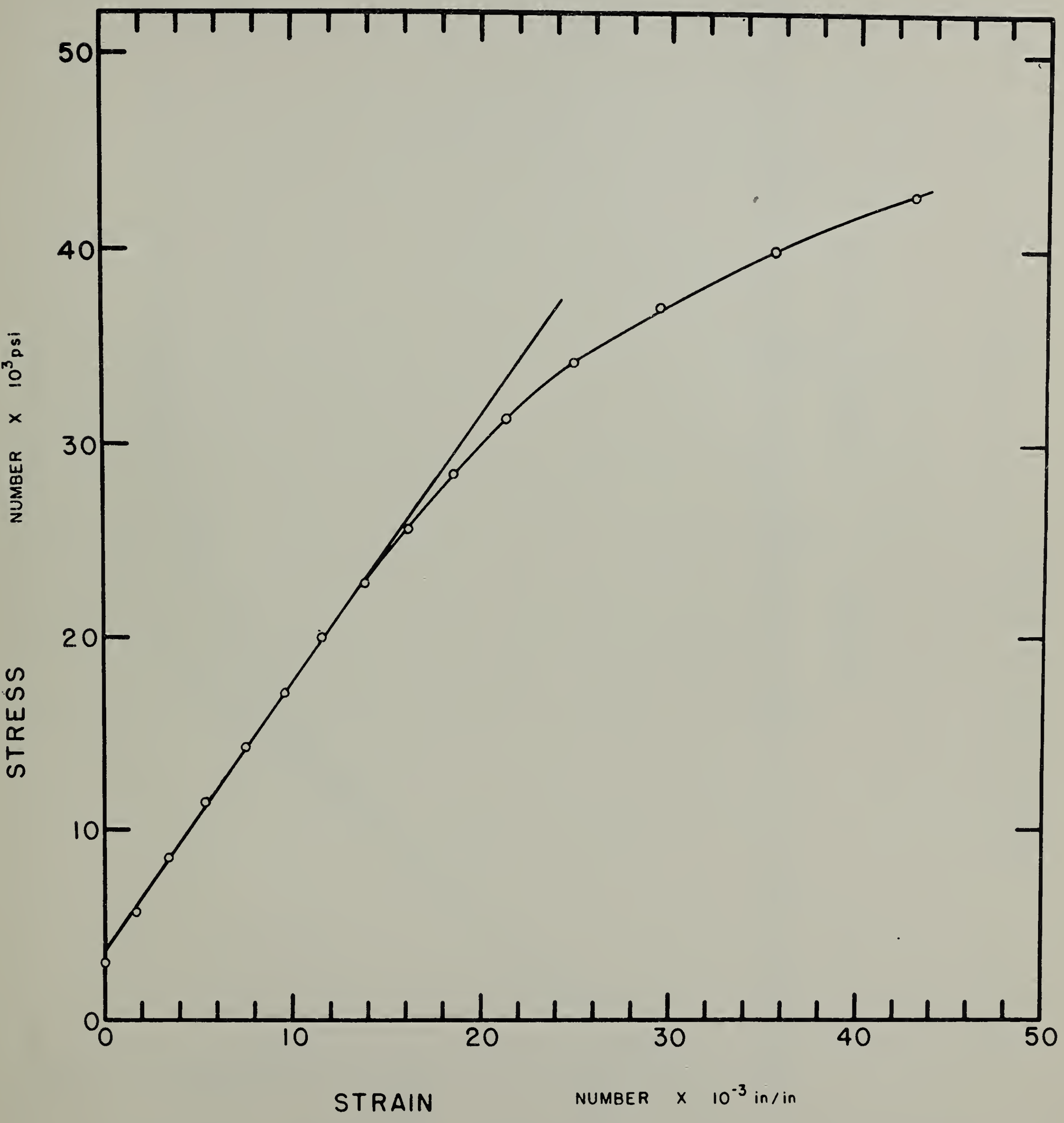

Figure 8. Representative stress-strain diagram for dentin.

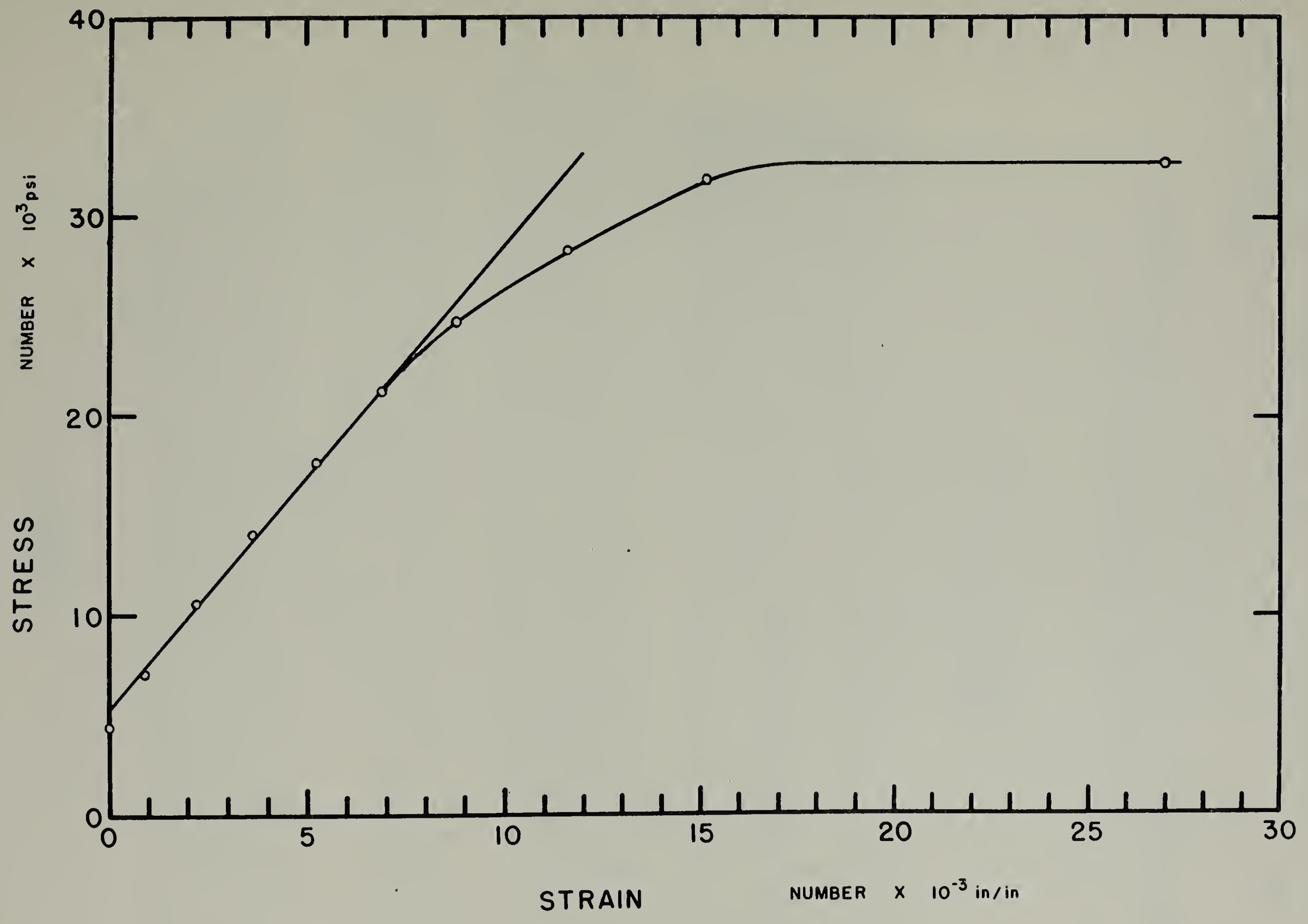

Figure 9. Representative stress-strain diagram for enamel and dentin combinations.

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

DETERMINATION OF SOME COMPRESSIVE PROPERTIES OF HUMAN ENAMEL AND DENTIN

by

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The data in this report were presented in a thesis by John W. Stanford in partial fulfillment of the requirements of the Graduate School, Georgetown University, Washington, D. C. for the degree of Master of Science.

NBS

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

DETERMINATION OF SOME COMPRESSIVE PROPERTIES OF HUMAN ENAMEL AND DENTIN

Abstract

A method of preparation of cylindrical specimens of hard tooth tissues by a grinding process has been developed. The results obtained show that the compressive properties of the tested enamel specimens fall into three categories depending on their original location: cusp, side and occlusal surface of the tooth. Values for enamel ranged from 4.0×10^6 to 8.2×10^6 psi for modulus of elasticity, from 15,000 to 34,000 psi for elastic limit and from 18,000 to 40,000 psi for compressive strength. Average values for dentin were 4.1×10^6 psi for modulus of elasticity; 25,000 psi for elastic limit; and 50,400 psi for compressive strength.

1. INTRODUCTION

A large amount of information on the physical properties of the restorative materials used in dentistry has been compiled during the past years. However, relatively few data have been published on the physical properties of the hard tooth tissue, the foundation for the restorative materials.

Knowledge of the physical properties of the hard tooth tissue is equally as important as knowledge of the restorative materials, since the success or failure of a restoration depends upon the properties of both the material and the tooth.

The objective of this research was to supply information on some mechanical properties of enamel and dentin. The properties determined, compressive strength, elastic limit, and modulus of elasticity, are defined as follows [1]:

1. Compressive strength is defined as the maximum compressive stress which a material is capable of developing, based on original area of cross-section. Standard tests for compressive strength specify test conditions such as size and shape of specimens in order that the stress at the critical cross-section will be, as nearly as practicable, uniaxially compressive. In an investigation of hard tooth tissue the quantity of material available is so limited that specimens cannot always be made to standard dimensions and the results obtained are not necessarily the same as would have been obtained under ideal conditions.

2. The elastic limit is defined as the greatest stress that a material is capable of developing without any permanent strain remaining upon complete release of the stress. Ordinarily, elastic limit and proportional limit of materials are considered to be approximately equal, and the elastic limit is determined as the highest stress on the straight-line portion

of the stress-strain diagram.

3. Modulus of elasticity is defined as the ratio of stress to the corresponding strain below the proportional limit. It is equal to the slope of the straight-line portion of the stress-strain diagram and is a measure of the stiffness of a material. The term modulus of elasticity alone generally refers to tensile modulus of elasticity. Moduli of elasticity in tension and compression are usually approximately equal for a given material.

An investigation of physical properties of tooth tissue was reported in 1895 by G. V. Black [2] who determined the crushing strength of 0.080 inch cubes of dentin. At that time he also reported an indication of the crushing strength of enamel. An average value for dentin was reported as 37,200 psi. With enamel specimens, whose dimensions were 0.080 inch x 0.080 inch x 0.040 inch, no matter how they were cut (as to direction of the enamel rods) or how the stress was applied, enamel rods would begin to split off with very light stress compared to dentin. The whole block collapsed at from 30 to 75 pounds load. (Approximately 4,700 to 11,700 psi).

Souder and Paffenbarger in 1942 [3] estimated the ultimate strength of sound enamel to be over 100,000 psi on the basis of its hardness compared to dentin. In 1952 Peyton, Mahler, and Hershenou [4] reported physical properties of cylinders of dentin prepared by a hollow drill coring method.

After the coring of the cylinders from the teeth, the ends of the specimens were finished to insure parallelism and flatness. Tuckerman Optical Strain Gages were used to determine the proportional or elastic limits of the dentin. The average values reported for dentin from this study were as follows:

1.	Modulus of Elasticity	1.67×10^6 psi
2.	Proportional limit	23,400 psi
3.	Compressive strength	36,100 psi

No values were reported on enamel.

2. EXPERIMENTAL PROCEDURE AND RESULTS

Cylindrical specimens as large as possible were prepared of enamel, dentin, and combinations of enamel and dentin including the dentino-enamel junction. The first method used in the preparation of specimens was a coring method similar to that reported by Peyton [4]. Hollow drills made of several different metals such as copper, bronze, and stainless steel were used. Different abrasives used varied from aluminum oxide to diamond dust. Also, diamond particles were embedded on a phosphor-bronze tool. Due to the shattering of the enamel it was impossible to obtain specimens with these tools. In an attempt to prepare specimens from dentin, only truncated cones could be produced by this method. The second method used consisted of grinding blocks of tooth tissue into cylinders. Freshly extracted teeth were mounted in rings with gypsum and slices were made into the tooth using the machine shown in

Figure 1. Slices were made approximately 0.1 inch apart. After these slices were made the teeth were remounted and slices were made at approximately 90 degrees to the previous ones. The resulting blocks were removed from the tooth and identified as to original location. These blocks were chucked in small collets in the milling machine shown in Figure 2. Different types and sizes of cutting wheels were used and it was found that the diamond cutting stone worked most efficiently. The tooth specimen and the diamond cutting stone were rotated in opposite directions. Light cuts were first made across the end of the block in order to true that end so that it would be perpendicular to the sides of the finished cylinder. Cuts were then made the length of the block until a cylindrical specimen was obtained as shown in Figure 3. At this point the tooth specimen was removed from the collet and turned end for end so that the excess could be removed and the ends made plane and parallel. All cutting and grinding operations were done with a steady dripping of water on the field of cutting, and the cylinders were stored in distilled water until tested. A typical specimen of hard tooth tissue is shown in Figure 4.

A Tinius Olsen testing machine operating over a range of 0 to 1000 lb. load was used as the loading device for applying stresses on the specimens. The platens were constructed of hardened tool steel (Figure 5). Two guide pins were fixed in the upper platen to align with holes in the

lower platen so that during loading the platens would not get out of line.

Because of the small size of the specimens of tooth tissue it was necessary in measuring the deformation to fasten the Tuckerman Strain Gages on the platens across the specimen length. A specimen in place between the platens is shown in Figure 5. The strain gages thus measured the deformation in both the specimen and that portion of the steel platens which lay within the gage length. The assumption that all the deformation measured took place over the length of the specimen would be a source of experimental error.

To determine the possible extent of this error, tests were conducted on materials for which the moduli of elasticity are well known. Small cylinders of carbon steel, AISI-1070; aluminum alloy, 2024-T4; and magnesium alloy, AZ31A, were prepared in a manner similar to that used in preparing those of tooth tissue, and tested in compression. Longer specimens of these three materials were also tested in tension. The results of the two types of tests did not agree. However, there are certain corrections which can be applied to this type of determination. The total deformation measured in conducting the compressive test involves four separate items which are designated as follows:

Item 1. Actual deformation or shortening of the specimen.

Item 2. Gap effect or apparent shortening due to imperfect fit of ends of specimens with platens. Included here would

also be the effect of friction between platens and ends of specimens restricting lateral expansion of the specimens near the ends.

Item 3. Elastic shortening of the platens over the gage length involved.

Item 4. Deformation of the platen surfaces or foundation effects.

There is no known equation for the correction of item 2 since it involves probability of how the platens contact the ends of the specimens.

The deformation correction, U, for item 3, the elastic shortening of the platens, is given by Hooke's law [5]:

$$U = \frac{P(L_g - L_s)}{E_p \times A_p} \qquad \text{(a)}$$

Where: P = load in pounds.

L_g = gage length of strain gage in inches.

L_s = length of specimen in inches.

E_p = modulus of elasticity of the steel platen.

A_p = cross-sectional area of platen.

The deformation correction, V, for item 4, the foundation effect for each platen, is given by the following equation [6]:

$$V = \frac{mP(1 - \nu_p^2)}{E_p \sqrt{A_s}} = \frac{P}{E_p \times d_s} \qquad \text{(b)}$$

Where: m = a function of the shape of section, 0.96 for circular cross-section.

ν_p = Poissons ratio of the platen, 0.28 for steel

A_s = Cross-sectional area of specimen,

$\frac{\pi d_s^2}{4}$, where d_s = diameter of specimen.

Then the corrected deformation, Δ, from (a) and (b) is given by:

$$\Delta = Z - (U+2V) = Z - \frac{P}{E_p}\left[\left(\frac{L_g - L_s}{A_p}\right) + \frac{2}{d_s}\right] \qquad (c)$$

Where Z = observed deformation, inches.

Then the strain, ε, = $\frac{\Delta}{L_s}$, and the modulus of elasticity of the specimen in compression is given by:

$$E_s = \frac{P}{A_s \varepsilon} \qquad (d)$$

Equation (d) was evaluated for the three known materials after corrections in deformations (equation c) were made. The results are shown compared to the observed moduli in compression and tension in Table 1. Also accepted or "True Moduli" in tension are shown for comparison.

Examination of Table 1 showed that the corrected values of moduli in compression still differed from the measured or accepted values in tension. Therefore, other factors are involved which cannot be corrected for by known equations. To compensate for these errors the accepted values of modulus of elasticity in tension were plotted as "True Moduli" versus

the corrected compression values and are shown in Figure 6. Also the modulus of elasticity of dental amalgam determined by Smith and Caul [7] using a direct measurement of deformation was plotted versus the modulus determined in compression using the same method employed in this research. The four plotted points in Figure 6 lie very nearly on a straight line. Tables 2, 3 and 4 of the results which are discussed in the following section include three average values for the modulus of elasticity. They are column 1, the observed experimental value; column 2, the corrected experimental value; and column 3, the average corrected value taken from the curve in Figure 6.

3. DISCUSSION OF RESULTS

The data for enamel, (Table 2), indicate that the values are related to the original location of the specimens in the teeth. The highest strength, modulus of elasticity and proportional limit were obtained for specimens of cusp enamel. This can possibly be explained by the presence of gnarled enamel rods in that area. The lowest values for these three properties determined on enamel were for specimens from the occlusal surface. Areas of possible decalcification may account for these lower values. Also during loading of this type of enamel specimen it was noted that at fracture the cylinder, instead of shattering, split lengthwise in tiny slivers. This type of failure would be expected if the general direction of the rods were lengthwise and if the pri-

mary failure were in the bonding material.

The values determined for specimens of enamel taken from the sides of the teeth fall between the above-mentioned determinations. In this location, the direction of enamel rods would tend to be perpendicular to the long axis of the specimen and this may account for the values obtained. Figure 7 shows a representative stress-strain curve for each area of the tooth enamel tested.

The data determined for dentin are shown in Table 3. No attempt was made to determine tubule direction in these specimens. The average value (50,400 psi) determined for compressive strength is higher than that reported by Peyton [3] (36,100 psi) whereas the values for the elastic limit and modulus of elasticity with the exception of the value for the modulus taken from Figure 6 are comparable. Figure 8 shows a representative stress-strain curve for dentin.

The data for the three properties on combinations of enamel and dentin are shown in Table 4. The values appear upon inspection to form two divisions depending upon the location of the dentino-enamel junction in the specimen. The higher values for the three properties were obtained on specimens in which the dentino-enamel junction peaked in approximately the center. The lower values obtained were on samples in which the dentino-enamel junction ran diagonally through the cylinder. However, the properties do vary from specimen

to specimen such that the differences may not be of significance. The average values for the three properties appear to fall between those determined for enamel and dentin separately. Figure 9 shows a representative stress-strain curve for dentin and enamel combinations.

4. SUMMARY

1. A method for preparation of small cylinders of hard tooth tissues was presented.
2. A calibration curve which may serve in evaluating determinations of moduli of elasticity in compression on small specimens of material was presented.
3. The average values determined in compression for the three properties are as follows:

Material	Modulus of Elasticity			Elastic Limit	Compressive Strength
	Observed	Corrected by Equations	From Curve Figure 6		
	x10^6 psi	x10^6 psi	x10^6 psi	psi	psi
Enamel					
Cusp	5.4	6.9	8.2	34,200	40,200
Side	3.8	4.4	6.3	21,200	28,200
Occlusal Surface	1.2	1.3	4.0	15,400	18,200
Dentin	1.5	1.6	4.1	25,100	50,400
Dentin and Enamel	2.4	2.7	5.0	23,900	34,200

5. BIBLIOGRAPHY

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TABLE 1

CALIBRATION DATA FOR DETERMINATION OF MODULUS OF ELASTICITY

Material	Observed E Compression	Corrected E Compression	Observed E Tension	Accepted* E Tension
	x10^6 psi	x10^6 psi	x10^6 psi	x10^6 psi
Magnesium alloy, AZ31A	4.2	4.8	6.5	6.5
Aluminum alloy, 2024-T4	7.2	9.6	10.5	10.6
Carbon Steel, AISI-1070	14.0	32.5	28.0	29.0

* Source: Metals Handbook, The American Society for Metals, 1948.

TABLE 2

PROPERTIES OF ENAMEL

Original Location of Specimens in Tooth	Dimensions of Specimens		Property Determined				
			Modulus of Elasticity			Elastic Limit	Compressive Strength
	Diameter	Length	(1) Observed	(2) Corrected[a]	(3) Average of Column 2 Corrected[b]		
	in.	in.	$x10^6$ psi	$x10^6$ psi	$x10^6$ psi	psi	psi
Tips of Cusps	0.038	0.079	6.1	7.4		38,900	42,500
	0.040	0.065	5.3	6.7		32,000	37,600
	0.038	0.050	5.7	7.8		35,000	39,800
	0.033	0.057	4.6	5.8		31,000	41,100
Average			5.4	6.9	8.2	34,200	40,200
Side	0.038	0.071	3.8	4.3		15,000	26,600
	0.040	0.064	4.0	4.8		25,600	26,400
	0.042	0.057	4.0	4.8		24,000	31,900
	0.040	0.061	3.2	3.8		20,000	28,000
Average			3.8	4.4	6.3	21,000	28,200

Table 2 (Continued)

Original Location of Specimens in Tooth	Dimensions of Specimens		Property Determined				
			Modulus of Elasticity				
			(1)	(2)	(3) Average of Column 2	Elastic Limit	Compressive Strength
	Diameter	Length	Observed	Corrected[a]	Corrected[b]		
	in.	in.	$x10^6$ psi	$x10^6$ psi	$x10^6$ psi	psi	psi
Occlusal Surface	0.062	0.065	1.4	1.6		10,000	11,200
	0.039	0.041	1.6	1.8		20,000	23,300
	0.040	0.028	0.4	0.4		16,000	20,800
	0.040	0.044	0.9	0.9		17,600	18,000
	0.039	0.059	0.8	0.8		20,000	22,500
	0.058	0.054	2.1	2.5		17,000	20,800
Average	...	...	1.2	1.3	4.0	16,800	19,400

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

TABLE 3

PROPERTIES OF DENTIN

Dimensions of Specimens		Property Determined				
		Modulus of Elasticity			Elastic Limit	Compressive Strength
		(1)	(2)	(3) Average of Column 2		
Diameter	Length	Observed	Corrected[a]	Corrected[b]		
in.	in.	x10^6 psi	x10^6 psi	x10^6 psi	psi	psi
0.056	0.091	1.8	2.0		20,400	45,000
0.042	0.068	1.4	1.5		26,000	47,800
0.047	0.068	1.6	1.8		27,500	47,500
0.052	0.052	1.2	1.3		26,000	52,400
0.039	0.055	1.3	1.4		24,000	56,000
0.057	0.047	1.4	1.5		28,000	54,900
0.052	0.071	1.6	1.8		24,500	50,000
0.054	0.087	1.8	1.9		24,000	49,600
Average		1.5	1.6	4.1	25,100	50,400

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

TABLE 4

PROPERTIES OF COMBINATIONS OF ENAMEL AND DENTIN

Dimensions of Specimens		Property Determined				
		Modulus of Elasticity				
		(1)	(2)	(3)	Elastic Limit	Compressive Strength
Diameter	Length	Observed	Corrected[a]	Average of Column 2 Corrected[b]		
in.	in.	$\times 10^6$ psi	$\times 10^6$ psi	$\times 10^6$ psi	psi	psi
0.052	0.088	3.3	3.7		26,600	38,600
0.038	0.102	2.5	2.7		23,000	32,700
0.057	0.082	2.7	3.1		25,000	35,300
0.048	0.101	2.7	2.9		28,000	38,300
0.045	0.074	1.8	1.9		18,600	25,300
0.040	0.100	1.6	1.7		22,000	35,200
Average		2.4	2.7	5.0	23,900	34,200

[a] Modulus of Elasticity corrected for elastic shortening of the platens and deformation of the platen surfaces.

[b] Average Modulus of Elasticity corrected as in (a) and then read from curve in Figure 6, thus correcting for factors which cannot be evaluated by known equations in testing small specimens.

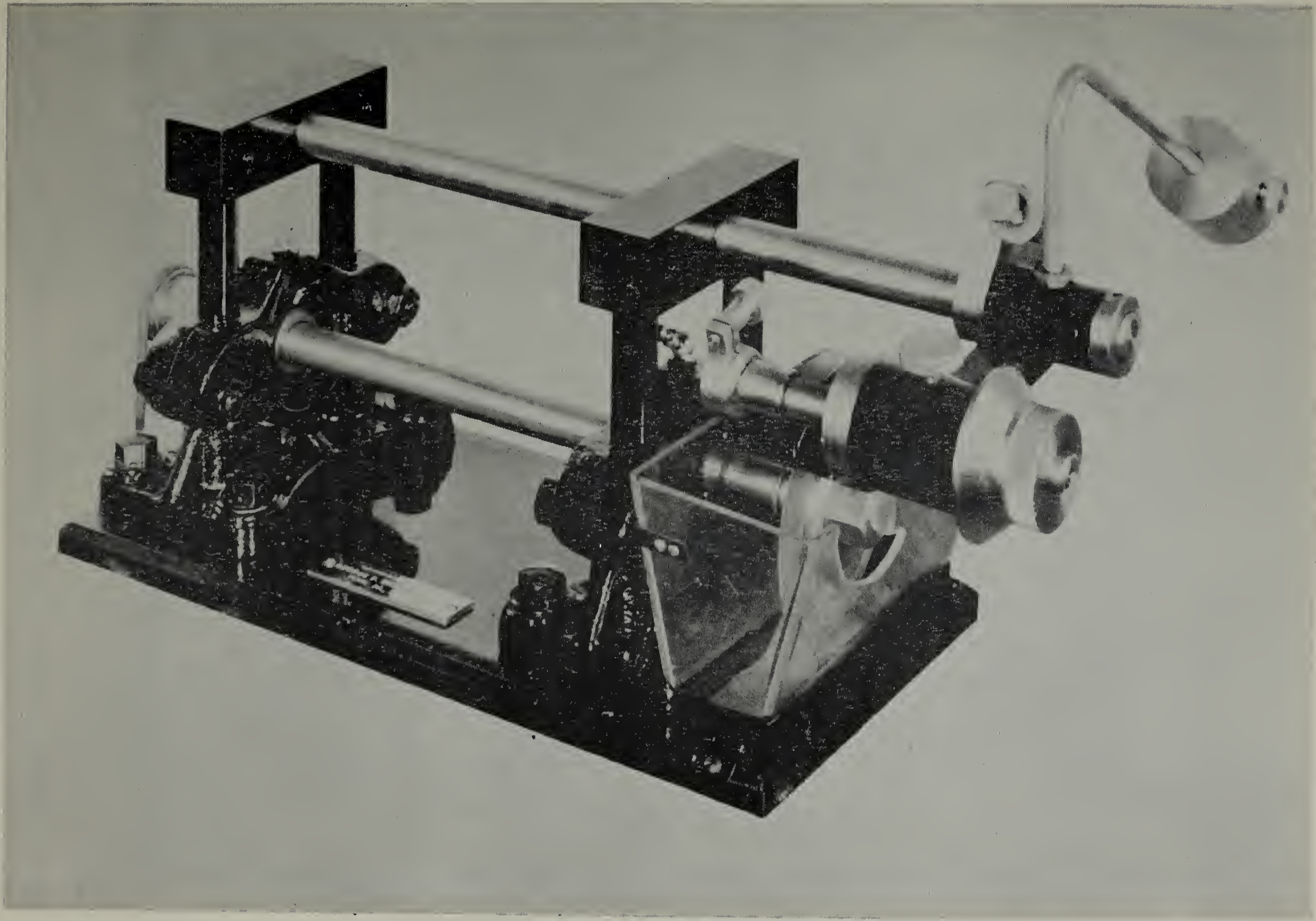

Figure 1. Tooth cutting machine.

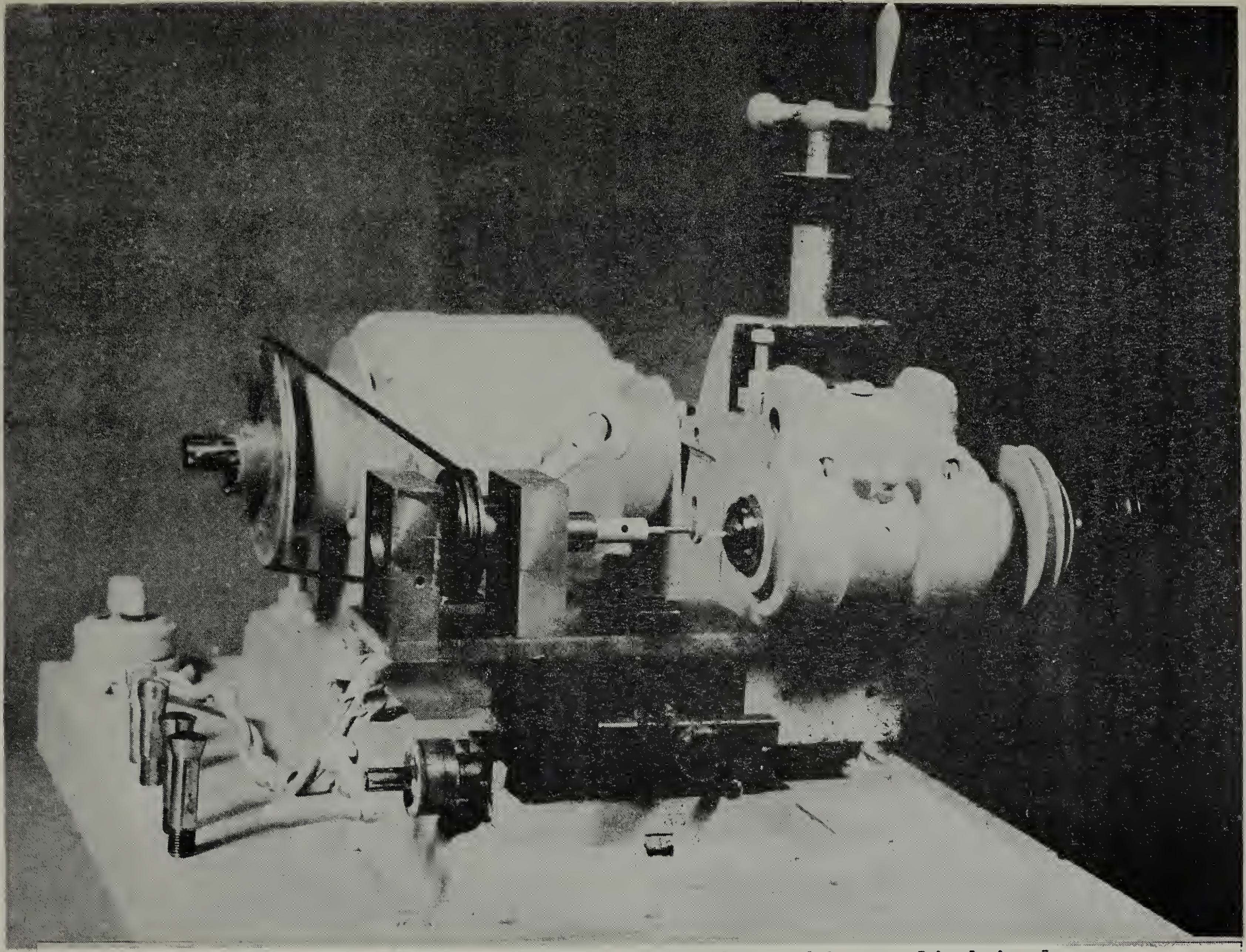

Figure 2. Milling machine used for making cylindrical specimens of enamel and dentin.

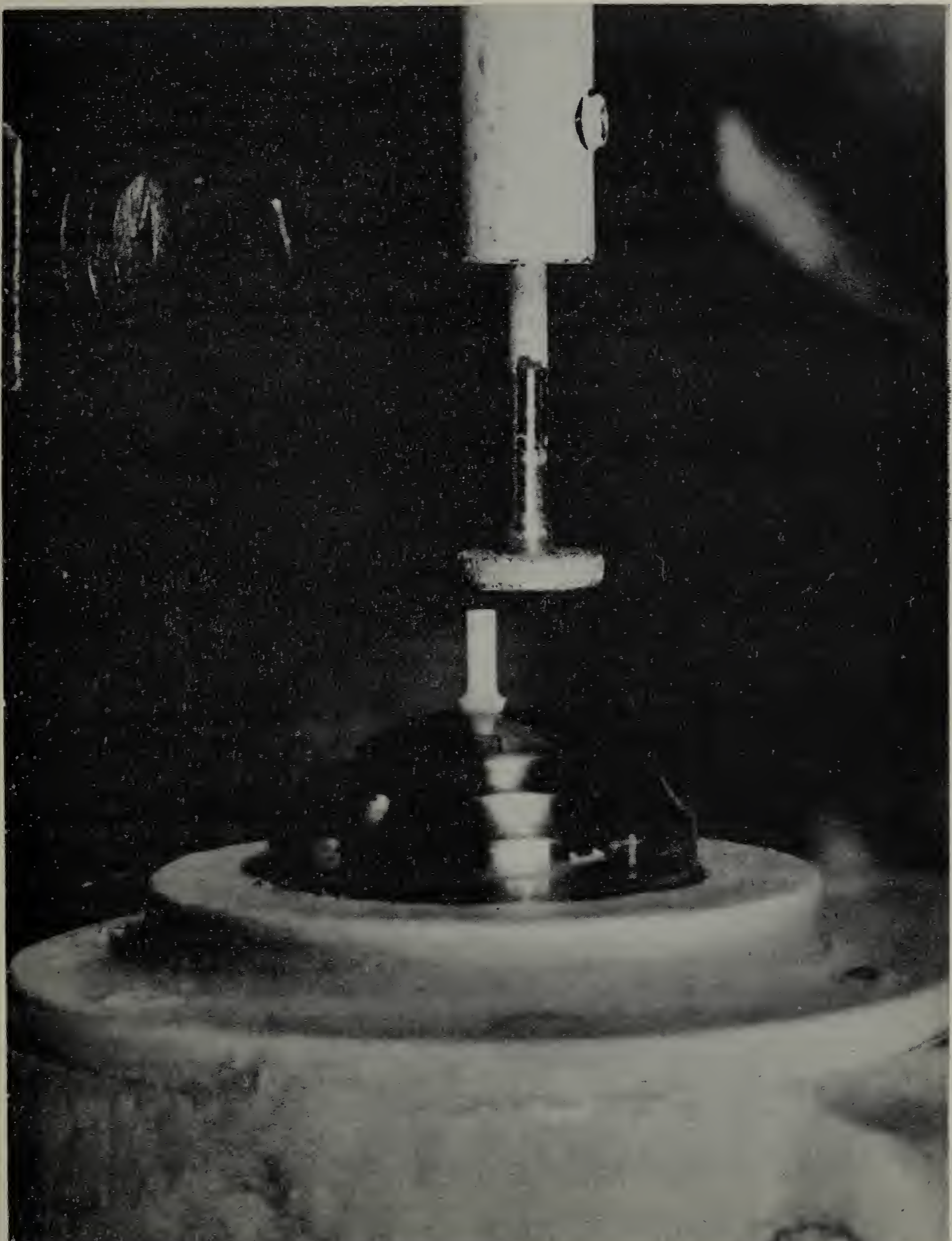

Figure 3. Close up of diamond wheel and tooth tissue in milling machine.

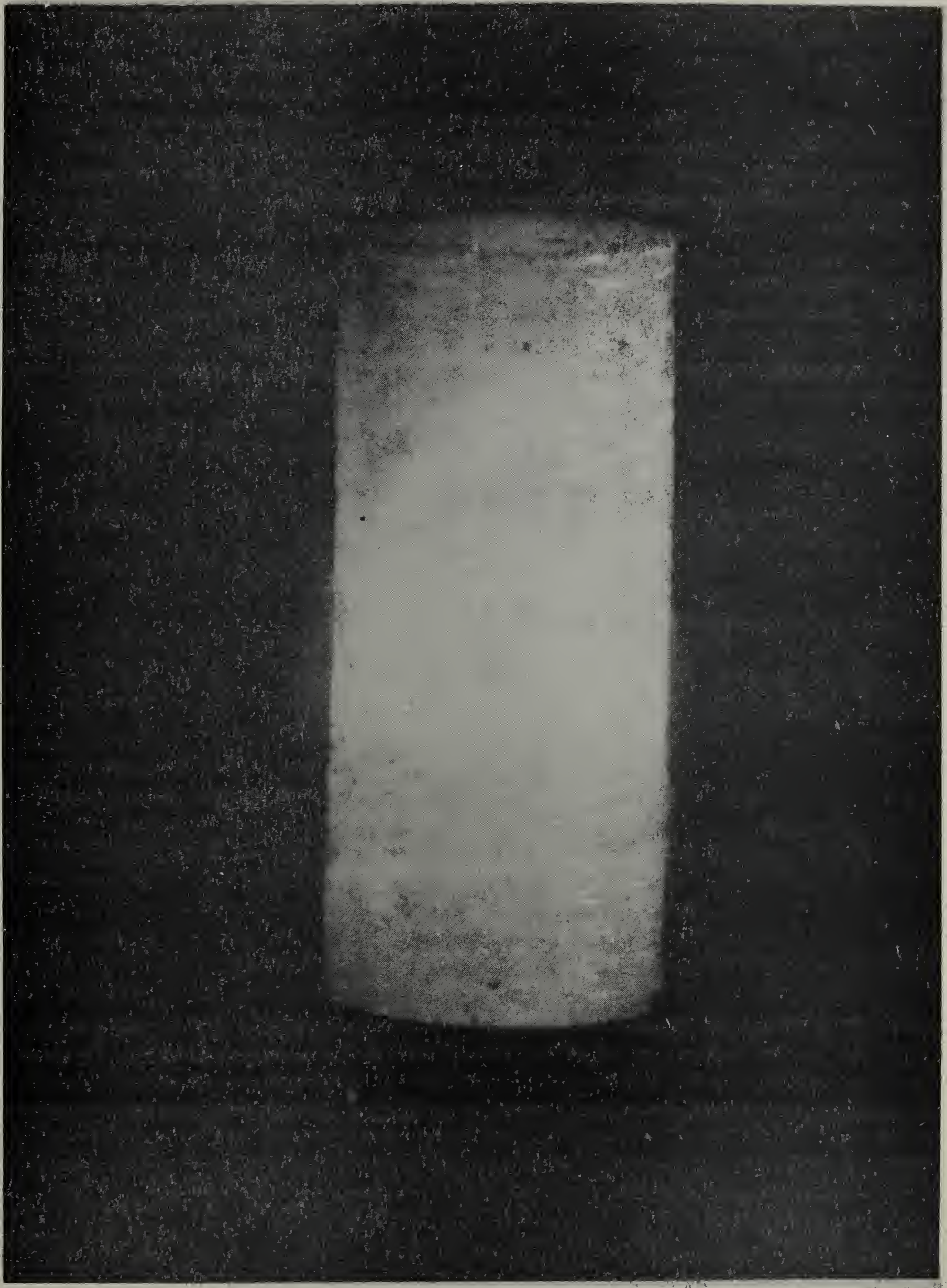

Figure 4. Specimen of hard tooth tissue.
Magnification 35X

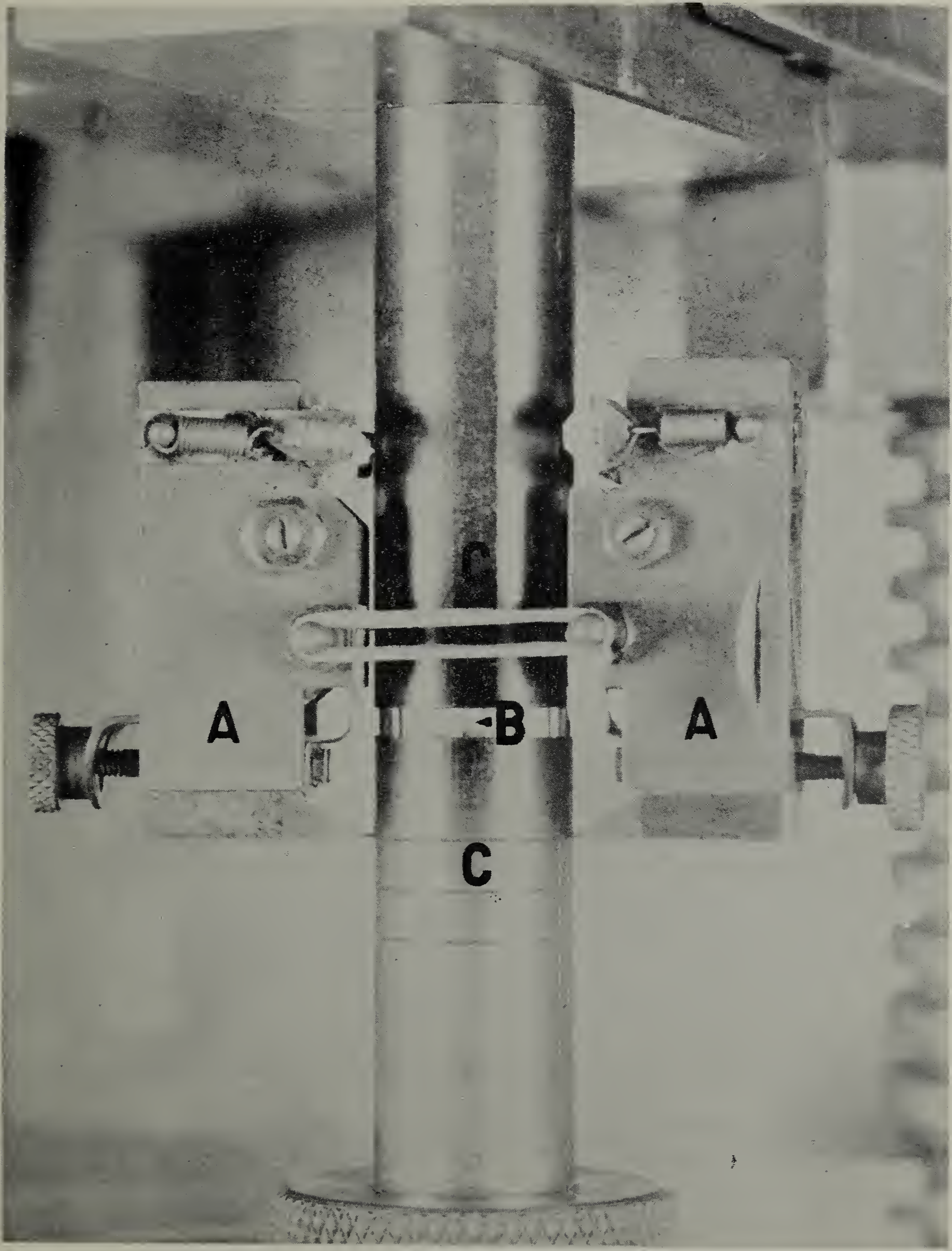

Figure 5. Specimen in position for determination of compressive properties.

A. Tuckerman strain gages
B. Specimen of hard tooth tissue
C. Platens

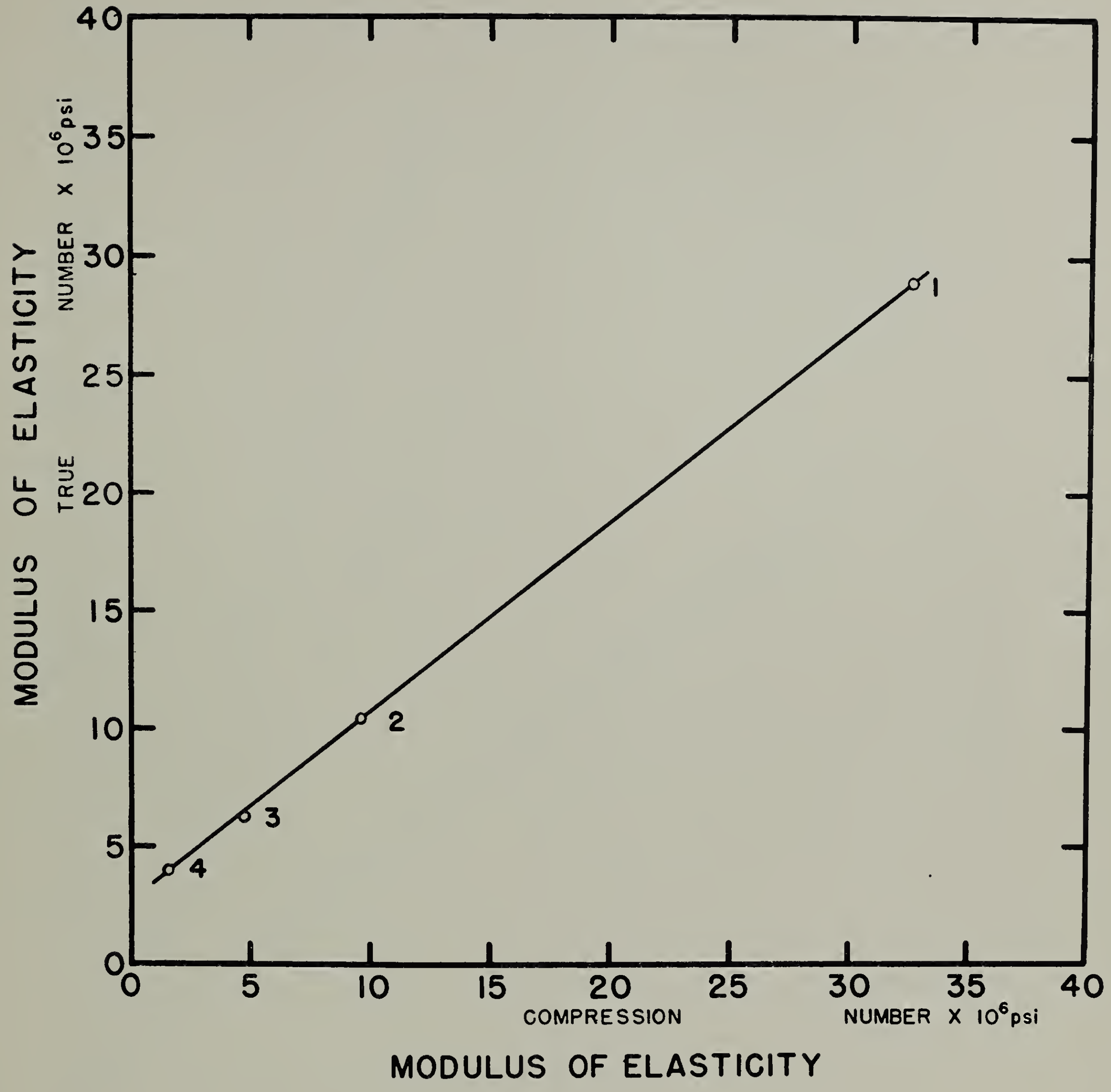

Figure 6. Calibration curve for modulus of elasticity determinations.

1. Steel
2. Aluminum
3. Magnesium
4. Dental Amalgam

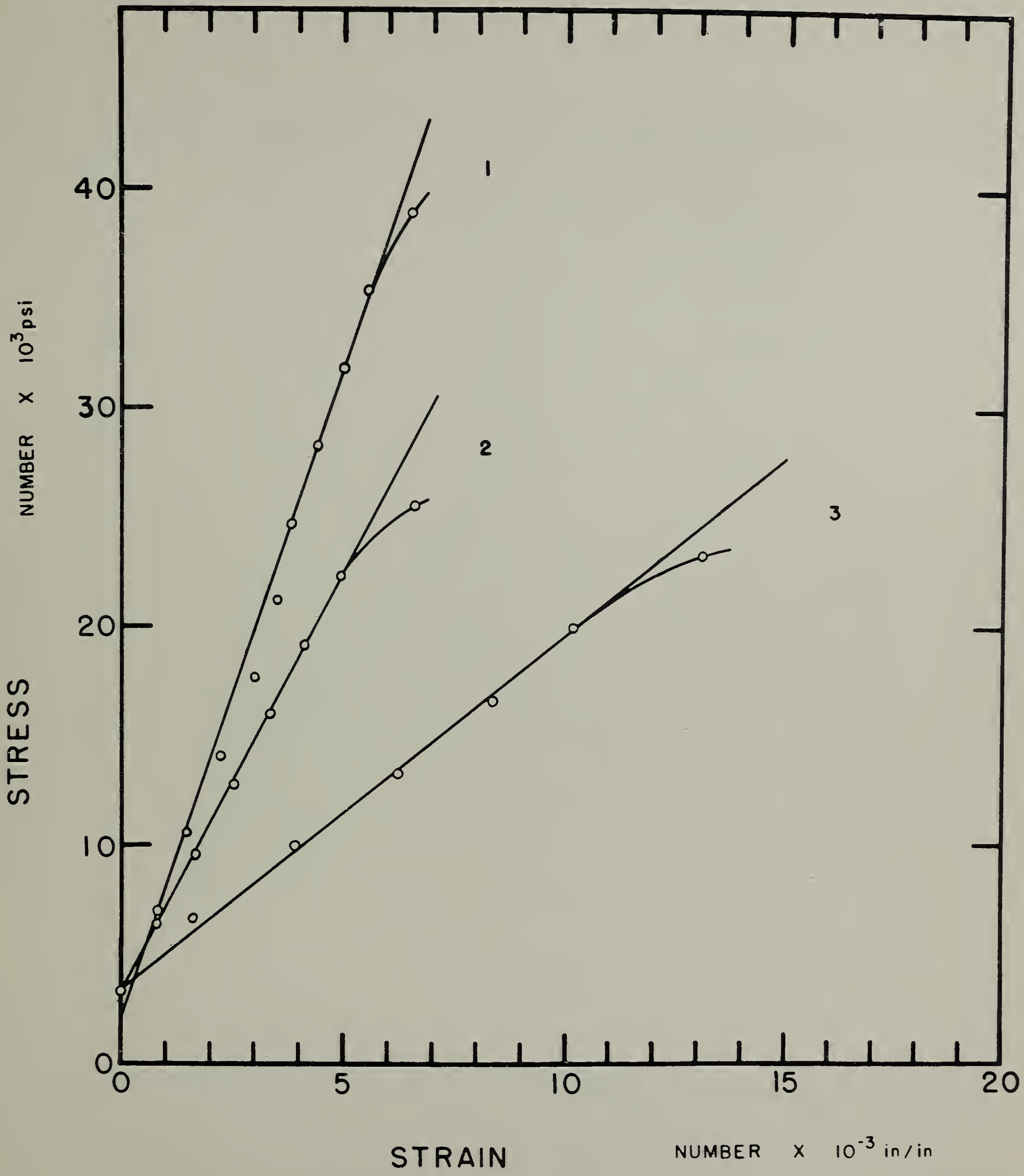

Figure 7. Representative stress-strain diagram for enamel.
1. Cusp
2. Side of tooth
3. Occlusal surface

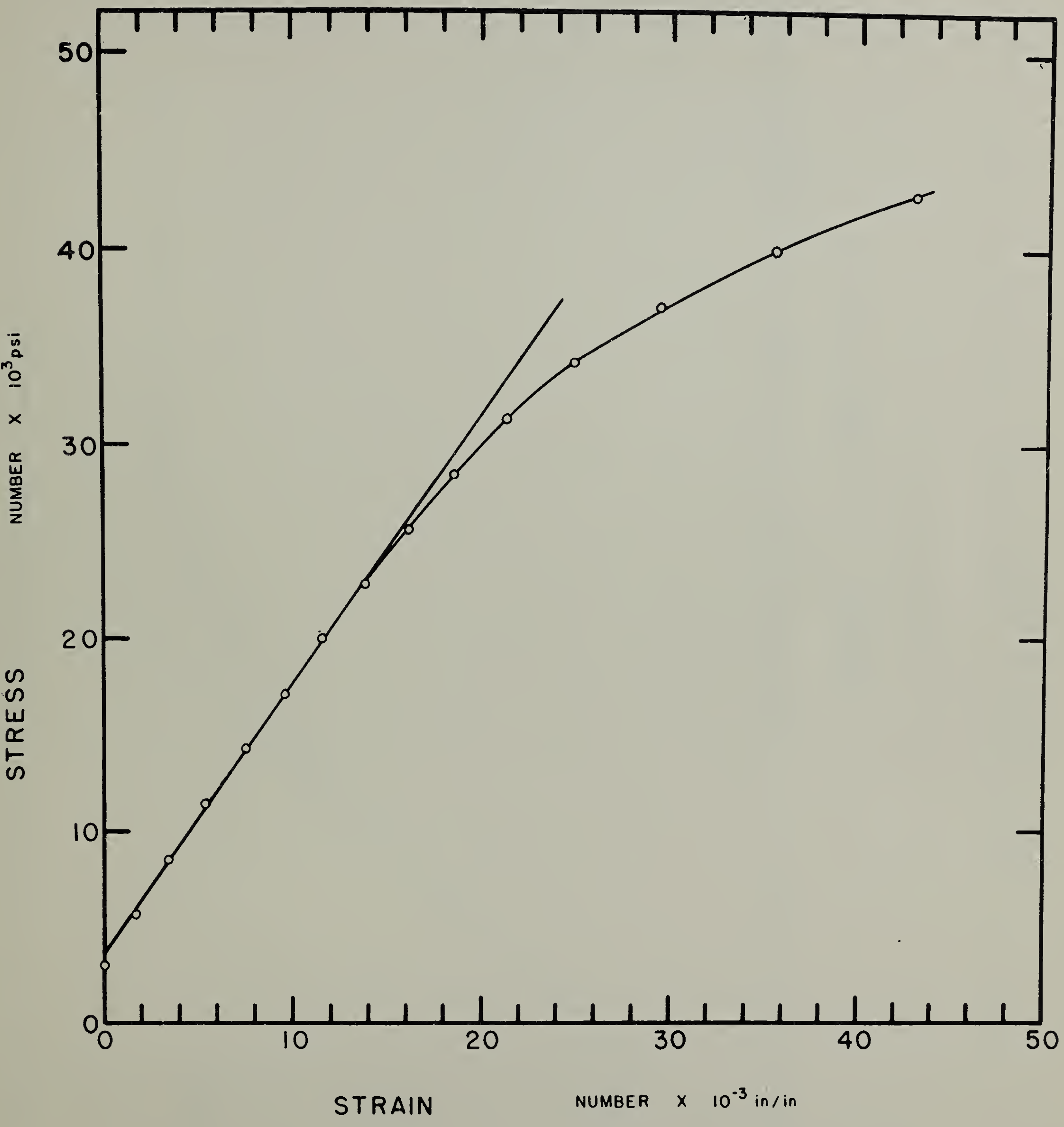

Figure 8. Representative stress-strain diagram for dentin.

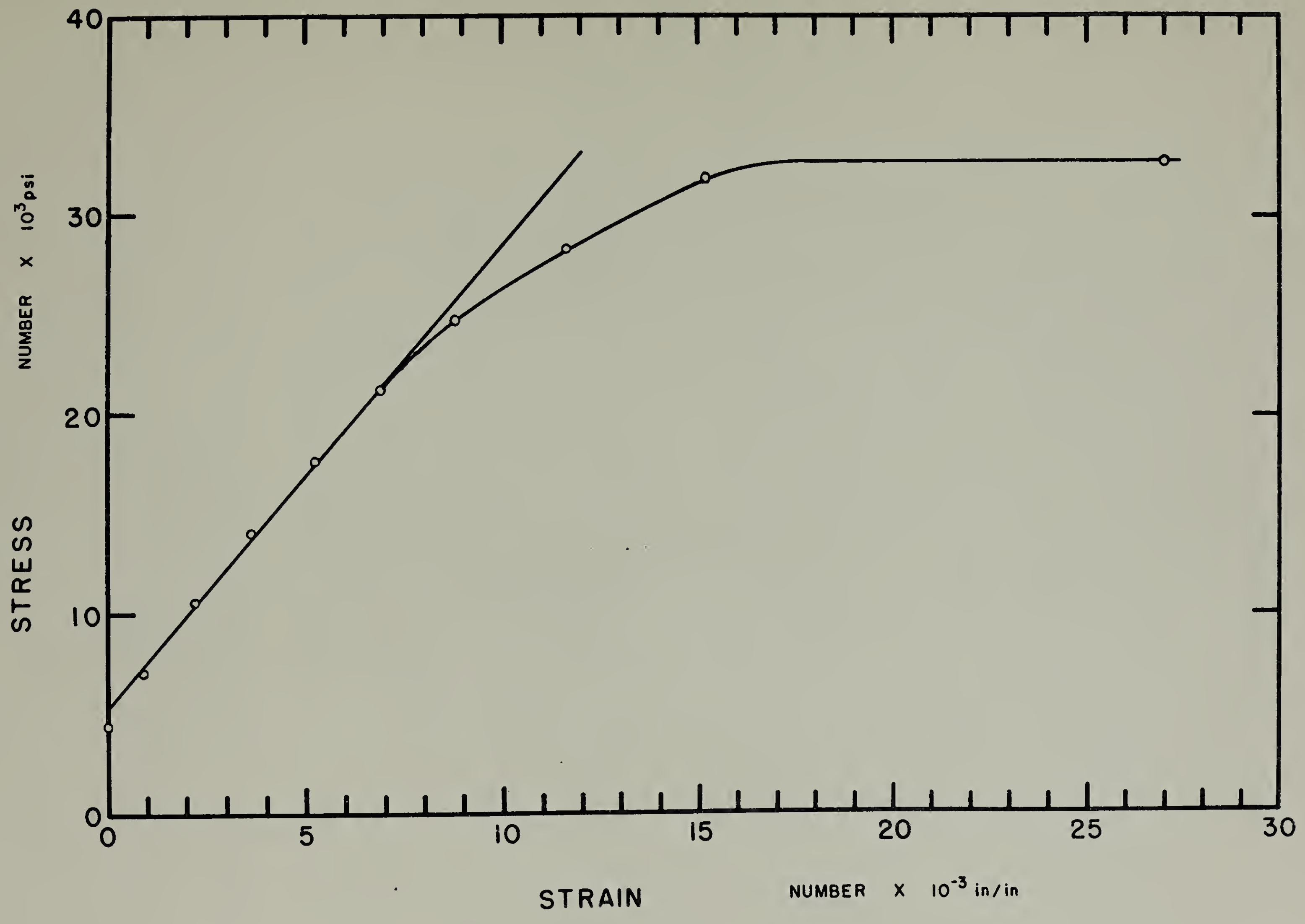

Figure 9. Representative stress-strain diagram for enamel and dentin combinations.

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