1955-2 Geo. C. Poffenberger

NATIONAL BUREAU OF STANDARDS REPORT

4548

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

July 1 to December 31, 1955

Dental Research Laboratory

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section is engaged in 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 of the back cover of this report.

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

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

Heat and Power. Temperature Measurements. Thermodynamics. Cryogenic Physics. Engines 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.

Mineral Products. Porcelain and Pottery. 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. Components and Techniques. Digital Circuitry. Digital Systems. Analogue Systems.

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

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services.

Radio Propagation Engineering. Frequency Utilization Research. Tropospheric Propagation Research.

Radio Standards. High Frequency Standards. Microwave Standards.

- Office of Basic Instrumentation
- Office of Weights and Measures

NATIONAL BUREAU OF STANDARDS REPORT

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0708-10-0707 0708-20-3824 0708-20-3857	January 31, 1956	4548

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

July 1 to December 31, 1955

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.

(Task 7756-41 BV No. 55-14)

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REPORT OF DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Investigations covering a wide variety of materials and equipment used in dentistry and studies of natural tooth structures have been carried on in the Dental Research Section of the National Bureau of Standards during the half year ending December 31, 1955. Lists of reports issued and papers published during this period are given below. Copies of the reports are appended.

2. REPORTS ISSUED

NBS Report 4312	The Polymerization of Methyl Methacrylate in the Presence of Amine Accelerators.
NBS Report 4313	Alloys of Gallium with Powdered Metals as Possible Replacement for Dental Amalgam.
NBS Report 4494	Resin Cements and Posterior-Type Direct-Filling Resins.
NBS Report 4495	Preliminary Study: Tropical Storage of Dental Materials.
NBS Report 4520	Dimensional Stability of Denture Base Resins.

3. PAPERS PUBLISHED

A Revision of American Dental Association Specification No. 3 for Dental Impression Compound. John W. Stanford, George C. Paffenbarger and W. T. Sweeney. J.A.D.A. 51:56 July (1955).

Ionization Chambers for Radiation Data During Dental X-ray Exposure. Donald C. Hudson and John W. Kumpula. U. S. Armed Forces Med. J. 6:(No. 8) 1131 August (1955).

Self-curing Resins for Repairing Dentures: Some Physical Properties. J. W. Stanford, Claire Burns and Geo. C. Paffenbarger. J.A.D.A. 51:307 Sept. (1955).

Setting Reaction of Zinc Oxide and Eugenol. Henry I. Copeland, Jr., Gerhard M. Brauer, W. T. Sweeney and A. F. Forziati. NBS J. Res. 55:133 Sept. (1955).

American Dental Association Specification No. 13 for Self-curing Repair Resins (Effective January 1, 1956). John W. Stanford, Claire L. Burns and George C. Paffenbarger. J.A.D.A. 51:425 Oct. (1955).

Dental Cements. Geo. C. Paffenbarger, W. T. Sweeney and P. J. Schouboe. Internat. Dent. J. 5:484 Dec. (1955).

4. WORK IN PROGRESS

4.1 Human Tooth Enamel and Dentin

(a) Fluorescence Investigation.

In an attempt to correlate intensity of fluorescence with organic content in calcified tissues, twelve serial sections cut from a dog femur were placed in an extractor and refluxed with ethylenediamine for a total of twelve hours. At the end of each hour one section was removed and preserved in ethanol. The fluorescence intensities of the twelve specimens were compared photographically and by means of the spectroradiometer. Although there appeared to be a general relationship between organic content and intensity of fluorescence, interpretation of the results must await a nitrogen analysis of the bone sections.

Specimens of human teeth which had been exposed in the artificial mouth constructed at the University of Alabama were examined by fluorophotomicroscopic methods. The fluorescence of caries-like lesions in these teeth was compared with that of naturally-occurring caries. The artificial lesions resembled natural caries to some extent but seemed to differ in pattern of tooth destruction. These differences may have been induced by the accelerated production of the artificial lesions. Further work is being done on this comparison. Fluorophotomicroscopic studies of human enamel and dentin in cooperation with the National Naval Medical Research Institute were continued.

(b) Crystallographic Investigation.

Efforts to produce in the laboratory crystals of non-stoichiometric calcium and lead apatites resembling bone and tooth mineral were continued. Attempts to leach out calcium ions preferentially from apatite crystals by means of organic chelating agents and to form perfect mixed crystals of calcium and copper apatites from which copper could be preferentially removed were unsuccessful. Presence of various foreign ions (iron, copper, molybdenum, magnesium, etc.) in hydrothermal bombs in which $CaHPO_4$ was hydrolized lead to the formation of βCa_3PO_4 or whitlockite. This unexpected reaction is of interest since the presence of whitlockite in dental calculi has been reported. (Formation of whitlockite in the presence of magnesium has also been reported by Trautz). Emphasis was placed on the formation of non-stoichiometric lead and calcium apatites by the hydrolysis of their acid phosphates. $CaHPO_4$ refluxed in water for up to two weeks did not appear to change. However, the addition of a base such as NaOH, tetramethyl ammonium hydroxide or triethylamine resulted in the formation of a material giving the typical apatite x-ray pattern. These solids

invariably had low indices of refraction and the few analyzed had low Ca to P ratios. This reaction is important since there is reason to believe that calcification of bone and teeth takes place with $CaHPO_4$ as an intermediate and apatite as the final structure.

Difference between normal and chalky human enamel were studied in cooperation with workers at Emory University. Production of chalky enamel by a mild acid leach did not change the x-ray diffraction pattern but did increase the index of refraction from 1.615 to 1.625. It is believed that the leach preferentially removed $CaCO_3$ and $MgCO_3$ from the enamel.

(c) Mechanical Properties.

In a study of methods of determining the mechanical properties of enamel and dentin an improved method for preparing suitable test specimens by sawing sections from teeth and grinding cylinders of uniform dimensions from the sections has been perfected. Preliminary results indicate that enamel is lower in compressive strength than dentin although it is approximately six times as hard. The modulus of elasticity determination presents difficulties in measuring the extremely small strain obtained with these small specimens (approximately 1 x 2 mm). Indirect methods using optical strain gages (Tuckerman) with small specimen between metal plattens have produced best results. Obtaining better data on the stress-strain relationship of enamel and dentin is of fundamental importance to the whole subject of the use of tooth restorative procedures. This work is being continued.

4.2 Low Temperature Alloys

Emphasis was placed on the investigation of the gallium-copper-tin system. The melting point of gallium can be reduced to about 15°C (59°F) by the addition of tin. This forms a eutectic alloy that is liquid at room temperature and makes possible mixing and packing without any special equipment. A number of physical properties of alloys formed by the combination of the gallium-tin eutectic with powdered copper and copper-tin alloys have been determined. The dimensional change is 20 μ/cm or less for several alloys with strengths from 43,000 to 55,000 psi. The modulus of elasticity in compression is being determined at the present time. Indications are that all gallium-copper-tin alloys are equal to amalgam and two alloys have a modulus between 2 and 3 times greater than that of amalgam. This, combined with adequate strength (45,000 to 55,000 psi) reasonable dimensional change (20 μ/cm or less), good hardness (100-130 Brinell) makes it appear that some alloys may be satisfactory for oral restorations.

Phase equilibrium studies of the Sn-Hg and Sn-Ag-Hg systems present in dental amalgams are in progress as a preliminary means of defining the location of the δ phase area on the Sn-Hg diagram, a series of diffusion experiments have been run at temperatures between 20°C and 100°C. The specimens were sectioned and mercury concentration measured by vaporization-weight loss methods. The resulting depth concentration curves indicate a narrow δ solid solution range centering near 22% Hg. A vapor effusion method will be used to substantiate these results and more closely define the limits. It is also hoped to use electrode potential measurements as an independent check, breaks in the curves of electrode potential vs composition indicating phase boundaries in a manner similar to the vapor pressure composition curve.

4.3 Resins

Additional studies of the reaction of benzoyl peroxide with tertiary amines were made. The formation of free radicals from benzoyl peroxide in the presence of dimethylaniline was determined in a series of solvents by measuring colorimetrically the disappearance of diphenyl pycrylhydrazyl (D.P.P.H.). In benzene and most solvents used two moles of D.P.P.H. react with the free radicals formed on decomposition of benzoyl peroxide. The kinetics of the reaction in air are complex and pass initially through an induction period, possibly until a steady state concentration of an intermediate peroxide-amine complex is obtained. In the later stages the benzoyl peroxide decomposition follows first order kinetics. Rate measurements at temperatures from 25° to 40°C have been made which allow the calculation of the activation energy in different solvents. A larger number of moles of D.P.P.H. per mole of benzoyl peroxide is used up when the reaction is conducted in chloroform instead of benzene. This may indicate a different reaction mechanism.

Apparatus has been assembled to measure the reaction rates in a vacuum. Results of such determination will be of interest in determining possible causes of the initial induction period.

The thermodynamic properties of solutions of polymers, particularly the intrinsic viscosity and volume expansion as functions of polymer-solvent system and concentration were studied. A new relation was found for determining the intrinsic viscosity by determining the relative viscosity at but one concentration. This relation holds for those systems in which the curve of log of relative viscosity vs concentration is a relatively straight line and the curve of specific viscosity vs concentration is a straight line. For those systems in which log of relative viscosity vs concentration deviates considerably from a straight line, plotting intrinsic viscosity as calculated from the equation vs concentration and extrapolating to zero concentration gives satisfactory results.

4.4 Agar-Agar Materials

Additional information was obtained on the deterioration of agar-agar materials. Viscosity, pH, and time required to fracture specimens under constant load were observed on agar-agar and a commercial reversible duplicating material. Specimens were boiled, placed in a water bath at 52°C and then allowed to gel at room temperature overnight. This cycle was followed for a period of weeks. At the end of this time the specimens were stored at 52°C for several weeks. Additional samples were first stored at 52°C and then subjected to the boiling gelation cycle. The viscosity decreased during the boiling-gelation cycle, and increased upon storage at 52°C. Changes in pH did not seem to be correlated with viscosity changes. Specimens made from the material maintained at 52°C fractured at constant load in a shorter time than did specimens made from material subjected to boiling and gelation. The affects of both storage at constant temperature and of boiling gelation cycle on viscosity, and time to fracture were reversible. A theory of micellar aggregation has been proposed to explain the change in properties of the materials.

4.5 Rubber Base Impression Materials

Properties of rubber base (thiokol) impression materials are being determined. Thus far values for strain, set, flow and setting time (as determined by a penetration test) have been obtained for 10 brands of material. Measurements of dimensional stability and temperature rise on setting are being made. After aging for 30 minutes all of the materials comply with the requirements for strain in compression of American Dental Association Specification No. 11 for agar type impression materials and most of the materials comply with the requirements for set after compression.

4.6 Inlay Casting Wax

The physical properties of a selected group of synthetic waxes and industrial casting waxes were investigated to determine their suitability as bases for dental inlay waxes. The coefficients of linear thermal expansion between 25 - 45°C varied from 212×10^{-6} to 556×10^{-6}. The polyethylene waxes showed fairly low coefficients as low as some of the industrial casting waxes. Solubility of most waxes was negligible as was their ash content. Carvability of the majority of waxes was fairly satisfactory for dental use. However, in all cases the melting points were too high to permit dental application without plasticization.

4.7 Fused Porcelain

The thermal expansion of various fused porcelains was determined using the interferograph. Values for the coefficients ranged from 6.4×10^{-6} per °C for specimens made from a high-fusing porcelain used for making porcelain restorations to 8.0×10^{-6} for specimens made from powdered porcelain teeth.

4.8 Hydraulic Turbine Handpiece

Work on the hydraulic turbine handpiece has been completed. The instrument has proven to be satisfactory for clinical use and is now being produced commercially by Bowen and Company, Inc., Bethesda, Maryland.

4.9 Panoramic X-ray Investigation

The panoramic dental x-ray machine for use in mass surveys and examinations has been developed to the point where extensive clinical tests are needed. The device produces full-mouth dental radiographs on a single 5 in. x 10 in. film using an extraoral technic. Patients are positioned either seated or standing beneath the moving arm of the machine, which carries an x-ray source and filmholder. Rotation of this arm about its axis, sweeps the x-ray source and film about the patient's head, producing a projection of the desired tooth images on the moving film. Adequate detail is secured to obtain a diagnosis of general mouth conditions. The panoramic dental x-ray device is not designed to supplant the conventional dental x-ray machine in cases where extreme sharpness and detail must be obtained. A detailed report on the machine is now being prepared.

4.10 Motion Pictures

The motion picture "A Porcelain Jacket Crown Technique" was completed. The picture presents a simplified method of making fused porcelain jacket crowns. The essential features of the method are the employment (1) of a prefabricated porcelain labial veneer made from a stock tooth and (2) of two porcelains having widely different fusing temperatures. By this technic the matching of the anatomy, the color and the translucency are largely determined by the porcelain veneer which can be tried in the patient's mouth when the preparation of the tooth is completed. Shrinkage on fusion is greatly reduced and the number of fusions is cut from four or five needed in the customary technics to two. The film is color-sound with a running time of 23 minutes.

4.11 Evaluation of Materials

Materials evaluated for the Federal dental services and the American Dental Association by specification or special test methods included amalgam, denture base resin, impression compound, inlay casting gold, inlay casting wax, mercury and plaster of paris.

For the Director
by

W. T. Sweeney

W. T. Sweeney, Chief
Dental Research Section

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
0708-10-0707	December 9, 1955	4312

Progress Report

THE POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF AMINE ACCELERATORS

by

G. M. Brauer
Ruth M. Davenport

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.

(Task 7756-41 BV No. 55-14)

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF AMINE ACCELERATORS

The accelerating effect of amines on the benzoyl peroxide-initiated polymerization of methyl methacrylate was studied. The reaction proceeds fastest in the presence of tertiary aromatic amines.

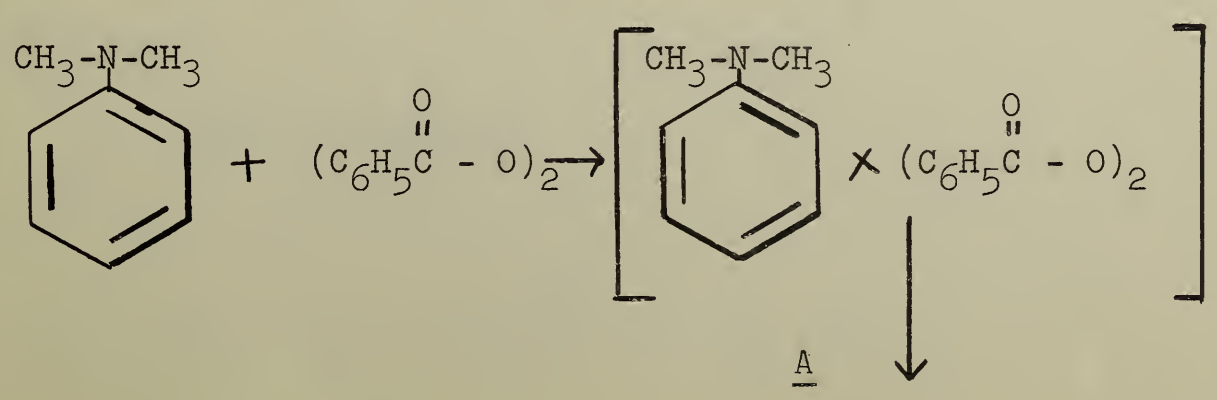
An ultrasonic viscometer was used to follow the course of the polymerization at 37°C in the presence of the most efficient peroxide-amine systems. The rate of polymerization often is different than one would expect from the relative rates of the amine-accelerated peroxide decomposition in non-polymerizable solvents. With many amine-peroxide systems, the polymerization reaction does not go to completion.

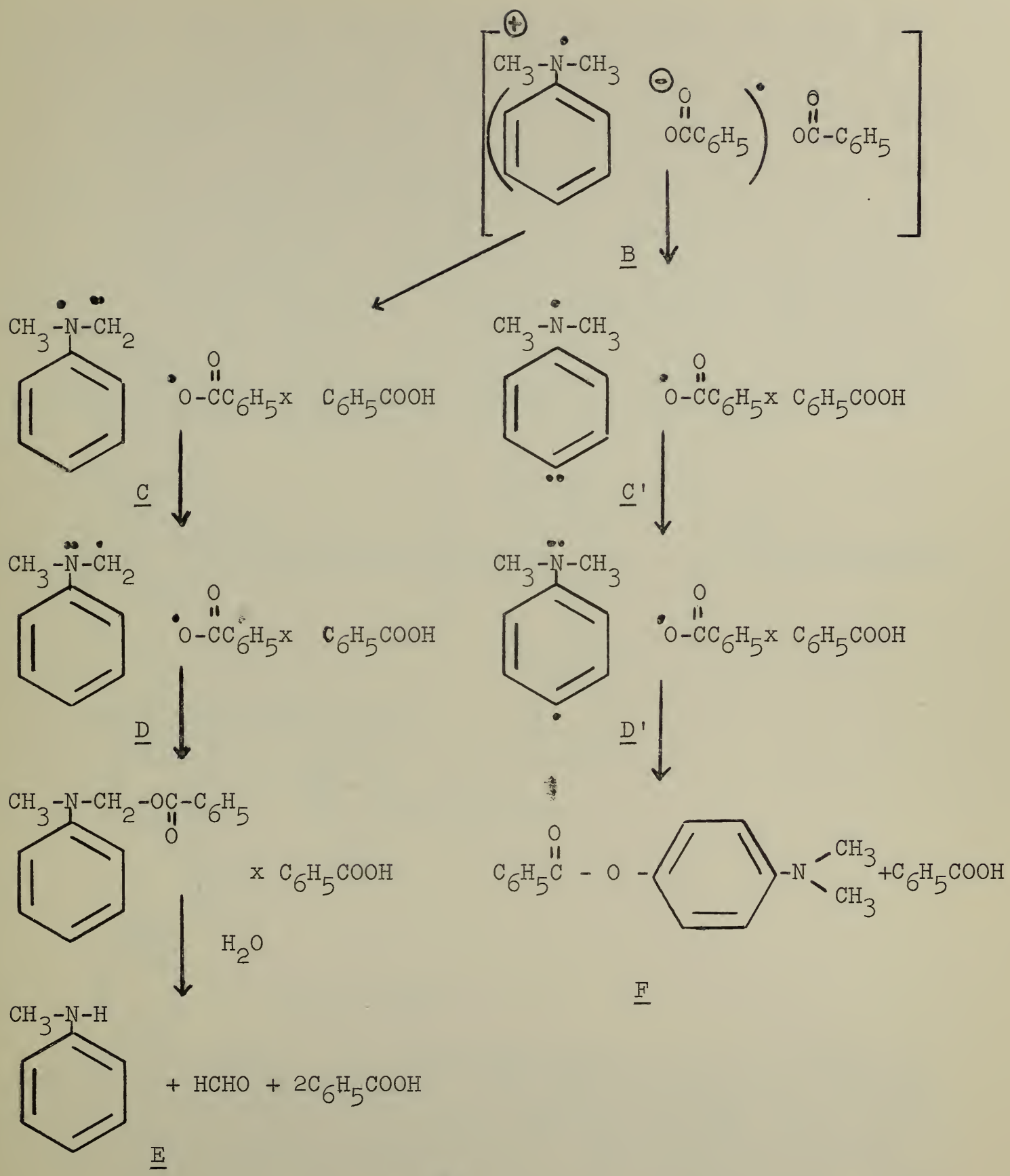
The relative order of efficiency of amines in the polymerization of monomer-polymer slurries does not always correlate with results obtained for the polymerization of monomer. Decreasing hardening time improves the indentation and recovery values of the polymers. Effective amine accelerators invariably produce colored polymers.

1. INTRODUCTION

Tertiary amines have been used for a number of years as accelerators for the peroxide-catalyzed polymerization of methyl methacrylate. These accelerators make possible the rapid polymerization of monomer or monomer-polymer slurries at room temperature [1-8]. Such mixtures have found considerable usefulness in dental filling resins, cements, and denture base materials.

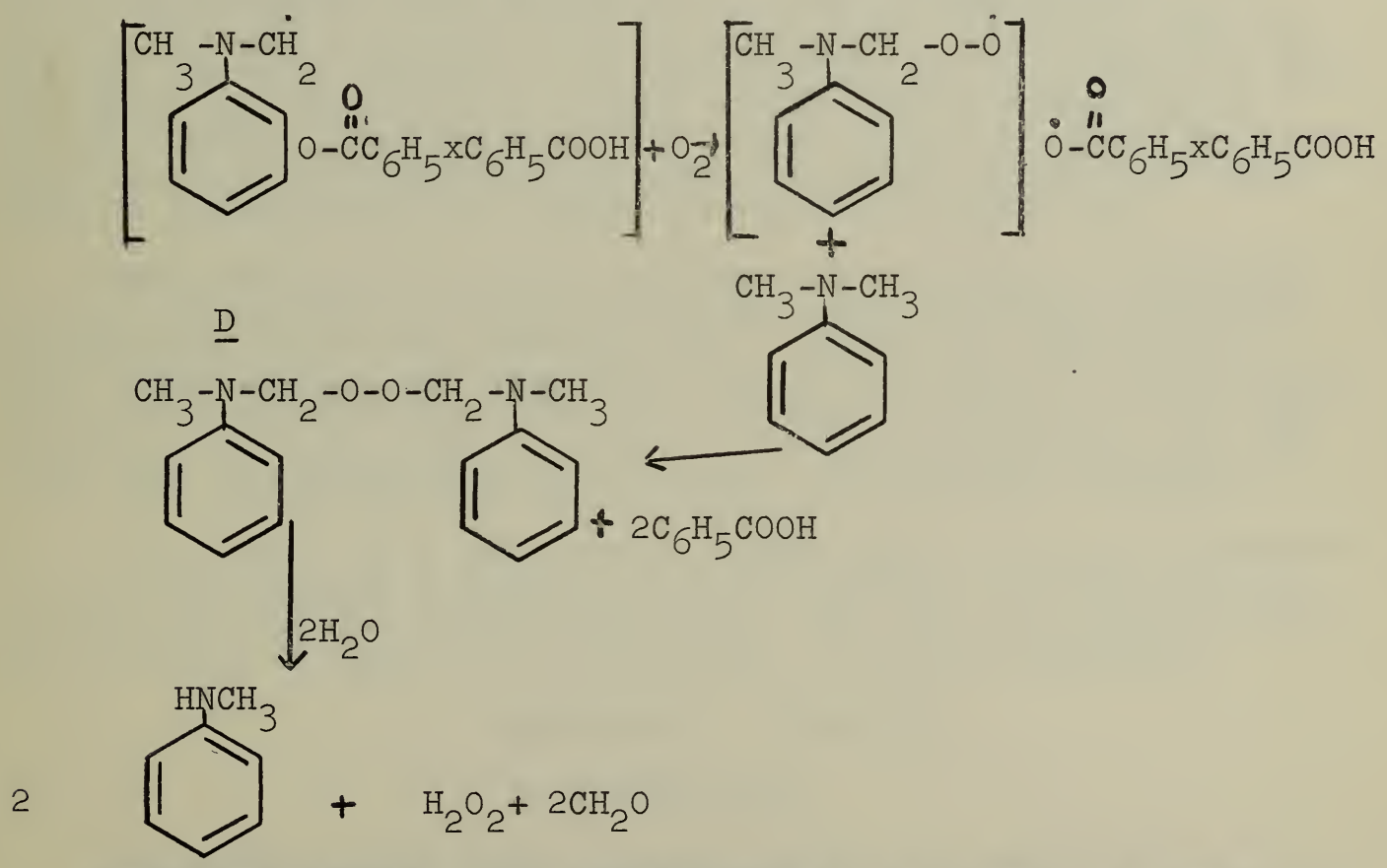
The increase in the polymerization rate is caused by the more rapid decomposition of peroxides in the presence of the amines. The kinetics of the decomposition of solutions of benzoyl peroxide with a number of amines was studied by Bartlett and Nozaki [9] and Meltzer and Tobolsky [10]. The latter showed that dimethylaniline in the benzoyl peroxide-dimethylaniline initiated systems does not affect the propagation or termination steps of the chain reaction. It must therefore change the initiation step. Horner and co-workers [11-18] proposed the following mechanism:





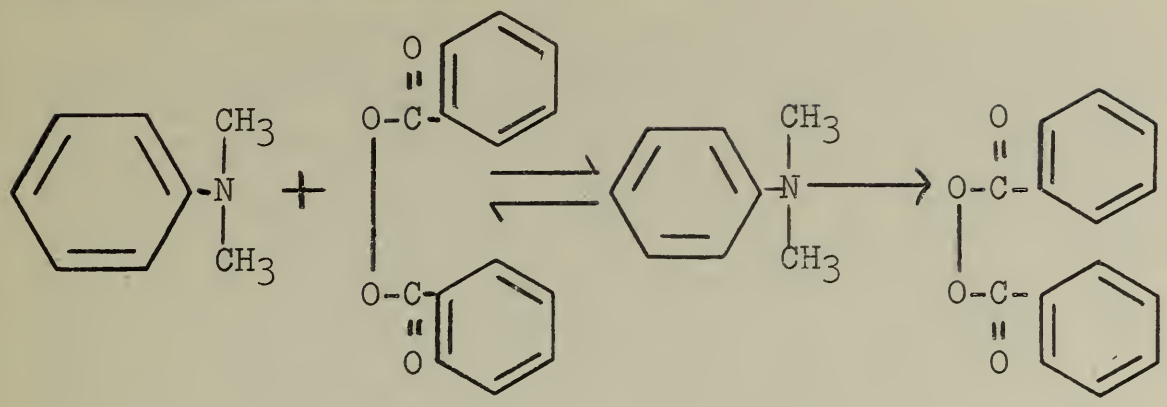
$$\underline{D} \text{ or } \underline{D}' + nCH_2 = \underset{R}{CH} \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}} - O \left(\underset{R}{CH} - CH_2 \right)_n$$

Presumably during the bimolecular reaction between the amine and the benzoyl peroxide, a transition state (A) occurs in which a transfer of an electron from the unshared pair of the nitrogen to the peroxide takes place. The benzoylate anion removes a proton from the aminium cation, either in the α position of the side chain (C) or from the aromatic nucleus - preferably from the para position (C'). On transfer of an electron from the carbon to the nitrogen, free radicals are formed (D and D') which may undergo (1) oxidative dealkylation, (2) substitution, (3) reaction with solvent or oxygen, (4) act as polymerization initiators in the presence of vinyl compounds. Identification of benzoic acid, carbon dioxide, formaldehyde, N-methylaniline (E), p-benzoxy-N,N-dimethylaniline (F), p,p'-tetramethyl diaminodiphenylmethane and chloride ion from reaction mixtures of benzoyl peroxide and dimethylaniline in chloroform [17] support this mechanism. When the reaction occurs in air, oxygen is absorbed and secondary peroxides are formed which decompose with the formation of hydrogen peroxide and N-methylaniline. This can be explained by the following mechanism:



Goode and Gratch [19] established that one mole of amine is required for the decomposition of one mole of peroxide in benzene. A large portion of the amine may be removed unchanged while small amounts of the amine are converted into formaldehyde, N-methylaniline and p-benzoxy-N,N-dimethylaniline. The decomposed peroxide can be accounted for nearly quantitatively as benzoic acid. Imoto and Choe [20] assume that the reaction of benzoyl peroxide with dimethylaniline starts with the formation of an intermediate complex produced by coordination of the unshared electron pair of the nitrogen atom in the dimethylaniline with the central -O-O- atoms

in the peroxide molecule.



This unstable intermediate decomposes into o,o'-dimethylaminodiphenyl, p-dimethylaminophenyl benzoate and benzoic acid. The ease with which the formation of the intermediate can be attained determines the decomposition rate of the benzoyl peroxide. When an electron-attracting group is introduced into the benzoyl peroxide molecule, the polarization of the carbonyl group decreases and the positive charge on the central oxygen atoms becomes larger. Formation of the intermediate coordination compound from dimethylaniline can take place more readily and the rate of decomposition of benzoyl peroxide is speeded up.

Some data on the relative efficiency of amines as accelerators in the benzoyl peroxide-catalyzed polymerization of methyl methacrylate have been reported [21]. Since the completion of this investigation, Lal and Green [22] have reported a qualitative study of the activating effect of a number of amines on the rate of polymerization. They recorded the peak temperatures and peak times for the polymerization of methyl methacrylate slurries.

The results of a qualitative investigation of the polymerization of monomer and a number of monomer-polymer slurries in the presence of various amines are given. The rate of polymerization was followed by means of an ultrasonic viscosity apparatus.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The methyl methacrylate monomer (Rohm and Haas) was inhibited with 0.006% hydroquinone.

The benzoyl peroxide (Eastman Kodak) was reagent grade.

Sources of the amines are given in Table 1. These amines were used without further purification.

The polymer powder* contained 1% by weight of benzoyl peroxide.

* The authors wish to thank the Research Dept. of the L.D.Caulk Co. for supplying the material.

2.2 Apparatus

The polymerization rate was determined by means of an ultrasonic viscometer (Ultra-Viscoson) manufactured by Rich-Roth Laboratories [23]. The instrument includes an analog-type computer which produces an electrical output that is a function of viscosity and density. Modifications of the instrument increased the sensitivity in the viscosity range below 1 cp. g/cm^3. This was accomplished by the inclusion in the system of a microammeter and a multiplier circuit which was developed by Hansen [24]. Ultrasonic measurements of the polymerization rate have the advantage of (1) ease of manipulation (2) speed and (3) simplicity. The Ultra-Viscoson reads in viscosity times density (cp. g/cm^3) units. These readings are affected by the following factors: (1) rise in temperature of the exothermic polymerization reaction; (2) increase in density on polymerization; and (3) modulus of rigidity of the solution which may not be negligible in comparison to its coefficient of viscosity.

Some of these variables will compensate each other. The course of polymerization showed extremely large variations of the viscosity-time curves in the presence of different amines. Because of this, it is unlikely that the above-mentioned variables (for which corrections are difficult to make) will greatly affect the results of this study. Hence, no corrections were made for these factors. Accurate measurements of the polymerization kinetics are preferably made by more time-consuming procedures such as dilatometric methods.

2.3 Polymerization Studies

2.3.1 Setting Time of Monomer

Preliminary studies were made using 18 x 150 mm test tubes with 5 ml monomer solutions containing 0.1 g benzoyl peroxide and 2% by volume of the amine under investigation. These solutions were maintained at 37° ± 1°C in an air bath. The test tubes were inverted at various time intervals until polymerization was evidenced by a marked increase in the viscosity. The time after which no further flow of the polymerized specimens could be observed was denoted as setting time. The color of the polymeric product was noted. If the solution did not harden, no further examination was made of that amine.

The setting time of monomer containing 2% benzoyl peroxide and various concentrations of dimethyl-p-toluidine was determined by the same procedure. The test tubes were stored at 21° ± 1°C.

Polymerization of the amine solutions which set within 2 hours was followed by means of the Ultra-Viscoson. About 22 ml of the monomer solution containing known concentrations of benzoyl peroxide and amine were placed in a Pyrex test tube (18 x 150 mm) in an air bath regulated to 37° ± 1°C. The Ultra-Viscoson probe was immediately inserted. Care was taken to ensure that the reed of the probe did not touch the sides of the tube at any time.

Reading of the Ultra-Viscoson, which had been allowed to "warm up" for at least one hour prior to the insertion of the probe into the solution, was started at one minute after the immersion of the probe. Readings were taken every minute or two, depending on the speed of the reaction, for the first hour and then at five minute intervals. Measurements were usually discontinued when the material reached a viscosity of about 2000 cp. g/cm^3 so that the probe could be removed.

2.3.2 Setting Time of Monomer-Polymer Slurries

In order to determine the setting time of monomer-polymer slurries, one ml of monomer solution containing different amine concentrations was mixed at room temperature with 1 g of polymer powder containing 1% benzoyl peroxide. The rate of hardening was measured in air at room temperature and at 37°C ± 1°C using the modification of the A.S.T.M. penetration test D-5-25 for bituminous materials described by Brauer and Burns [25]. All measurements were made in duplicate.

2.4 Evaluation of Physical Properties

The Rockwell Superficial Hardness Tester was used to determine the indentation and recovery of polymeric products. One ml of monomer containing 1% or 2% amine and 1 g of polymer containing 1% benzoyl peroxide were mixed. Indentation and recovery values were obtained after the mixture had been held at 37°C for 10 min., 30 min., 1 hour, 3 hours, 1 day, 3 days and 5 days by the procedure of Sweeney, Sheehan and Yost [26]. Most of the mixes were too soft to test at 10 minutes and some at 30 minutes. However, all mixes could be measured after 1 hour. All tests were made in duplicate at room temperature.

3. RESULTS AND DISCUSSION

The results of the preliminary experiments on the efficiency of commercially available amine accelerators are given in Table 1. It will be noted that only a small number of secondary or tertiary amines produce rapid polymerization under the experimental conditions.

Among the tertiary amines, dimethylaniline is an effective accelerator. The substitution of two β-hydroxyethyl groups for the methyl groups in N,N-dimethylaniline increases the polymerization rate. (β-Hydroxyethyl)methylaniline and N-ethyl-N-(β-hydroxyethyl) aniline show a much reduced efficiency. A methyl group substitution in the ortho position of dimethylaniline reduces the decomposition rate of benzoyl peroxide to such an extent that polymerization does not take place readily. An aliphatic group in the meta position increases peroxide decomposition as compared to the ortho-isomer [15].

Substitution of electron-repelling groups in the para position of dimethylaniline will increase the accelerating efficiency. In the presence of dimethyl - p - toluidine, and N,N - dimethyl - p -

phenylene-diamine, the polymerization rate is very rapid. This is in agreement with Horner's mechanism since an increase in the electron density of the unshared pair of electrons of the nitrogen atoms of substituted dimethylanilines should produce a larger accelerating effect.

Electron-attracting groups such as aldehydes have a retarding effect on the polymerization rate. The slow rate of polymerization in the presence of diethyl-p-toluidine and p-diethylamino-diphenyl is unexpected. Horner and Scherf [14] showed that dimethylaniline and diethylaniline decompose benzoyl peroxide at approximately the same rate. Absorption of oxygen in the benzoyl peroxide-diethylaniline solutions is much slower and is one-fourth of that of the equivalent peroxide-dimethylaniline systems [18]. Steric effects of the larger ethyl groups may reduce formation of a free radical similar to D. Formation of secondary peroxide would therefore be reduced. Rate of formation of free radicals by abstraction of a proton from the para position of the aromatic nucleus to form free radicals similar to D' is little affected by the presence of N,N-diethyl groups. This would explain the formation of equivalent amounts of p-benzoxy-N,N-dimethyl- and p-benzoxy-N,N-diethylaniline and the same decomposition rate of benzoyl peroxide in the presence of the two amines [19].

Aromatic compounds with amine groups in the side chain, such as secondary and tertiary benzylamine derivatives, are poor polymerization accelerators. None of these compounds produce polymerization in less than 24 hours. Since tribenzylamine rapidly decomposes benzoyl peroxide in solution [14], steric effects must again be responsible for the lowered reactivity. Dimethyl-1-naphthylamine, probably for the same reason, shows little accelerating efficiency.

With few exceptions, the aromatic amines form colored products which range from yellow for dimethyl-p-toluidine to black for N,N-dimethyl-p-phenylenediamine. Substituents which produce a deepening of the colors (bathochromic groups) often increase the polymerization rate. Introduction of a second dimethylaniline group in p,p'-benzylidenebis (N,N-dimethylaniline) produces a deepening of the color of the polymeric product.

Most aliphatic amines have little effect on the rate of polymerization. The decrease in reactivity compared with the aromatic amines may be due to the formation of a salt of the benzoic acid (which is formed from the decomposition of benzoyl peroxide) with the more basic aliphatic amine. Such a salt does not accelerate peroxide decomposition. In the presence of secondary amines, the solutions show no appreciable increase in viscosity, even on prolonged standing. Monomer solutions containing diethylenetriamine and triethylenetetramine polymerize after 24 hours at 37°C. Tri-n-hexylamine is the most efficient of the tertiary aliphatic amines. Further increase in the aliphatic chain length increases the setting time. Products usually show a lighter shade than those polymerized with the aromatic amines.

Heterocyclic amines have little effect on the setting time. An exception is phenylmorpholine which, when added to monomer, gives a pale yellow polymer in less than 2 hours.

The course of the polymerization in the presence of the more efficient benzoyl peroxide-amine systems was followed viscometrically. A summary of the results is given in Table 2 and Figures 1 and 2. After a short induction period, the polymerization rate increases rapidly. Some curves show an increase in rate after a considerable amount of polymer has been formed. This effect is caused by a rise in temperature due to the exothermic polymerization reaction. It can also be attributed to a decrease in the rate of bimolecular termination of growing chains with increasing viscosity of the monomer-polymer medium [27-29].

Eventually the concentration of free radicals or monomer becomes very low. Chain growth and termination become small, resulting in a levelling off of the viscosity-time curves. Variations in the ratio of the benzoyl peroxide-dimethyl-p-toluidine concentration greatly change the location at which the slope of the curves becomes small (Figure 1).

Dimethylaniline is a more efficient accelerator than the diethyl-, di(β-hydroxyethyl), or p-chloro-N,N-diethyl- derivatives. The substituted toluidines (Figure 2) show a rapid initial rise in viscosity. Complete polymerization is not reached with di(γ-phenyl-n-propyl)-p-toluidine. With di(β-hydroxyethyl)-m-toluidine, a 1000 cp. g/cm^3 is reached in the shortest period of time (19½ min.). No levelling off in this viscosity-time curve is observed.

The effect of the different concentrations of dimethyl-p-toluidine on the rate of polymerization is shown in Figure 1. A 2% solution of the amine has the largest initial polymerization rate but the increase in viscosity with time becomes small in the neighborhood of 50 cp. g/cm^3. Solutions containing 0.25%, 0.50% and 1% amine have similar increases in viscosity below 1 cp. g/cm^3. After 5 minutes, more rapid polymerization takes place for the 0.50% and 1% solutions. From Figure 3, showing the effect of the accelerator concentration on the hardening time of the monomer, it will be seen that the amine concentration between 0.75% and 1.0% gives the shortest setting time. Further increase or decrease in the amount of amine dissolved in the monomer produces a very rapid increase in the setting time.

The setting time of each monomer-polymer slurry is given in Table 3. Typical penetration-time curves are shown in Figure 4. Mixtures containing 2% amine concentration in the monomer set faster than those containing 1% amine. With 2% dimethyl-p-toluidine in the monomer, polymerization is fastest. On increasing the polymerization temperature from 22° to 37°C, a shorter setting time is observed. Relative efficiencies of amines in the polymerization of monomer do not always correlate with those obtained for monomer-polymer slurries. The reason for this lack of correlation cannot be explained readily. Short setting times are only obtained if

complete polymerization takes place rapidly. This may explain the decrease in the accelerating efficiency of di(β-hydroxyethyl)-m-toluidine and di(β-hydroxyethyl) aniline in monomer-polymer slurries. Hagger [30] has suggested that the heat of swelling of the polymer powder particles initiates polymerization. It is conceivable that uncoiling of the polymer chains and the subsequent expansion (swelling) of the network may vary in the presence of different amines and amine concentrations. The possibility that the rate of solution of benzoyl peroxide, which is incorporated in the powder, varies somewhat in the different amines must also be considered. The relative rate of reaction of free radicals with monomer and polymer chains and the chain transfer rate may also be altered by varying the amine.

In order to evaluate the physical properties of the polymer specimens, indentation and recovery were determined. Results of these measurements are shown in Tables 4-7. With 1% amine concentration in the monomer (Tables 4 and 5), most products were too soft to measure at 30 minutes. After 1 hour, the specimens polymerized with di(β-hydroxyethyl)-m-toluidine had the lowest indentation and the highest recovery values. Values for dimethyl-p-toluidine followed closely. Otherwise, the results correlated well with the setting time data; the longer the setting time, the larger the indentation and the smaller the recovery. Specimens polymerized with the different amines showed little variation in indentation at 5 days. Recovery values of products of the slower setting amines were slightly lower than those for dimethyl-p-toluidine. With 2% amine concentration, (Tables 6 and 7), polymerization occurred more rapidly as evidenced by the lower indentation and higher recovery values after one hour. Five day indentation values for the specimens polymerized with dimethyl-p-toluidine were lowest. In the presence of the other amines, indentation and recovery were slightly poorer and showed little variations for the various amines. Generally, amines which were polymerized with 2% amine showed improved physical properties compared to those polymerized with 1% amine. The data are in agreement with previous studies which show that the molecular weights of the polymer formed increase with an increase in the polymerization temperatures[31-32]. Since the faster setting resins have higher peak temperatures[33], improved indentation and recovery values should be expected.

4. SUMMARY

The polymerization of methyl methacrylate has been investigated in the presence of various benzoyl peroxide-amine systems.

Only a small number of tertiary aromatic amines are efficient polymerization accelerators.

The course of the polymerization, in the presence of the fastest setting peroxide-amine systems, has been followed with an ultrasonic viscometer. With many amines, the initial reaction rate is

fast but the polymerization does not go to completion. The polymerization rate is often different than one would expect from the relative rate of decomposition of benzoyl peroxide in the presence of the amine.

The setting time of monomer-polymer slurries containing different amines has been determined. The relative order of efficiency of amines in the polymerization of monomer-polymer slurries is not always the same as that found in the polymerization of monomer. Polymerization with dimethyl-*p*-toluidine or di(β-hydroxyethyl)-*m*-toluidine give products having the best physical properties.

Improvement of some physical properties, such as indentation and recovery, is obtained on decreasing the setting time. With effective amine accelerators, colored products are formed.

The authors wish to thank Mr. Francis R. Burns for assisting in the experimental work.

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TABLE 1

POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF VARIOUS AMINES

Benzoyl peroxide concentration - 2%
Amine concentration- - - - - - - 2%

romatic Amines	Source**	Setting Time hrs.	Color
N,N-Dimethylaniline	E reagent	<1	amber
N,N-Diethylaniline	F reagent	<1	dark brown
N,N-Di-n-propylaniline	E reagent	<2	amber
2-Anilinoethanol	E reagent	np.[1]	-----
N,N-(β-Hydroxyethyl) methylaniline	E reagent	np.	-----
N,N-Di(β-hydroxyethyl)-aniline	TE	<1	gold
N-Ethyl-N-(β-hydroxyethyl)-aniline	TE	>24	layered brown-yellow
N-Phenylglycine	E reagent	np.	yellow-brown
Phenylhydrazine	F reagent	np.	amber
N,N-Dimethyl-o-toluidine	E reagent	np.	red-brown
N,N-Dimethyl-m-toluidine	E reagent	< 2	pale yellow
N,N-Diethyl-m-toluidine	E reagent	<2	dark brown-yellow
N,N-Di(β-hydroxyethyl)-m-toluidine	TE	<24	amber
2-Aminobenzenethiol	C	>24	dark (brown or black)
m-Dimethylaminophenol	M technical	>24	blue-black
m-Diethylaminophenol	E practical	>24	black
N,N-Dimethyl-p-toluidine	E reagent	<1	medium yellow

TABLE 1 (cont.)

Aromatic Amines(cont.)	Source**	Setting Time hrs	Color
N,N-Diethyl-p-toluidine	E reagent	< 24	yellow
p-Dimethylaminobenzaldehyde	F reagent	> 24	yellow
p-Dimethylaminoazobenzene	F reagent	< 1	red-brown
N,N-Dimethyl-p-phenylene-diamine	E practical	> 24	black
p-Diethylaminodiphenyl	E reagent	np.	-----
N,N-Bis(γ phenyl-n-propyl)-p-toluidine	E practical	> 24	yellow
p-Chloro-N,N-diethylaniline	E reagent	< 2	amber - dark on top
p,p'-Tetramethyl diamino-diphenylmethane	F technical	< 1	muddy yellow
p,p'-[p-Hydroxybenzylidenebis-(N,N-dimethylaniline)]	E reagent	np.	red
p,p'-Benzylidenebis(N,N-dimethylaniline)	E reagent	< 1	blue-green
p,p',p"-Methylidynetris(N,N-dimethylaniline)	E reagent	np.	purple
Dibenzylamine	E reagent	np.	yellow-orange
α Methylbenzylmonoethanolamine	C+C	np.	-----
Benzyldimethylamine	R+H	np.	-----
α-Methylbenzyldiethanolamine	C+C	> 24	medium yellow
Dimethyl-1-naphthylamine	E reagent	> 24	colorless
Tribenzylamine	E reagent	> 24	colorless
liphatic Amines			
Ethylenediamine	E reagent	np.	-----
Di-n-propylamine	E practical	np.	deep rose
Di-isopropanolamine	E practical	np.	dark

TABLE 1 (cont.)

Aliphatic Amines(cont.)	Source**	Setting Time hrs	Color
Di-isobutylamine	E reagent	np.	-----
Di-sec-butylamine	E reagent	np.	-----
Di-n-hexylamine	E reagent	np.	-----
Dicyclohexylamine	E practical	np.	dark
Methylcyclohexylamine	D	np.	amber
Diethylenetriamine	E technical	> 24	yellow
Triethylenetetramine	E technical	> 24	yellow
Hexamethylenetetramine	E reagent	np.	-----
Dimethylaminoethanol	R + H	> 24	layered, red to yellow
Triethanolamine	E reagent	< 4	brown-yellow
2-Di-n-butylamino-1-propanol	E practical	np.	brown
Tri-isopropanolamine	E practical	> 24	yellow
Tri-n-butylamine	E practical	> 24	-----
Tri-n-hexylamine	E reagent	< 2	pale yellow
Diethylcyclohexylamine	E practical	np.	dark
N,N-Dimethyldodecylamine	A	> 24	medium yellow
N,N-Dimethyl tallowamine	A	np.	-----
Armeen 2HT	A	> 24	mauve to pale yellow
Amine C	A1	> 24	dark amber
Amine S	A1	> 24	dark amber
Sequestrene Na-2 (disodium ethylenediamine tetraacetate dihydrate)	A1	> 24	colorless
Petrolite Wax Amine C	P	> 24	pale yellow

TABLE 1 (cont.)

Aliphatic Amines(cont.)	Source **	Setting Time hrs	Color
Petrolite Wax Amine B	P	> 24	pale yellow
Petrolite Wax Amine A	P	> 24	pale yellow
Diethylthiocarbamylchloride	S	> 24	pale yellow
Heterocyclic Amines			
2-(2-Dimethylaminoethylamino)-pyridine	Mo	np.	-----
Piperidine	F reagent	np.	dark
Pyrrole	F reagent	np.	black
Pyrrolidine	E practical	np.	dark
Phenylmorpholine	E practical	< 2	pale yellow
Phthalamide	E reagent	np.	colorless

1 np. - no polymerization took place within 48 hours

*

Al	Alrose Chemical Co.*	M	Matheson, Coleman + Bell*
A	Armour and Co.*	Mo	Monsanto Chemical Co.*
C + C	Carbide and Carbon Chemical Co.*	P	Petrolite Corporation,Ltd*
C	American Cyanamid Co.*	R + H	Rohm and Haas Co.*
D	E.I. DuPont de Nemours + Co.*	S	Sharples Chemical Co.*
E	Eastman-Distillation Products Industries	TE	Tennessee Eastman Co.*
F	Fisher Scientific Co.		

* The authors wish to thank these companies for generously supplying the samples.

TABLE 2

POLYMERIZATION of METHYL METHACRYLATE with BENZOYL PEROXIDE-AMINE SYSTEMS

Benzoyl peroxide concentration - 2%

Viscosity - cp. g/cm^3	5.0			100.0			1000.0		
Amine Concentration - %	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
	min	min	min	min	min	min	min	min	min
Dimethylaniline	42	18	12	75	26½	21½	---	35	43
Diethylaniline	45	---	19	70	43	29	100	63	41
p-Chloro-N,N-diethylaniline	np.	np.	33	np.	np.	44	np.	np.	61
Di(β-hydroxyethyl)-aniline	np.	30	20	np.	42	25	np.	45½	32
Dimethyl-o-toluidine	- - - - - - - - - - - -				-np.-		- - - - - - - - - - -		
Dimethyl-m-toluidine	np.	10½	7	np.	21	23	np.	30½	100
Diethyl-m-toluidine	19	16	14	44	32	30	73	52½	110
Di(β-hydroxyethyl)-m-toluidine	11	12½	10	14	17	13½	np.	19½	np.
Dimethyl-p-toluidine	10	8	5	21½	18	46	34	34	185
Di(γ-phenyl-n-propyl)-p-toluidine	np.	13	np.	np.	41	np.	np.	np.	np.
Tri-n-hexylamine	39	29	20	np.	113	76	np.	119	88
Triethanolamine	25	np.	77	120	np.	200	np.	np.	215

np. - No polymerization took place

TABLE 3

SETTING TIME of MONOMER-POLYMER SLURRIES

Penetration Test

Mixture: One gram of ground polymer containing 1% benzoyl peroxide
One milliliter of hydroquinone-stabilized monomer

Material	Time of Set in min.			
Temperature	37°C		22°C	
Amine Concentration in Monomer	2%	1%	2%	1%
Dimethyl-p-toluidine	7	9	9	9½
Di(β-hydroxyethyl)-m-toluidine	9	12	18	24½
Diethyl-m-toluidine	11	14	--	--
Dimethylaniline	12	17½	19½	--
Di(β-hydroxyethyl)aniline	15	21½	--	--
Diethylaniline	18	--	--	--
Commercial monomer and polymer	8		14	

TABLE 4

INDENTATION of POLYMERS DURING STORAGE

Material 1% amine concentration	Age of Specimen						
	10 min	30 min	1 hour	3 hour	1 day	3 days	5 days
	Depth of Indentation*						
	mm	mm	mm	mm	mm	mm	mm
Dimethyl-p-toluidine	------	0.223	0.148	0.135	0.107	0.106	0.099
Diethyl-m-toluidine	------	------	0.167	0.144	0.120	0.102	0.096
Di(β-hydroxyethyl)-m-toluidine	------	------	0.145	0.124	0.108	0.108	0.099
Dimethylaniline	------	------	0.184	0.162	0.125	0.107	0.101
Diethylaniline	------	------	0.215	0.157	0.129	0.104	0.096

* Average of at least two specimens. Major load applied for 10 minutes.

TABLE 5

RECOVERY of POLYMERS DURING STORAGE

Material 1% amine concentration	Age of Specimen 10 min	30 min	1 hour	3 hour	1 day	3 days	5 days
	Recovery**						
	%	%	%	%	%	%	%
Dimethyl-p-toluidine	*	36	48	53	69	71	76
Diethyl-m-toluidine	*	*	44	53	63	75	76
Di(β-hydroxyethyl)-m-toluidine	*	*	48	58	69	67	72
Dimethylaniline	*	*	36	45	58	70	73
Diethylaniline	*	*	33	46	59	73	74

* Too soft to measure

** Recovery computed as percent of indentation depth recovered 10 minutes after the major load (30 kg) was released and minor load (3 kg) remained. Average of at least two determinations.

TABLE 6

INDENTATION of POLYMERS DURING STORAGE

Material 2% amine concentration	Age of Specimen						
	10 min	30 min	1 hour	3 hour	1 day	3 days	5 days
	Depth of Indentation*						
	mm	mm	mm	mm	mm	mm	mm
Dimethyl-p-toluidine	0.216	0.190	0.133	0.115	0.109	0.099	0.093
Diethyl-m-toluidine	------	------	0.149	0.134	0.115	0.106	0.098
Di(β-hydroxyethyl)-m-toluidine	------	0.188	0.133	0.119	0.111	0.098	0.101
Dimethylaniline	------	------	0.174	0.143	0.128	0.104	0.097
Diethylaniline	------	------	0.185	0.152	0.119	0.104	0.097
Di(β-hydroxyethyl)aniline	------	------	0.164	0.142	0.120	0.103	0.098

* Average of at least two specimens. Major load applied for 10 minutes.

TABLE 7

RECOVERY of POLYMERS DURING STORAGE

Material 2% amine concentration	Age of Specimen						
	10 min	30 min	1 hour	3 hour	1 day	3 days	5 days
	Recovery **						
	%	%	%	%	%	%	%
Dimethyl-p-toluidine	22	34	48	64	70	76	79
Diethyl-m-toluidine	*	*	46	53	66	74	78
Di(β-hydroxyethyl)-m-toluidine	*	40	53	61	70	76	77
Dimethylaniline	*	*	41	52	63	69	78
Diethylaniline	*	*	40	49	65	72	77
Di(β-hydroxyethyl)aniline	*	*	42	53	63	71	74

* Too soft to measure

** Recovery computed as per cent of indentation depth recovered 10 minutes after the major load (30 kg) was released and minor load (3 kg) remained. Average of at least two determinations.

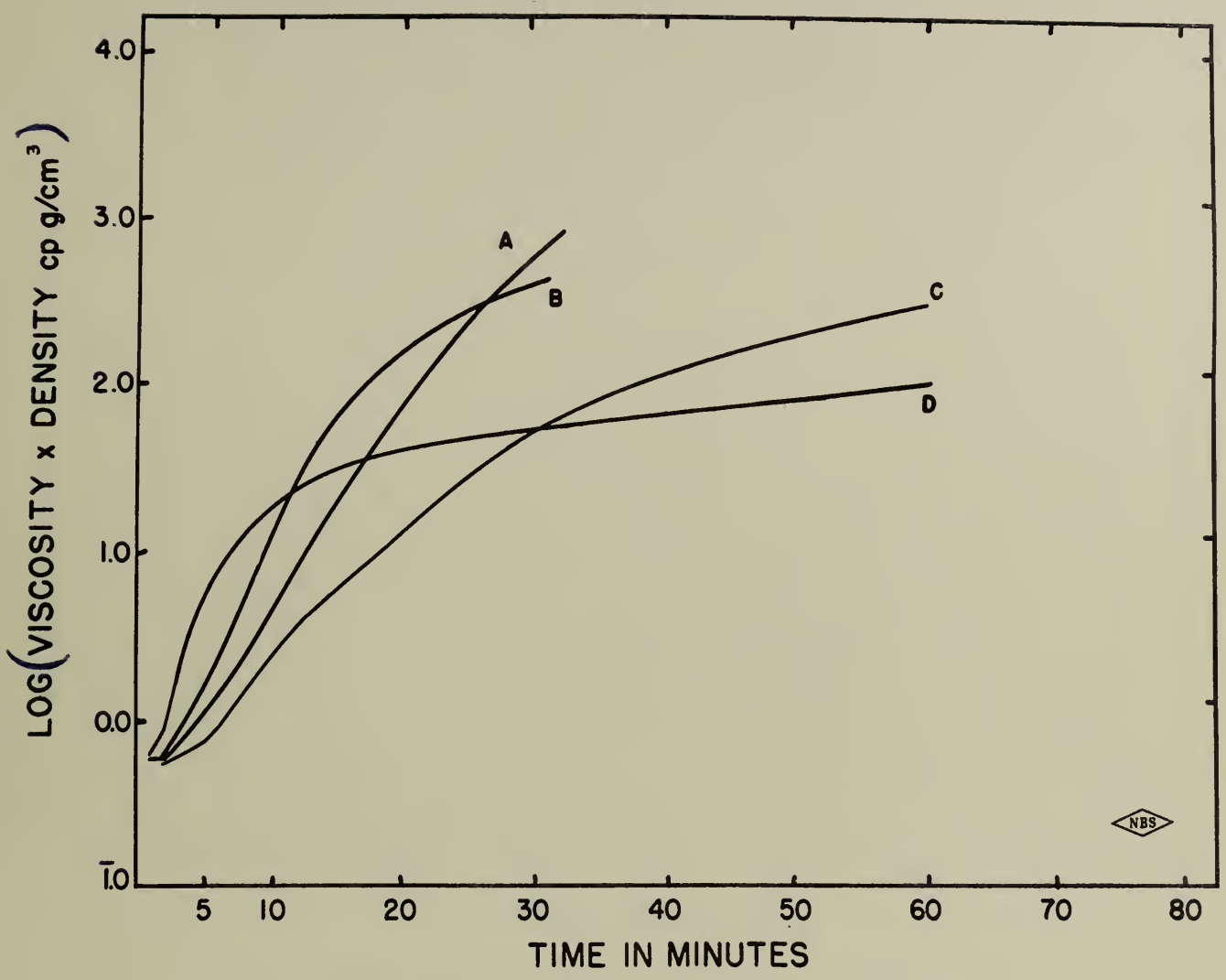

Fig. 1 POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF VARYING CONCENTRATIONS OF DIMETHYL-p-TOLUIDINE

Temperature - 37°C Benzoyl Peroxide Concentration - 2%

Dimethyl-p-toluidine concentration -

A = 0.50%, B = 1.00%, C = 0.25%, D = 2.00%

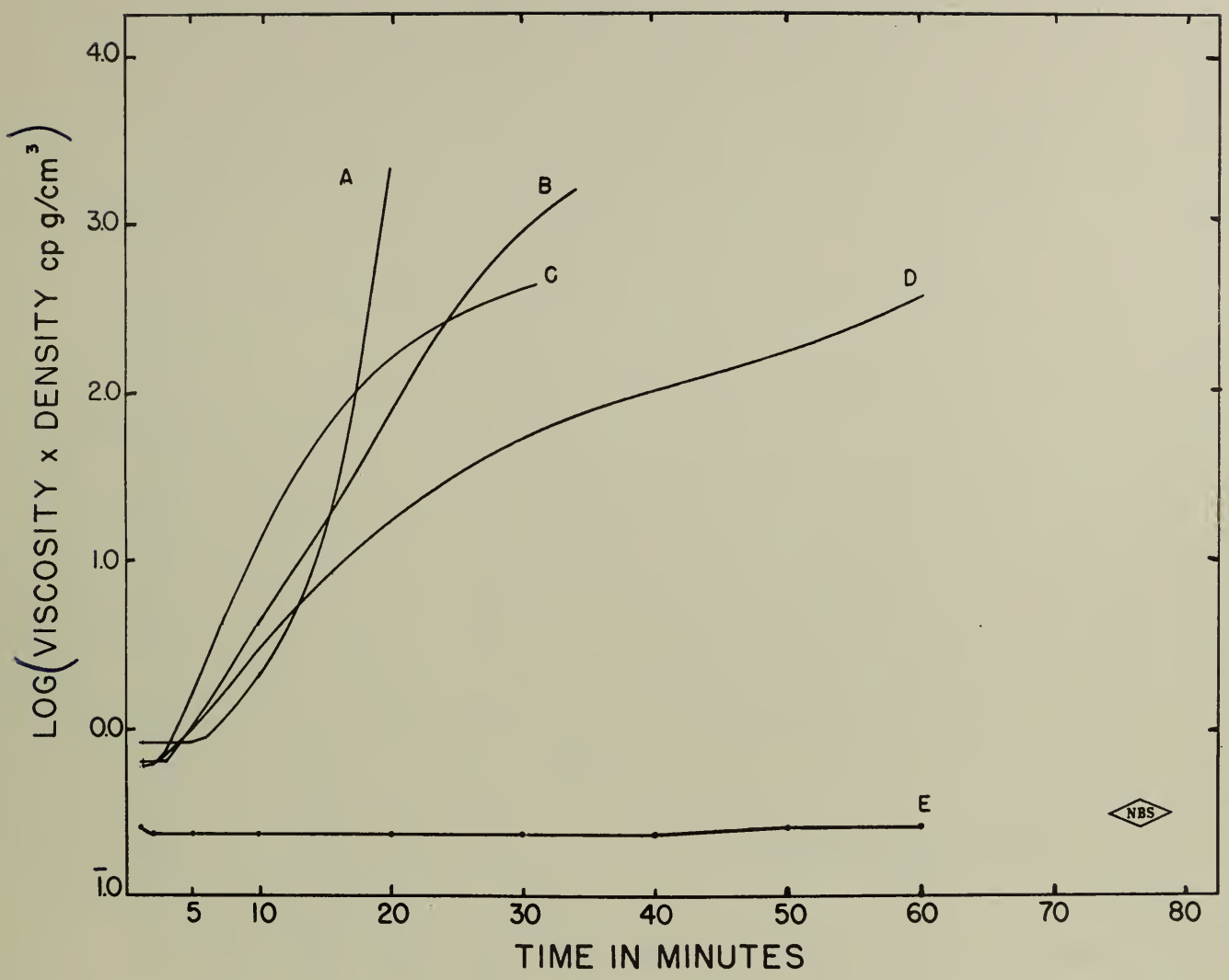

Fig. 2 POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF SUBSTITUTED TOLUIDINES

Temperature - 37°C Benzoyl Peroxide Concentration - 2%

Toluidine Concentration - 1%

A - Di(β-hydroxyethyl)-m-toluidine
B - Dimethyl-m-toluidine
C - Dimethyl-p-toluidine
D - Di(γ-phenyl-n-propyl)-p-toluidine
E - Dimethyl-o-toluidine

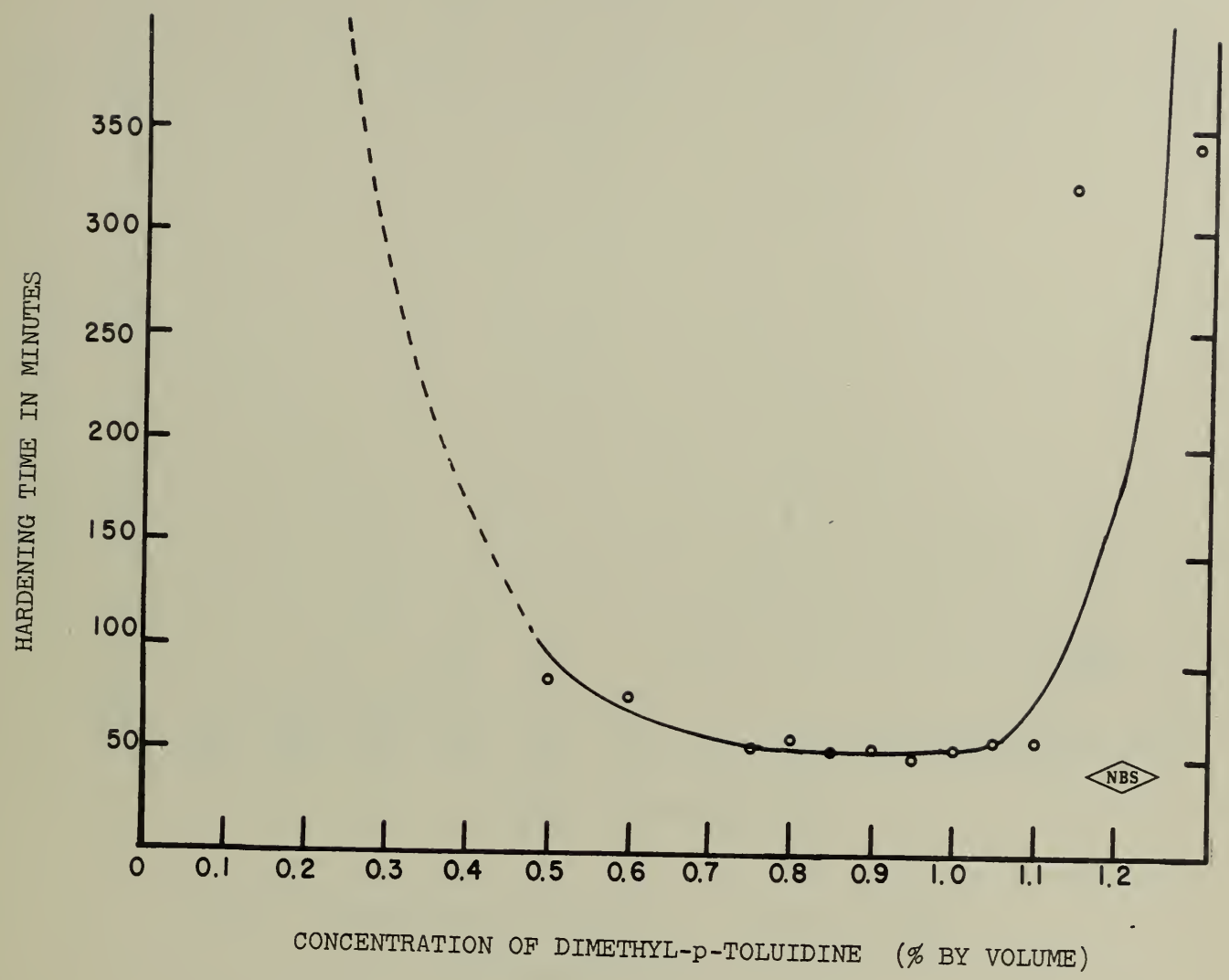

Fig. 3 EFFECT OF ACCELERATOR CONCENTRATION ON THE HARDENING TIME OF SELF-CURING RESIN

Temperature - 21.1°C Catalyst Concentration - 2%

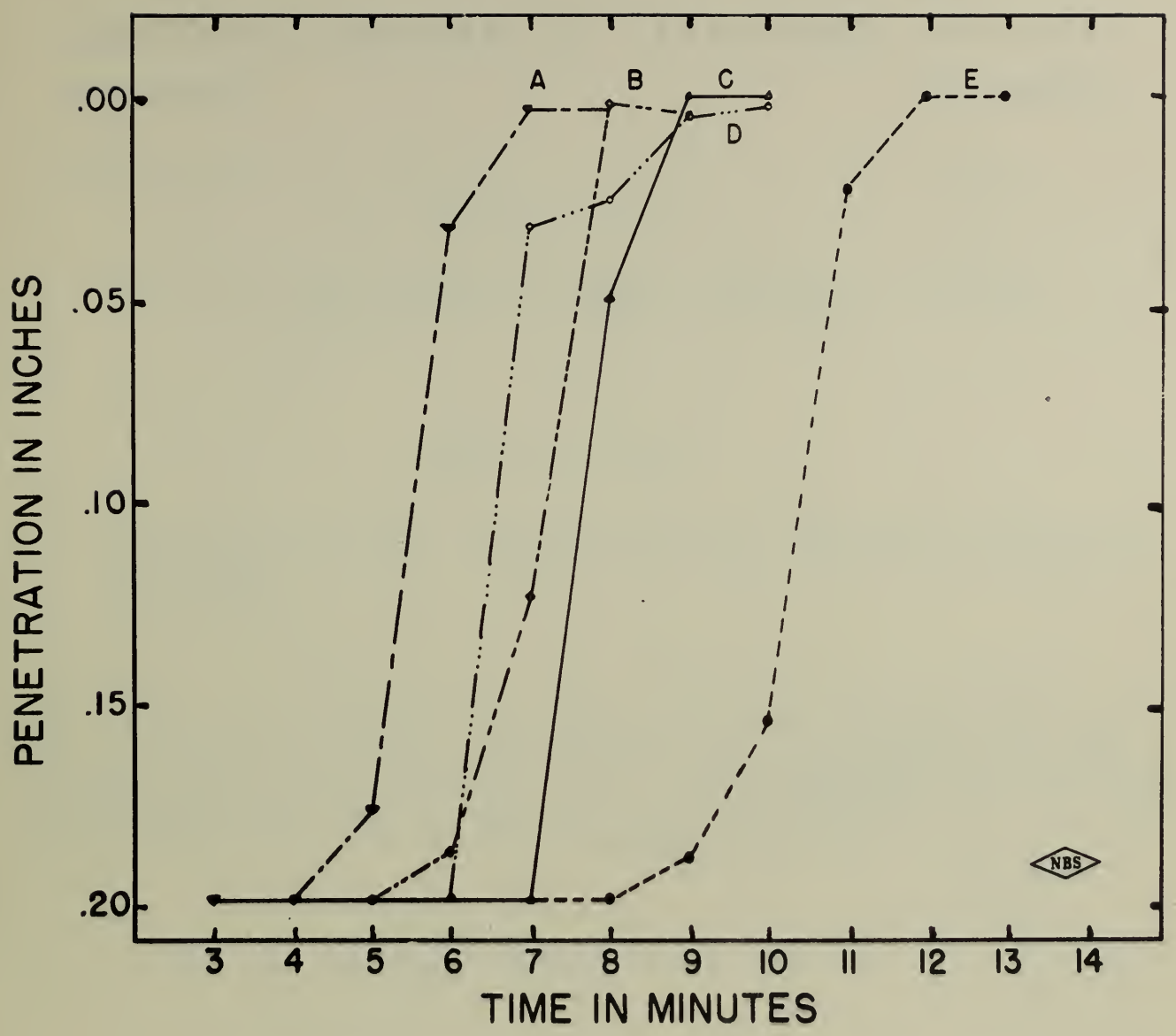

Fig. 4 SETTING TIME OF MONOMER - POLYMER SLURRIES

(Penetration Test)

Mixture: One g ground polymer containing 1% benzoyl peroxide and 1 ml of 0.006% hydroquinone-stabilized monomer

Temperature - 37°C

A - Dimethyl-p-toluidine 2%
B - Commercial monomer-polymer slurry
C - Di(β -hydroxyethyl)-m-toluidine 2%
D - Dimethyl-p-toluidine 1%
E - Di(β -hydroxyethyl)-m-toluidine 1%

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT **NBS REPORT**

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Progress Report

ALLOYS OF GALLIUM WITH POWDERED METALS AS POSSIBLE REPLACEMENT FOR DENTAL AMALGAM

by

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

ALLOYS OF GALLIUM WITH POWDERED METALS AS POSSIBLE REPLACEMENT FOR DENTAL AMALGAM

Abstract

The possibility of using gallium as a liquid metal to replace mercury in dental restorations was investigated. It was found that gallium would not combine at room or mouth temperature with body-centered cubic metals such as tantalum, chromium and molybdenum. Gallium did combine with powdered face-centered cubic metals such as nickel, gold, copper, with alloys of copper and tin, and with cobalt.

With the exception of gallium-cobalt these alloys had adequate compressive strength and hardness but expanded excessively during hardening. Gallium-cobalt had low compressive strength but exhibited shrinkage during hardening.

Gallium alloys have been made that have some physical properties that are better than dental amalgam. None of the alloys investigated possess all the desired physical properties for oral restorations.

1. INTRODUCTION

The metallic element gallium was first predicted by Mendeleff in 1871 in his work on the correlation of the properties of the elements with their atomic weights [1]. It was also predicated at about the same time by de Boisbaudran who concluded, while studying the spectral lines of the elements, that there was an element missing between aluminum and indium in the periodic table. Gallium was first isolated by de Boisbaudran in 1875 [2].

The amount of gallium present in the earth's crust is about the same as lead, roughly 15 g per ton [3]. Unlike lead which is concentrated in localized areas, gallium is widely distributed. The low concentration of the ore and lack of demand for the metal make gallium relatively expensive at $2.50 to $5.00 per gram [3].

Gallium has several interesting physical properties. Its melting point is 29.78°C (85.60°F) [4] while its boiling point is 1983°C (3601°F) [4], thus giving it one of the longest liquid ranges of the metals. The metal has a low vapor pressure even at high temperatures, a pressure of 1 mm of mercury being attained at 1315°C (2399°F) [4]. Gallium expands 3.4% in volume during solidification, the solid having a density of 5.90 g/cm^3. It has the property of wetting many materials including tooth structure.

The true nature of this property has not been determined but the wetting characteristic is generally attributed to a thin oxide film on the surface of the metal [6]. It has also been reported that gallium is essentially nontoxic [7].

This combination of physical properties indicates that gallium instead of mercury might be used as a component in a filling material. Some alloys of gallium begin to melt at higher temperatures than does dental amalgam. These factors make it desirable to investigate its possible use in oral restorations. It is expected that gallium, instead of mercury, might be used as a liquid metal to be combined with a powdered metal or alloy to form such a filling material. To be successful the combination should readily mix and condense, preferably using implements similar to those already familiar to the dentist. The gallium alloy should harden at mouth temperature within a reasonable length of time and possess strength, dimensional stability and corrosion resistance equal to or greater than those of dental amalgam.

2. MATERIALS AND METHODS

Gallium metal of 99.9+% purity was used in the experiments described here. The powdered metals and alloys used were obtained from laboratory supply houses, powdered metal manufacturers, or by alloying and comminuting in the Dental Research Section at the National Bureau of Standards. All metallic powders passed a No. 325 sieve of the U.S. Standard Sieve Series. For laboratory control, all mixing and condensing of specimens was at 37°C (98.6°F) which is above the melting point of gallium. Mixing was accomplished either in a mortar or in a mechanical amalgamator. All of the triturated mass was condensed. No liquid metal was expressed prior to or during condensation with one exception as noted.

Determinations of the dimensional change were made at 37°C (98.6°F) using unrestricted specimens 10 mm long and 5 mm in diameter in a differential interferometer with a fiducial reading 15 minutes after mixing was started. The compressive strength was determined at 21°C (69.8°F) using cylinders 8 mm long and 4 mm in diameter. The strength of one series of gallium-nickel-silicon alloys was determined at 37°C (98.6°F) and at 50°C (122°F). The rate of loading of the compressive strength specimens was in all cases 80 lbs (36.3 Kg) per minute.

3. RESULTS

Gallium-tantalum mixture. Two mixes of gallium and powdered tantalum were made, one containing 40% gallium and the other 25% gallium. The first was mixed with a mechanical amalgamator, the second with a mortar and pestle. Both specimens could be easily packed. These metals did not alloy. At room temperature the specimens hardened by the freezing of the gallium but readily softened when reheated to mouth temperature.

Gallium-chromium mixture. Gallium and finely divided chromium did not mix well. A specimen containing 35% gallium hardened by the solidification of the free gallium present. As in the case of the gallium-tantalum mixture, the gallium-chromium specimen softened by the melting of the gallium when heated to body temperature. A mix containing 50% gallium was too crumbly to pack.

When these mixtures of gallium and chromium were heated over an open flame the two metals combined with an exothermic reaction causing the mass suddenly to become bright red. The combination, after cooling, was a black friable powder.

Gallium-molybdenum mixture. Powdered molybdenum was mixed with 35, 40 and 50% gallium, respectively, in a mortar and in a mechanical amalgamator. The 50% gallium mixture was too wet to pack satisfactorily, while the 35% gallium mixture was too dry to pack well. The resultant mixtures did not harden during a 5-week period at room temperature. Small droplets of what appeared to be gallium were observed on the surface of the specimens.

Mixtures of gallium and molybdenum also combined exothermically when heated over an open flame to form a brittle, black mass.

Gallium-silver-indium alloys. Silver alloys containing 22½, 30 and 34% indium were prepared and chill cast into a steel mold. These alloys were then comminuted on a lathe. None of these alloys when combined with gallium hardened during storage at 37°C (98.6°F) for 1 month. The combinations remained soft and were easily deformed in the hand.

Gallium-gold alloy. A mixture containing 60% precipitated gold powder and 40% gallium hardened. These components react exothermically to form the intermetallic compound $AuGa_2$ [7]. The rate at which the reaction occurs is apparently dependent on the temperature at which the metals are mixed. Mixing temperatures of about 22°C (73°F) resulted in no appreciable heat generation; but when the components were mixed at a temperature of approximately 55°C (131°F) and packed into a 4 x 8 mm cylinder containing a thermocouple, temperatures as high as 450°C (842°F) were recorded.

The blue color, characteristic of $AuGa_2$ [7], was noted to extend throughout the specimen. These alloys had a linear expansion of about 12.5% during hardening.

Gallium-cobalt alloy. A mixture of 40% gallium with cobalt powder contracted approximately 3 μ/cm in 24 hours and was stable for 4 days thereafter. This is the only alloy investigated that contracted during hardening. The 7-day compressive strength of this alloy was 12,700 psi with a standard deviation of 1,100 psi. This low compressive strength makes the gallium-cobalt alloys unsuitable for oral use, but powdered cobalt may be introduced into an experimental gallium-powdered metal alloy to control an excessive expansion.

Gallium-nickel alloys. Nickel powder that passed a U.S. Standard Sieve No. 325 combined readily with gallium in several proportions. For practical purposes a gallium content from 20 to 40% was desirable. Less than 20% gallium resulted in a dry granular material that could not be readily packed and more than 40% gallium made a sloppy alloy that was difficult to handle. The data on compressive strength and hardness of four gallium-nickel alloys are summarized in Table 1. When triturated 70 revolutions in 30 seconds, the 35% gallium alloy expanded from 128 to 136 μ/cm at the end of 24 hours and was about constant at 140 to 149 μ/cm from 2 to 5 days (Fig. 1, Curves 1 and 2). Mixing this alloy in a mechanical amalgamator for 1 minute instead of a mortar for 30 seconds resulted in a 24-hour expansion of about 60 μ/cm (Fig. 1, Curve 3). This increased to about 75 μ/cm expansion after 3 days and remained constant for 14 days thereafter. Increasing the amount of work done on the mix appears to reduce the expansion and increase the compressive strength of the 35% gallium-nickel alloy.

Either powdered cobalt or powdered silicon reduced the large setting expansion of gallium-nickel alloys. For example, an alloy of 35% gallium, 55% nickel, and 10% cobalt expanded about 55 μ/cm at the end of 24 hours (Fig. 1, Curve 4). It continued to expand for about 6 days until a total expansion of approximately 70 μ/cm had occurred. No additional expansion had occurred at the end of 16 days. A specimen containing 36% gallium, 62% nickel and 2% silicon expanded 37 μ/cm in 24 hours. However, this method of reducing the high expansion of the gallium-nickel alloys also reduced their strength. A comparison of the 24-hour compressive strengths is given in Table 2.

The compressive strength of the 38% gallium, 60% nickel and 2% silicon alloy remained constant from 20°C (68°F) to 50°C (122°F). The strength of amalgam at mouth temperature was reduced approximately 21% and at 50°C (122°F) the strength was decreased about 43% (Table 3).

The tarnish resistance of gallium-nickel alloy was superior to amalgam when exposed to ammonium polysulfide vapor. The sulfide film that did form on the gallium-nickel alloy was easily removed by wiping with the finger, whereas the sulfide film on amalgam was adherent.

Gallium-copper and gallium-copper-tin alloys. Gallium combined with copper and copper-tin alloys of several compositions. Copper powder and a powdered alloy containing 90% copper and 10% tin were obtained from a manufacturer of powdered metals. Alloys with compositions corresponding to the γ (73% copper-27% tin), δ (68% copper-32% tin), ϵ (62% copper-38% tin) and η (41% copper-59% tin) phases of the copper-tin phase diagram (Fig. 2) [9] were made and comminuted. The compressive strengths of these,

when combined with 35% gallium, are shown in Figure 3. The alloy made by the combination of gallium and speculum metal (68% copper-32% tin) was readily mixed and packed and had good strength. This alloy hardened slowly as shown in the strength-time curve in Figure 4, and expanded from 46 to 50 μ/cm on hardening (Figure 5). This expansion is less than that of the 35% gallium-65% nickel alloy but is still high when compared to the expansion of dental amalgam (3 to 13 μ/cm is the range of expansion permitted by American Dental Association Specification No. 1 for Dental Amalgam Alloy) [10]. The hardness of this alloy varied from 100 to 119 Brinell which corresponds to the upper range of a type II (medium) or the lower range of a type III (hard) inlay casting gold alloy [10].

Gallium-copper-beryllium alloys. Gallium combined with a powdered copper-beryllium alloy (98% copper-2% beryllium) to form an alloy that hardened rapidly. The compressive strength (average of 2 specimens) of this copper-beryllium alloy when combined with 35% gallium was 19,500 psi at 1 hour and 18,500 psi at 24 hours. This would indicate that little or no reaction between the gallium and copper-beryllium alloy occurred after 1 hour. This does not agree with the data on dimensional change on hardening as shown in Figure 6. The technique for preparing the compressive strength specimens was the same as that for Curve 1, Figure 6. Different trituration times used in preparing this alloy resulted in different rates at which the expansion occurred (Figure 6). The discrepancy in the order of the expansion curves was not investigated because the alloy had unsatisfactory compressive strength.

When the gallium content was increased to 40%, liquid gallium squeezed out of a 1-hour-old specimen during crushing. This specimen had a compressive strength of 14,000 psi.

Gallium and commercial dental amalgam alloys (silver 65% min., tin 25% min., copper 6% max., and zinc 2% max.).* The combination of gallium with commercial dental amalgam alloys was unsatisfactory. The compressive strength of these alloys when mixed with gallium varied from a maximum of 14,000 psi after 1 week for a specimen containing 20% gallium, with a powdered alloy containing 69.1% silver, 26.8% tin, 2.8% copper and 1.4% zinc, to a minimum of 1,000 psi after 1 day when 35% gallium was triturated with an alloy containing 74.5% silver, 25% tin and 0.5% zinc. Trituration in all cases was in a mortar using 70 revolutions in 30 seconds with a 3 lb load on the pestle. The 1-day compressive strength of the 74.5% silver, 25% tin, 0.5% zinc alloys, when combined with gallium in this manner, decreased with an increasing gallium content as shown in Figure 7. The compressive strength of any of these is too low for use in the mouth.

* Composition limits for dental amalgam as per American Dental Association Specification No. 1 for Dental Amalgam Alloys (First revision 1934) [10].

4. DISCUSSION

This investigation indicates that powdered face-centered cubic metals such as gold, nickel, copper and some intermetallic compounds of copper and tin will, when triturated with gallium, harden at room or mouth temperature. Powdered body-centered cubic metals such as tantalum, chromium and molybdenum, when triturated with gallium, if they harden at all, do so too slowly to be of practical value.

The strength of alloys containing 35% gallium-65% copper, 35% gallium-65% speculum metal, 35% gallium-65% nickel is adequate for oral use but the expansion on hardening may be excessive as clinical experience with alloys having a setting expansion of about 50 μ/cm (35% gallium-65% speculum metal) has not been reported.

The wetting action of gallium should give good adaptation when the alloy is condensed in a cavity. Packing a 35% gallium-65% nickel alloy into a glass tube gave a mirror-like appearance to the inside of the tube. This wetting action is also a handicap when handling gallium alloys. The glass and metal mixing and condensing instruments become coated with gallium alloy making cleaning difficult. Since gallium does not wet wax and wax-like materials and smooth surfaces of some resins such as Teflon and Nylon, it may be possible to make satisfactory mechanical amalgamator capsules and pluggers from these resins.

The indication that gallium alloys retain their strength at mouth temperature and above, whereas amalgam does not, may be significant. Failure of amalgam at the margins of a restoration may be due, in part, to the reduced strength of the amalgam at body temperature.

5. SUMMARY

The following alloys of gallium with powdered metals and alloys have been made and found to harden at room or body temperature: 40% gallium-60% gold, 35% gallium-65% nickel, 38% gallium-60% nickel-2% silicon, 35% gallium-55% nickel-10% cobalt, 35% gallium-65% copper, 40% gallium-60% cobalt; and 35% gallium with the following copper-tin alloys; 90% copper-10% tin, 73% copper-27% tin, 68% copper-32% tin (speculum metal), 62% copper-38% tin, and 41% copper-59% tin.

Mixtures of gallium with tantalum, chromium, molydenum and some commercial amalgam alloys would not harden or were too weak to be of practical value.

The 40% gallium-gold alloy reacted exothermically under certain conditions and was therefore impractical for oral restorations.

The 35% gallium-nickel alloy had good strength and hardness but expanded 140 to 149 μ/cm in 2 days. The expansion was reduced to about 75 μ/cm by increasing the amount of work done on the mix during trituration.

Cobalt powder or silicon powder added to gallium-nickel alloys also reduced the expansion but the 1-day strength of the alloy was decreased by this treatment.

The 35% gallium-speculum metal alloy had good strength and hardness but set slowly. It continued to gain strength during 10 days storage at body temperature. This alloy had a setting expansion of 46 to 50 μ/cm.

Gallium alloys have been made with some physical properties that are adequate for oral restorations. However, sufficient data on the physical properties of gallium-powdered metal alloys are not available to recommend any so far investigated as possible replacements for dental amalgam. Prior to any such recommendations the alloy or alloys must be assessed biologically.

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TABLE 1

Compressive Strength and Brinell Hardness of Some Gallium-nickel Alloys

Composition Gallium-Nickel Wt %	Wt %	Compressive Strength psi	Baby Brinell hardness 15 Kg load 1/16" ball	Remarks
23	77	14,000	48	Triturated 2 min. 3 lb load on pestle. Specimen 3 days old
33	67	32,000	90	Triturated 2 min. 3 lb load on pestle. Specimen 1 day old.
35	65	49,000	90	Triturated 1½ min. 3 lb load on pestle. Specimen 1 day old
44	56	33,000	70	Triturated 2 min. 3 lb load on pestle. Specimen 1 day old
		62,000	100	As above except excess gallium was expressed during condensation.

Above values are individual or average of two determinations.

TABLE 2

Effects of Addition of Cobalt and Silicon to the Compressive Strength of Gallium-nickel Alloys

Composition Wt %	Compressive Strength Average psi	Compressive Strength Standard Deviation psi
35 gallium 65 nickel	39,600	5,500
35 gallium 58½ nickel 6½ cobalt	31,100	2,300
38 gallium 60 nickel 2 silicon	25,500	800

All specimens made by triuration in a mortar, 70 revolutions in 30 seconds under a 3 lb load.

TABLE 3

Compressive strength (1 day) of amalgam and an alloy of 38% gallium, 60% nickel, and 2% silicon at 21°C, 37°C and 50°C (70°, 99° and 122°F)

Temperature	Amalgam*	38% gallium, 60% nickel, 2% silicon	
		Average	Standard Deviation
°C	psi	psi	psi
21	49,500**	25,500	800
37	39,000**	26,700	1,300
50	28,600**	25,200	2,000

* Alloy composition - Silver 70.3%, Copper 2.4%, Tin 25.5% and Zinc 1.8%

** Average of two determinations

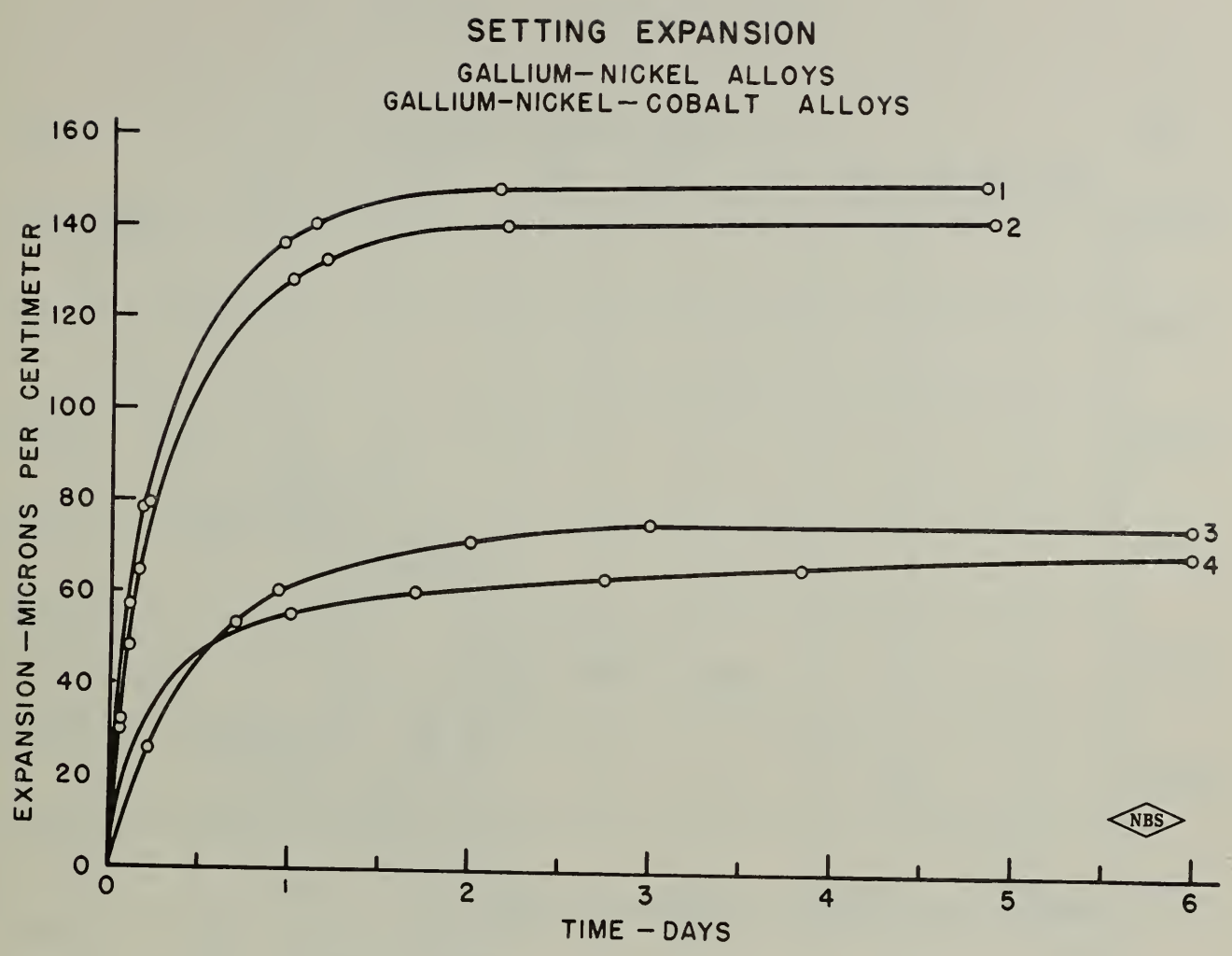

Figure 1. Dimensional Change on Hardening of Gallium-Nickel and Gallium-Nickel-Cobalt Alloys at 37°C (98.6°F)

Curves 1 and 2. 35% gallium-65% nickel triturated 70 revolutions in 30 seconds at 3 lb load.

Curve 3. Same as 1 and 2 except triturated 1 minute in a mechanical amalgamator.

Curve 4. 35% gallium-55% nickel-10% cobalt triturated 75 revolutions in 30 seconds at 3 lb load.

Cu-Sn Copper-Tin

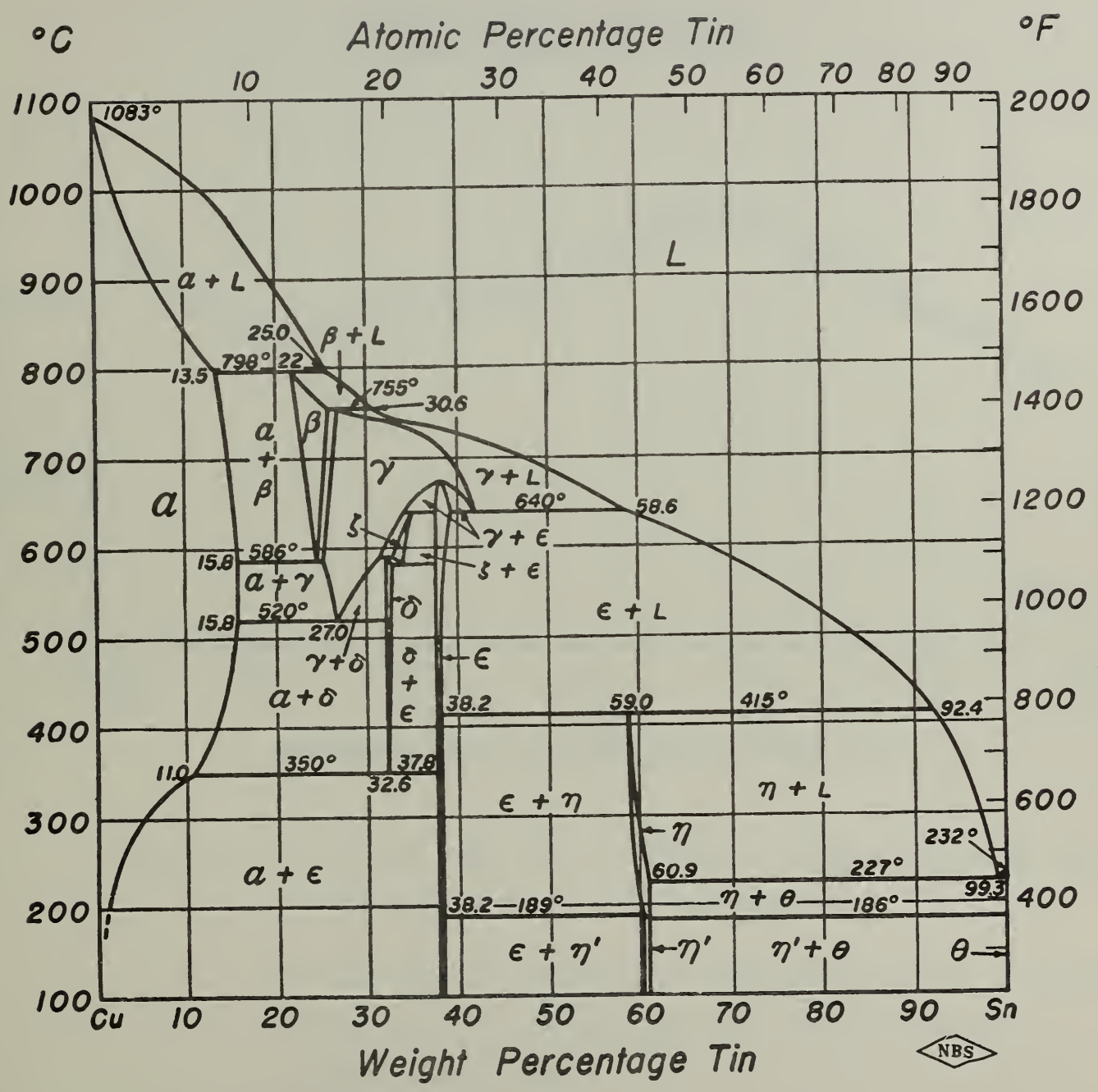

Figure 2. Copper-tin Constitution Diagram[9].

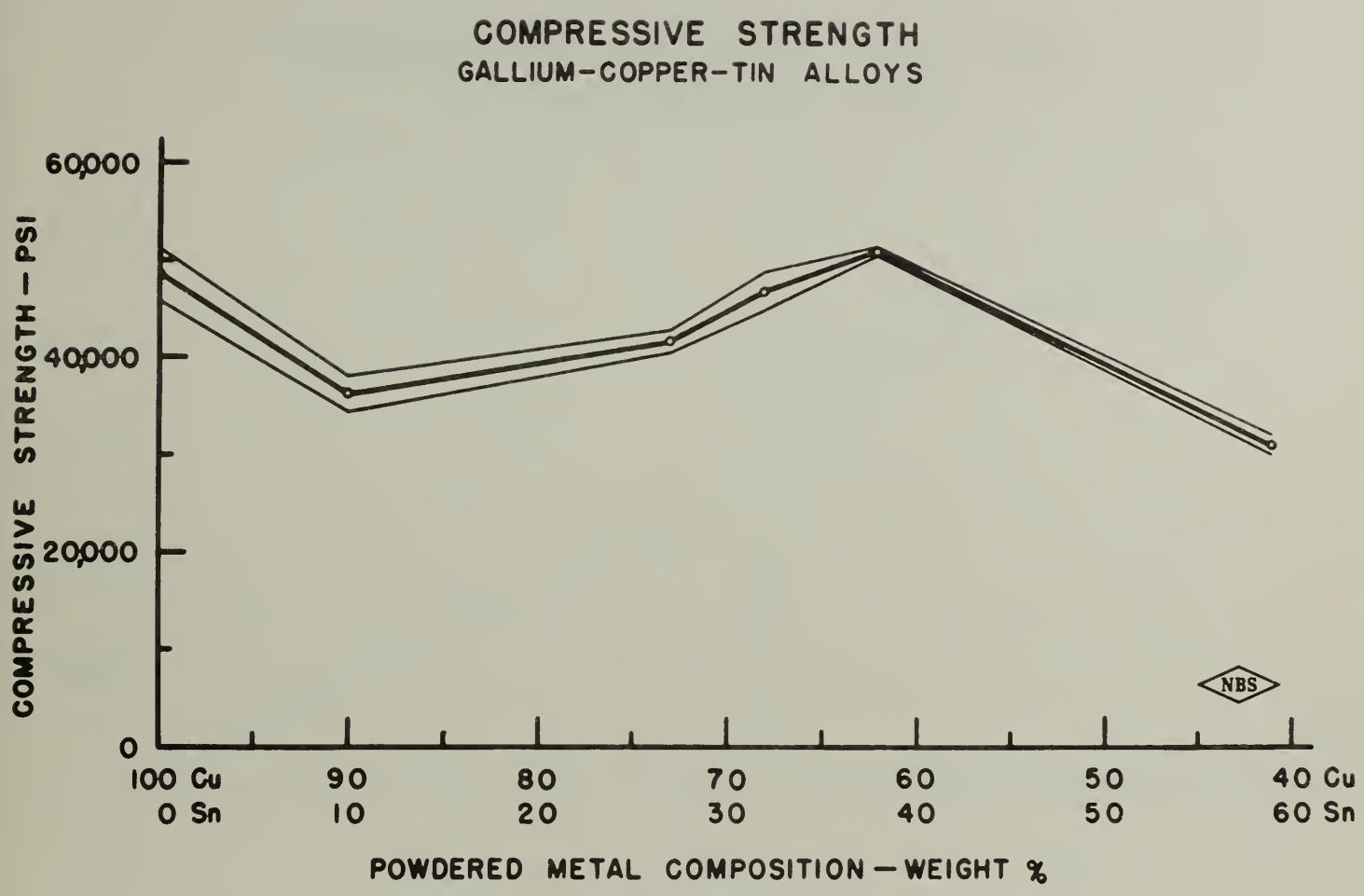

Figure 3. Three-day Compressive Strength of Copper and Copper-Tin Alloys when Combined with 35% Gallium.

Trituration in a mortar, 70 revolutions with a 3 lb load. Center line is average; upper and lower lines are standard deviations.

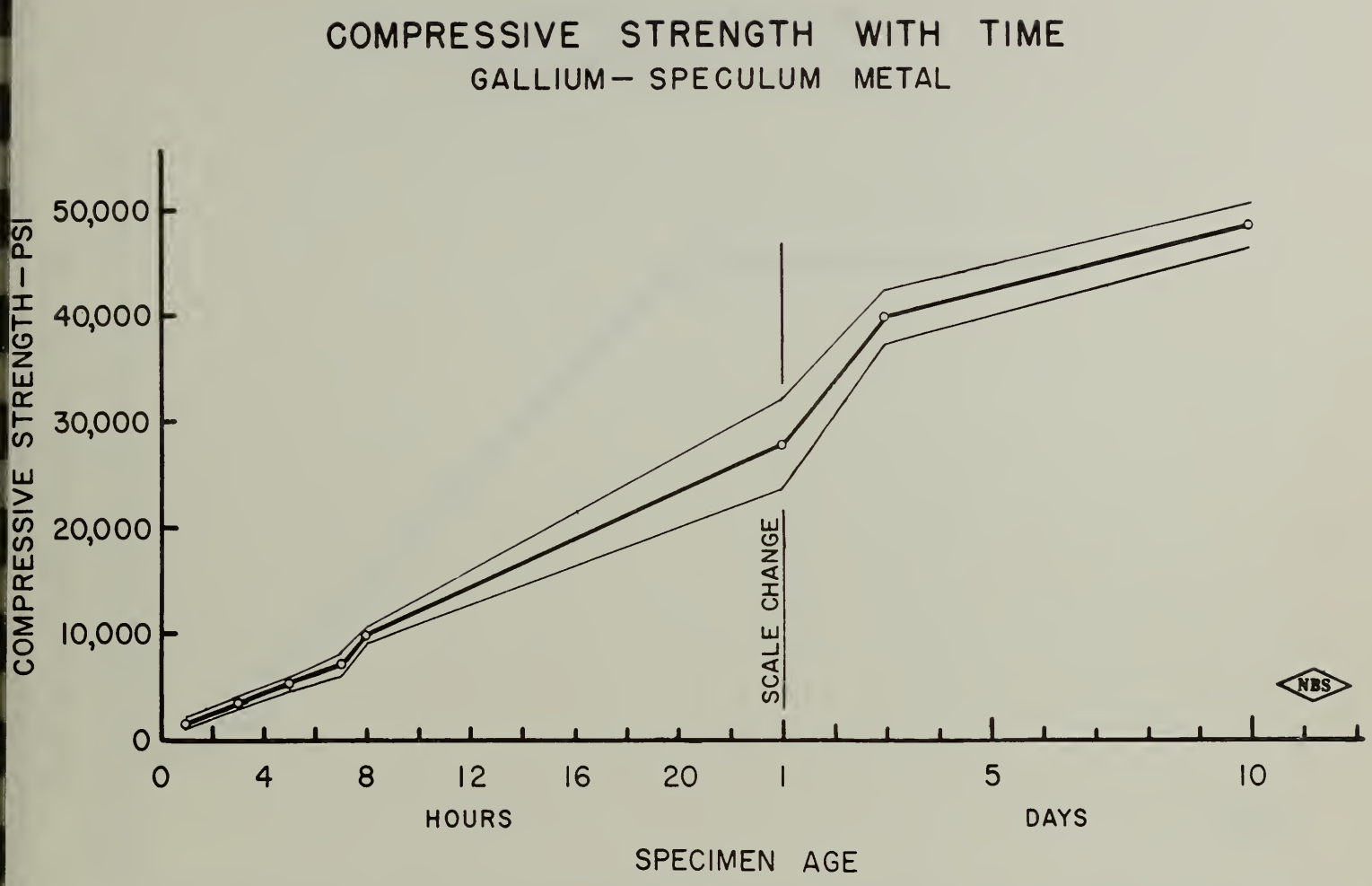

Figure 4. Compressive Strength of 35% Gallium, 65% Speculum Metal (68% copper-32% tin).

Triturated 70 revolutions in 45 seconds with a 3 lb load. Center line is average; upper and lower lines are standard deviations.

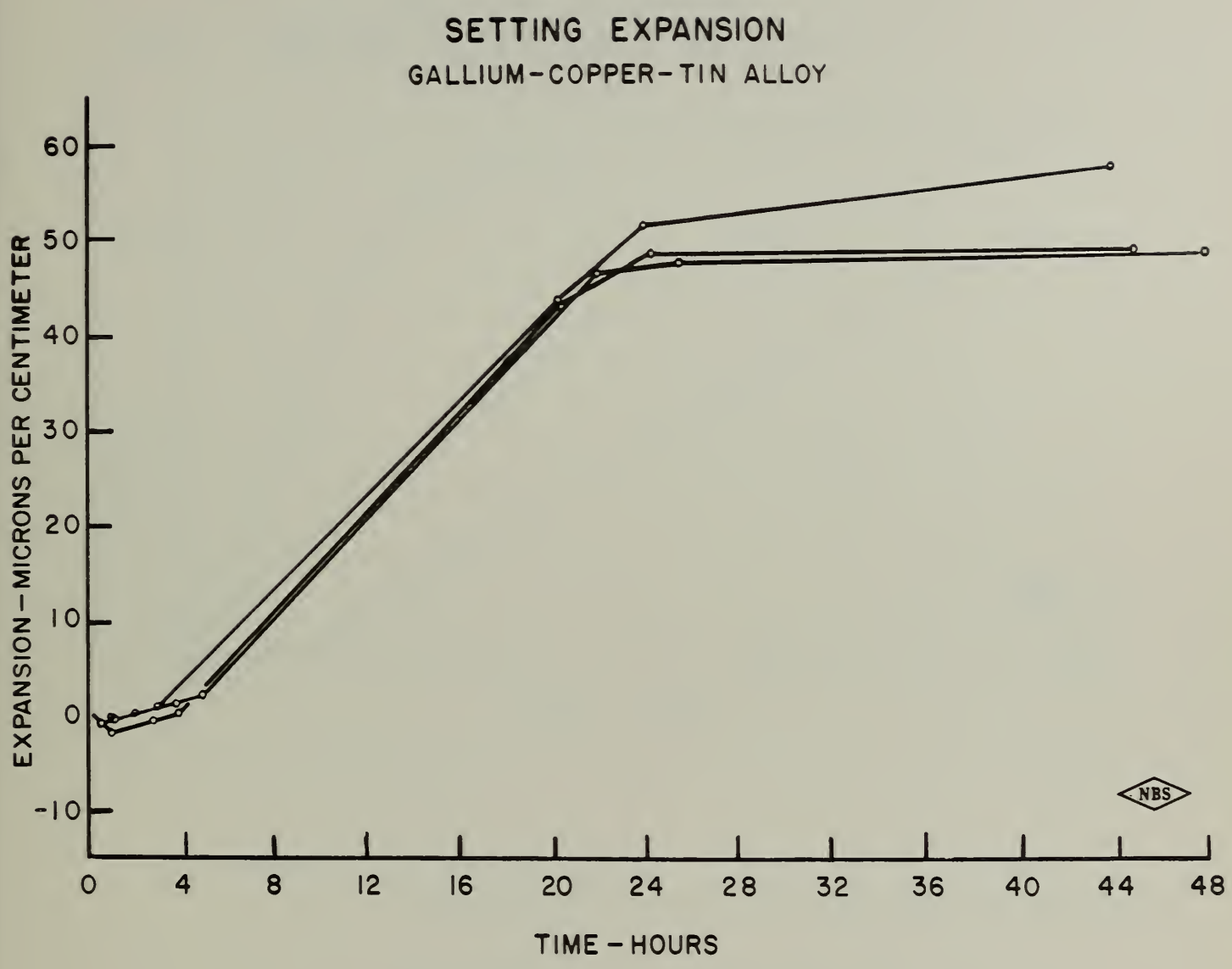

Figure 5. Dimensional Change on Hardening of Three Specimens of 35% Gallium-65% Speculum Metal (68% copper-32% tin).

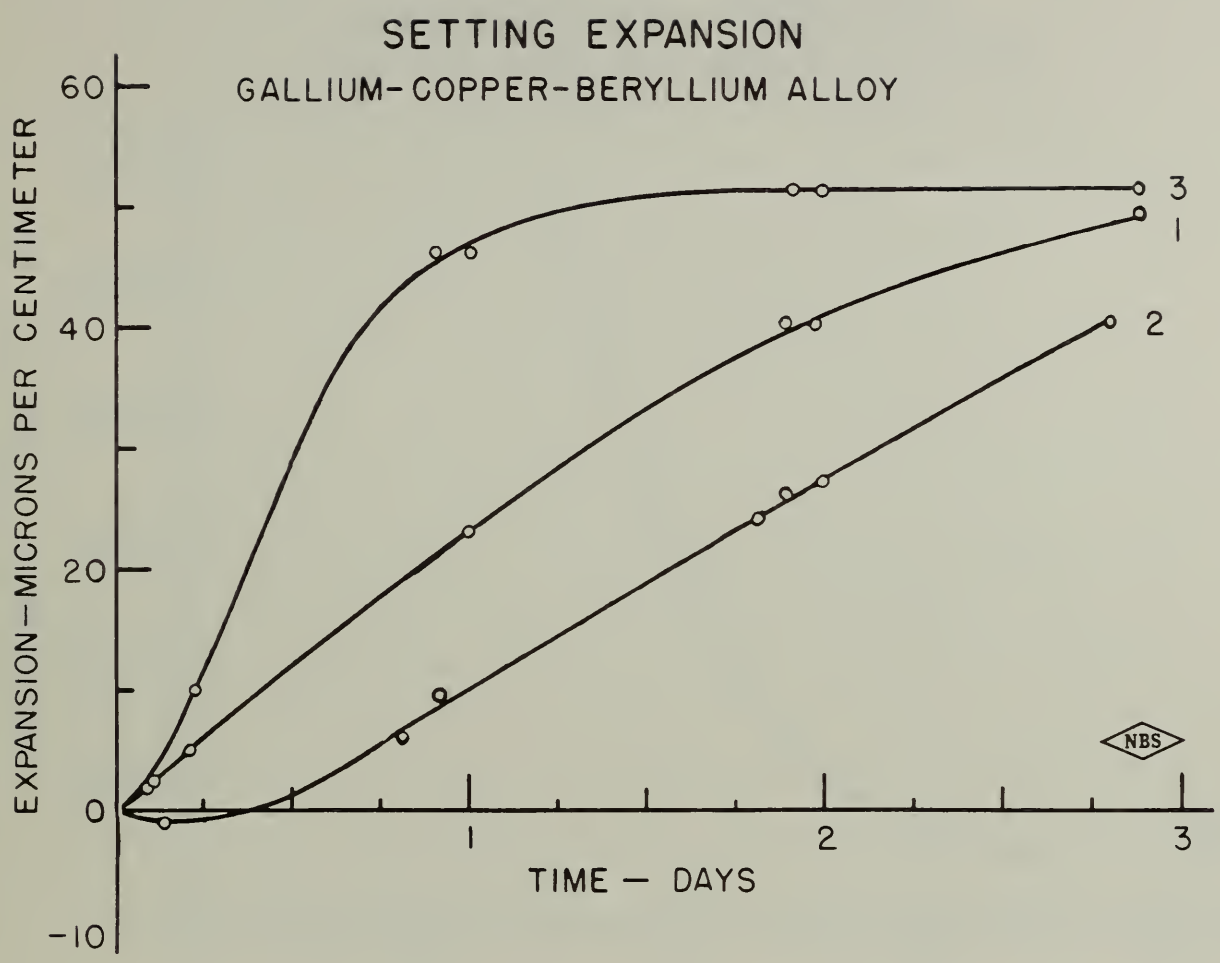

Figure 6. Dimensional Change on Hardening 35% Gallium-65% Copper-Beryllium Alloy (98% copper-2% beryllium).

Trituration in a mortar with 3 lb load.

Curve 1 - 50 revolutions in 30 seconds.

Curve 2 - 70 revolutions in 45 seconds.

Curve 3 - 100 revolutions in 60 seconds.

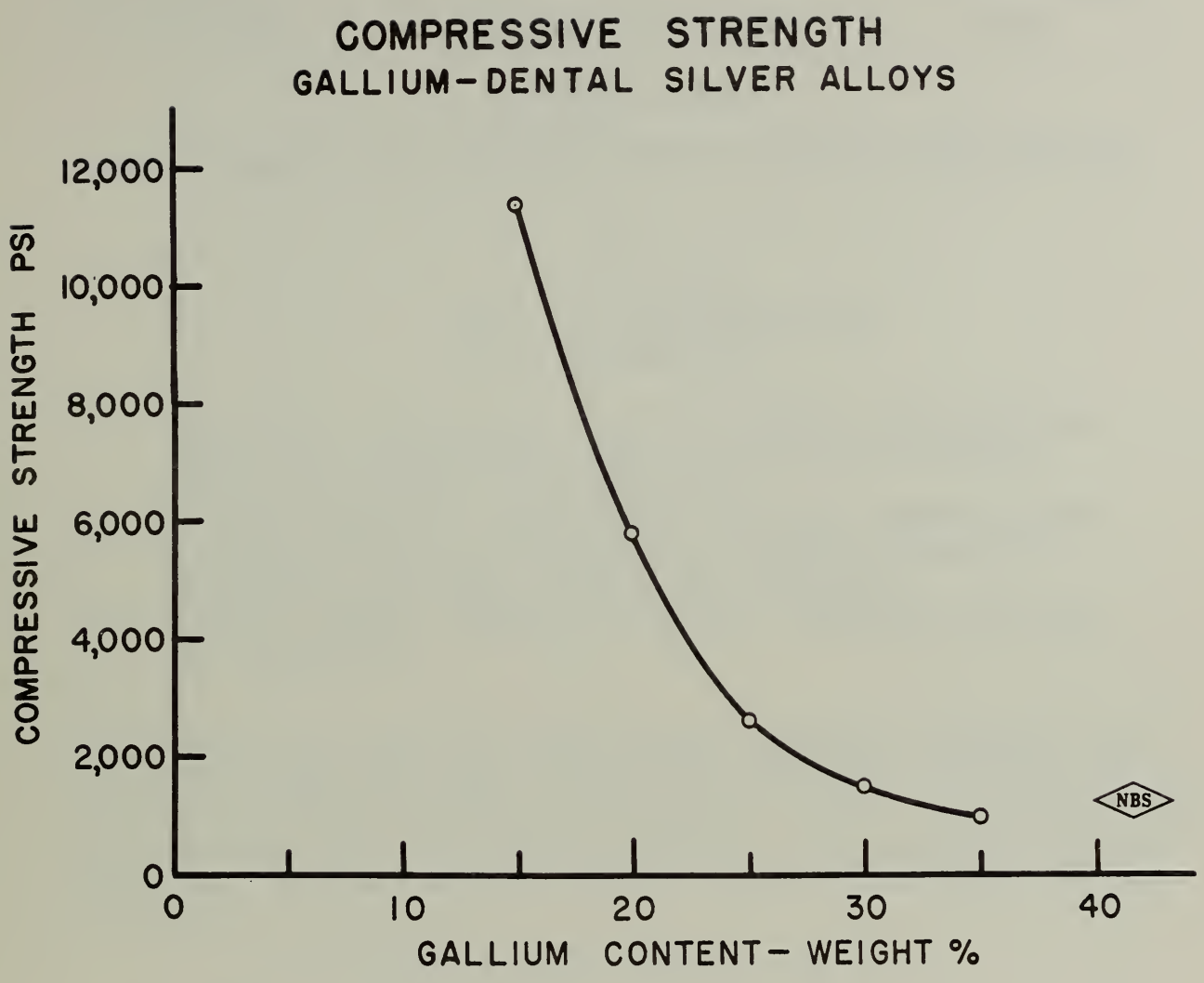

Figure 7. Compressive Strength at 24 hours of Gallium-Silver-Tin-Zinc Mixtures (powdered alloy composition, silver 74.5%, tin 25%, zinc 0.5%). Triturated 70 revolutions in 30 seconds with 3 lb load.

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

RESIN CEMENTS AND POSTERIOR-TYPE DIRECT-FILLING RESINS

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NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

RESIN CEMENTS AND POSTERIOR-TYPE DIRECT-FILLING RESINS

Abstract

A physical property survey of nine resin cements and two posterior-type direct-filling resins used in dentistry showed (a) times of setting ranging from 4 to 12 minutes; (b) a temperature rise of from 10 to 41°C above 37°C on 200 mm^3 specimens; (c) a polymerization shrinkage of 3 to 8 percent by volume; (d) an expansion on sorption of water of 0.2 to 0.6 percent linearly; (e) slight solubility in distilled water; (f) some with optical opacities that approximate enamel and dentin; (g) one with a radio-opacity equal to that of zinc phosphate cement; (h) a compressive strength about the same as that of zinc phosphate cement; (i) no adhesion to the hard tooth tissues under oral conditions; and (j) color instability under ultra-violet light. At the present stage of development the resin cements should be considered as experimental materials and not as a complete substitute for zinc phosphate cement.

1. INTRODUCTION

Dentistry has long awaited the development of a cement with such superior properties that it would displace zinc phosphate cement. Since 1952 some synthetic resin cements have been available commercially for dental use, but little informative literature about them is available. It is the purpose of this report to supply some data on the physical and chemical properties by which these resin cements may be compared with each other and with zinc phosphate cements.

2. MATERIALS INVESTIGATED

The materials surveyed are listed in Table 1 according to type, batch or control numbers of the manufacturer and date of procurement. Standard deviations are given in the tables presenting test results if more than two specimens were tested. Otherwise the data are the average of duplicate tests.

3. EXPERIMENTAL PROCEDURE AND RESULTS

3.1 Composition

Powder. The proportion of organic and inorganic constiuents of the powders was determined quantitatively (Table 2) by extraction with chloroform. The resins in P. F. and Replica

powders would not dissolve in chloroform; hence, these two resins are omitted from Table 2. The resins were not identified. The chloroform-insoluble portions of the powders referred to in Table 2 did not contain organic materials (as no charring occurred on heating) and were, therefore, considered inorganic. Some of these inorganic fillers were identified by spectrographic, petrographic and X-ray diffraction analyses (Table 3).

Liquid. The refractive indices of the various resin liquids ranged from 1.413 to 1.424 at 25°C. The index of refraction of methyl methacrylate monomer is 1.412 at 25°C. The density of the liquids ranged from 0.938 to 0.944 g/ml at 25°C. The density of methyl methacrylate monomer is 0.938 at 25°C. The liquids had an odor characteristic of methyl methacrylate monomer but no chemical identification was attempted. All of the monomers except P.F. and Replica were apparently free of cross-linking agents, as all of the powders and all of the hardened resins except P. F. and Replica dissolved in chloroform.

Cement. The water-soluble arsenic content of all of the resins was determined by the modified Gutzeit Method [1]. The specimens were prepared according to the method outlined in the American Dental Association Specification No. 9 for Dental Silicate Cement [2] except that the resin specimen was not powdered. Instead, films of resin approximately 300 microns thick were used. All of the resins were within the maximum permissible limit of 0.0002 percent (2 parts per million) of arsenic [2,3] required by the silicate cement and zinc phosphate cement specifications.

3.2 Consistency of Mixed Unset Resin Cement

The method for determining the consistency of the unset cement was patterned after those in the American Dental Association specifications for silicate cement [2] and zinc phosphate cement [3].

Apparatus. A diagram of the apparatus used in determining the consistency is shown in Figure 1. The glass measuring tube (A) is employed in the test for consistency for silicate cements. The method of forming the disk (B) is used in the test for consistency of zinc phosphate cements.

Method. The following technic was used in preparing all specimens unless otherwise stated. The resin powder was placed in a heap on one end of a glass slab (3 in. wide, 6 in. long and 1 in. thick). A crater was made in the powder with a flexible stainless steel spatula (S.S.White No. 324). Then 0.5 ml of monomer was ejected into the crater in 5 seconds with a luer-type, tuberculin, hypodermic syringe having a capacity of 1 milliliter. The monomer was allowed to soak into the powder

for 5 seconds, after which the mixture was spatulated vigorourly for 20 seconds, using approximately 1 square inch of the surface of the mixing slab in order to obtain as homogeneous a mixture as possible. The glass measuring tube (A in Fig. 1) was then slightly overfilled with the mix and struck off flush on the end of the tube with the spatula.

These operations were completed in 20 seconds, after which 0.5 ml of the mix was ejected on the glass plate in 10 seconds. Fifteen seconds later the glass plate weighing approximately 20 ± 2 grams and the 100 gram weight (total weight, 120 grams) were placed on the cement as shown in B, Figure 1. The weight was removed 10 minutes after the mixing was started. The average of the major and minor diameters of three disks was recorded to the nearest 0.5 mm. The tests were conducted at 21°C (70°F) and at a relative humidity of 60 ± 10 percent.

Test Results. The diameter of the disk is a measure of the consistency of the resin under test conditions. The effect of powder-liquid ratio on consistency is shown in Figure 2. In a former investigation of the zinc phosphate cements [4] a consistency that produced a disk 30 mm in diameter was the average cementing consistency preferred by dentists. With the exception of Justi, Tyton, Vitacril and Grip, the resins had a suitable cementing consistency when a 30 millimeter disk was produced. The consistencies of the four foregoing materials were too heavy for use as a cement at a 30 millimeter disk. For these four materials, a disk diameter of 40 millimeters was judged to coincide with a proper cementing consistency.

The slope of the lines in the graph (Fig. 2) indicates the degree of change in consistency with the powder-liquid ratio. As the slope of the lines approaches the horizontal, the more critical is the effect of slight changes in the powder-liquid proportions on consistency. In other words, the slope of the lines indicates the rate of polymerization which in turn is governed by a number of factors, the principal ones being the proportions of catalyst and promoter present and the solubility of the polymer (powder) in the monomer (liquid).

The data fell on a straight line when testing many of the resins. Considerable scatter from a straight line occurred with some other resins. Repeated check tests confirmed this experience and indicated that the reproducibility of the data is connected with inherent characteristics of the individual products. The maximum standard deviation for a sample of any color (Table 1) was less than 1 millimeter, except Tyton and Surgident, in which cases the standard deviations were 2 and 1.5 millimeters, respectively.

Because the relative amount of monomer in a mix governs the shrinkage during polymerization, there should be some correlation between the powder-liquid ratios and the polymerization shrinkage. The resins in the upper portion of the graph (Fig. 2) should have less shrinkage than those in the lower part. As is shown in Figure 3, this relationship is generally present.

The test for consistency provides a simple and rapid method of detecting small differences among lots or batches and colors of the resin and could serve as a simple production control test.

3.3 Time of Setting

In this report the time of setting is the elapsed period between the beginning of the mix and the time at which a standard 1 lb. Gillmore needle does not leave a perceptible circle on the surface of the cement specimen.

Apparatus and Method. The test was conducted as described in American Dental Association Specification No. 8 for Zinc Phosphate Cement [3] except that the specimen was transferred to an atmosphere of 100 percent relative humidity at 37°C (98.6°F) in 1 minute, instead of 3 minutes after starting the mix. This change was made because a proper mix of the resin may be made in 30 seconds while at least 1½ minutes are required for making a proper mix of zinc phosphate cement. Also if the resin cement sets unprotected in the air, the monomer evaporates quickly causing the formation of a crust. This was especially true when thin, slow-setting mixes having a high monomer content were tested. In this case the crust became thick enough to support the weight of the needle even though the resin cement was not polymerized in the center of the specimen.

Test Results. The times of setting determined at three consistencies on all of the resins show a much narrower spread (with the exception of Surgident) than either zinc phosphate or silicate cement (Table 4). In some instances (P.F., Tyton and Vitacril) there was as little as 30 seconds difference in the time of setting of very thin and very thick mixes. Therefore, the resin cements are far less critical than the zinc phosphate cements in variation of time of setting among different consistencies of mix.

As the Gillmore needle test for setting time uses a cylindrical specimen 6 mm high and 10 mm in diameter, it departs from clinical practice where a thin film of cement is used. Consequently data obtained by a rough test for setting time that employs thin films were compared with data obtained by the standard Gillmore needle test. The film setting-time test

consisted of cementing two glass microscope slides together under a load of 100 grams, with an overlap of approximately 25 mm^2 on the ends and applying a 1 kilogram load axially. This force would shear the unset but not the set film of cement. A new specimen was tested every 30 seconds until one was found that would sustain the load. Times of setting by this film test were approximately 2 minutes longer than the times of setting obtained by the Gillmore needle method.

Substances like eugenol interfere with or prevent the polymerization of the self-curing resins, hence prolong the time of setting indefinitely.

3.4 Temperature Rise During Polymerization

Some dentists may feel that sufficient heat is generated during the polymerization of these resins to be of consequence clinically. It was decided, therefore, to measure the temperature rise during hardening of the resins. The method employed was that used in other investigations [4, 7, 8]. The data show that the temperature rise of resin cements on setting of a cylinder having a volume of 200 mm^3 ranged from 10 to 41°C above 37°C which is comparable with the direct filling resins. As the cements are used in much smaller volumes than 200 mm^3, no danger of overheating the pulp is anticipated.

3.5 Shrinkage on Polymerization

The volume shrinkage of the resins, of a zinc phosphate cement and of a silicate cement as they pass from a fluid to a solid state was measured by a displacement method previously described [9]. The data (Fig. 3) show that at the end of 30 minutes, the resins shrink from 3.4 to 8.3 percent by volume; the silicate cement, 1.3 percent; while the zinc phosphate cement had an expansion of 0.3 percent. However, the slope of the terminal portion of the curves shows that the shrinkage of the resins is almost over at 30 minutes but that the shrinkage of the zinc phosphate cement persists. The silicate cement continued to shrink for 24 hours after which there was little change from the final value of 2 percent by volume [9]. The zinc phosphate cement shrinkage was not followed beyond 30 minutes. A final volume shrinkage for a zinc phosphate cement in water was computed from data on the linear shrinkage in another report [5] as 0.15 percent at the end of 30 days, after which no additional change was noted. Thus, the resins have considerably more shrinkage on hardening than do either the silicate or the zinc phosphate cements.

Shrinkage may not be as critical when the resin is used as a cement as when it is used as a filling. The film of cement pressed between two rough surfaces (those of an inlay and cavity) is restrained and stretched so that the shrinkage is localized.

The amount of shrinkage of a thin cement film is of little practical significance. If a cement film 100 microns thick shrank 8 percent by volume on hardening, the linear shrinkage would be 2.7 percent. On a film 100 microns thick this would amount to about 3 microns.

3.6 Expansion on Sorption of Water

In common with denture base resins [10] and the direct filling resins [9], the resin cements expand on sorption of water. The data in Table 5, obtained on single specimens by a previously described method [9], show the expansion at 1 day and at 3 months. These data are of the same order as those obtained on direct filling resins [9]. The clinical significance of expansion caused by water sorption is not definitely known. It may be responsible for the resin cements not adhering to tooth structures under mouth conditions. As in the case of the shrinkage on polymerization, the actual dimensional change in the thickness of the film of a cement between an inlay and the tooth would be very small.

All of the resins and a zinc phosphate cement were placed in small cylindrical cavities prepared in stainless steel and in aluminum blocks, which were kept submerged in water at body temperature for 9 months. None of the materials expanded visibly above the surfaces of the blocks except Tyton. This behavior is not consistent with the data in Table 5.

3.7 Solubility and Disintegration

Fully polymerized pure methyl methacrylate resin should be highly insoluble in water. However, the resin cements and filling materials contain catalysts, promoters, mineral fillers, and often considerable quantities of residual monomer. Therefore, it was decided to determine the solubilities by the method outlined in the American Dental Association Specification No. 8 for Zinc Phosphate Cement [3] with some modifications. These modifications were: (a) the two flat plates were covered with 0.003 inch tin foil to facilitate removal of the specimens; (b) the plates and cement were placed in the 37°C (98.6°F) - 100 percent relative humidity atmosphere at 2 instead of 3 minutes after start of mix; (c) after the water was evaporated, the weighing bottles were dried to constant weight at 120°C (248°F) instead of 149°C (300°F).

The residue obtained by this method is the amount of material dissolved and eroded by the distilled water from the specimens and is reported in Table 6 as the percentage of their original weight. The average solubility and disintegration of the resins is approximately the same as the maximum of 0.3 percent permitted by the American Dental Association Specification for Zinc Phosphate Cement [3]. However, the zinc phos-

phate cements are attacked readily by sulfides while the resins are not. Since sulfides are present in the mouth, they may be at least partially responsible for the failure of zinc phosphate cements in service. The silicate cements are not attacked by sulfides. This, too, may account for the silicate cements lasting longer in the mouth than zinc phosphate cements, even though the silicate cements are more soluble in water [8]. Thus this solubility test does not appear to represent some mouth conditions and should not be used to intercompare different types of dental materials. However, experience has shown the test to be useful in comparing cements of the same type.

A 1 percent solution of glucose was mixed with saliva in a ratio of 3 to 1 and allowed to ferment until it reached a ph of 3.4. When films of resins, 0.5 mm thick, were immersed in this glucose-saliva mixture, bubbles developed on the surfaces of Acrynamel and Dura Cement in 24 hours. The color of the surfaces of Acrynamel, Dura Cement, Dura Kore, and Smith's Resin Cement in contact with the mixture were bleached. The surface of the zinc phosphate cement darkened, The gloss was not removed from the surface of the resins after a week's immersion. The surface of the zinc phosphate cement was so severely attacked that it could be rubbed off easily.

When the resin films were immersed in 5 percent solutions of acetic acid (pH 2.4), citric acid (pH 1.9), and lactic acid (pH 1.8) all of the cements which contained carbonate fillers - namely, Acrynamel, Dura Cement, Dura Kore, Smith's and Tyton - had gas bubbles form on the surface and were bleached severely. The other resins were not visibly affected. A 5 percent solution of ammonium hydroxide had little or no visible effect on any of the resins.

3.8 Opacity

The dentist is interested in the opacity of cement to both visible light and X-rays; the former for esthetic purposes and the latter for oral diagnosis.

Optical Opacity. The optical opacities of enamel, dentin and silicate cements were given in a previous report [8] wherein the limits of opacity for silicate cements were set at a range of 35 to 55 percent on specimens 1 mm thick. This range was based largely on the average opacity of enamel - 39 percent, and of dentin - 70 percent. It would therefore be desirable for any filling material to have an opacity in the range of 35 to 55 percent. This opacity range would also be desirable in a cement used with translucent materials such as fused porcelain and synthetic resins.

The optical opacity of the resins was determined by the method outlined in American Dental Association Specification

No. 9 for Dental Silicate Cement [2], except that the glass plates, between which the 1 mm thick specimen was molded, were covered with tin foil (0.003 in. thick) to facilitate removal of the specimen. Also the time of placing the mix between the plates was 1 minute instead of 3 minutes after beginning the mix.

Opacities for the various resins are given in Table 7. The color of some of the resin cements has a pronounced effect upon the opacity, the lighter colors being less opaque. However, it is possible, as the data in Table 7 show, to produce a resin cement with the proper optical opacity for cementing translucent filling materials. The red and black copper phosphate cements, the zinc phosphate cements and the zinc oxide-eugenol cements are all 100 percent optically opaque on specimens 1 mm thick [11].

Radio-opacity. When using cements as a base under other restorations or for cementing opaque materials, the cements should be as radio-opaque as possible in thin sections so that there will be no confusion on the X-ray picture between the cement and decayed areas.

The radio-opacity was determined by X-raying a six-step wedge of cement (Fig. 4) under a set of standard conditions. As each step was approximately 0.5 mm thick, the six-step wedge ranged in thickness from 0.5 to 3.0 mm. The exposures were made at normal incidence with a film-target distance of 16 inches at 10 milliamperes and 65 kilovolt peak. Kodak Radiatized film was exposed for 1 second. The solutions were Eastman Kodak liquid developer and fixer made up according to the manufacturer's directions. The film was agitated constantly during processing, developed 4½ minutes at 20°C, rinsed for 2 minutes in running water, shaken as dry as possible, fixed for 10 minutes and washed for 20 minutes in running water.

Film densities for various thickness of the cement wedges were read on the zero to three scale of an Ansco densitometer. The data on the 2 mm thick step in the wedge are presented in Table 8. The lower readings indicate the greater radio-opacity. The resin cements should be as radio-opaque as zinc phosphate cements, if used as a base or as a cement for opaque filling materials. Only Grip had such a radio-opacity. Most of the resins were less radio-opaque than silicate cements.

3.9 Film Thickness

If a cast restoration of lost tooth structures is to be seated accurately, the cement film between the casting and the tooth should be as thin as possible. Thus, the cementing medium should have only small particles on it. One method for determing the effect of particle size of the cement powder

on the cement film is to measure the thickness of a film between optically flat plates. Such a test which is a part of American Dental Association Specification No. 8 for Zinc Phosphate Cement [3] was employed except that the load was applied to the plates 1 minute instead of 3 minutes after mixing was started. The data (Table 9) show that a film thickness as low as 10 microns may be obtained with one resin cement (Grip). Six of the cements would comply with the film thickness requirement of the American Dental Association Specification for Zinc Phosphate Cement [3] as they had a film thickness of 40 microns (0.0016 in.) or less at the standard consistencies (Fig. 2). Thinner than standard consistencies produced films less thick and thicker than standard consistencies produced films of greater thickness. This is probably so because monomer in excess softens the polymer grains in the powder which permits them to be flattened before the cements harden. Evidently the particle size of the inorganic fillers was less than that of the polymer particles in the cement.

The data on film thickness in Table 9 show that resin cements can be formulated that have thinner films than any of the currently certified zinc phosphate cements.

3.10 Compressive Strength

The compressive strength of a dental filling material should give some indication of its resistance to masticatory forces. The compressive strength of a cement should be useful in evaluating the ability of a cement to hold restorations in place. As will be subsequently shown, the retention is not due to the true adhesion of the cements to tooth structure or to the restorations being cemented, but to a mechanical interlocking when the cement flows into the irregularities of the surfaces of the cavity and the restoration. To displace the restoration it is necessary to shear off these minute projections; the higher the compressive strength, the higher the force required to shear them. The strength of the individual particles of powder in the set cement would influence the amount of shear required to dislodge a cemented restoration if the particle was large enough to wedge between the surfaces of the cavity and the restoration.

The compressive strength of the resins was determined on specimens 1 hour and 1 week old by the procedure used in determining the compressive strength of silicate cement [2] except as follows; (a) the test cylinders were 6 mm (0.236 in.) in diameter and 10 mm (0.394 in.) high; (b) tin foil [0.076 mm (0.003 in.) thick] covered the glass plates used in forming the ends of the molds in which the test cylinders were prepared; (c) these plates and the stainless steel molds were lubricated sparingly with a silicone (Dow-Corning high vacuum grease); (d) the ends of the test cylinders were made plane and parallel by facing the specimens on a lathe. The aluminum oxide filler

present in P. F. dulled the cutting tool so badly that it had to be resharpened after cutting each specimen. (This dulling of instruments by the aluminum oxide abrasive has been observed by dentists in cutting P. F. with a dental bur and should not be interpreted as indicating that this resin is extremely hard).

It was difficult to obtain smooth-sided cylinders with some of the cements having high shrinkage values (Fig. 3). Better specimens of these cements were obtained by filling a retaining ring approximately half full of the resin and by inserting the mold inside this ring causing the powder-liquid mixture to rise from the bottom to the top surface of the mold, in much the same manner as specimens used in the test for compression of the hydrocolloidal impression materials are formed [15].

The resins did not fracture on failure in compression in the same manner as the various dental cements and amalgam which, being brittle, suddenly go to pieces at the ultimate load. Instead the test cylinders of the resin barrel-out and sometimes shear diagonally.

The compressive strengths of the resins and various other dental restorative materials are given in Table 10. As is common with most restorative materials formed by a chemical reaction between a powder and a liquid, the resin cements generally increase in strength with time. The strength at 1 week is usually more than that at 1 hour. These data also show that the compressive strength of the resin cements at 1 week is on the average roughly two to five times that of zinc oxide-eugenol cement; seven-eights of the minimum value (12,000 lb/in^2) for zinc phosphate cement in American Dental Association Specification No. 8 [3]; less than one-half the 24-hour minimum value (23,000 lb/in^2) for silicate cements in American Dental Association Specification No. 9 [2]; and from one-third to one-fifth that of amalgam. The clinical use of zinc oxide-eugenol cements, zinc phosphate cements, silicate cements and dental amalgam has placed their lasting qualities against masticatory stresses in the mouth in the same order as their compressive strength (Table 10). Since the resins have about the same compressive strength as the zinc phosphate cements which do not hold up well in the mouth, it is reasonable to assume that the direct filling resins cannot be used successfully for restorations subject to masticatory forces. In fact, experience with the indirect filling resins proved this. It is believed that the resin cements would retain an inlay or other appliance in place to about the same degree as zinc phosphate cements on the basis of their comparative compressive strength.

3.11 Indentation Hardness

The hardness of the resins, as determined by the Knoop indenter, fell within a range of 9 to 16 kg/mm^2 indicating

that these resins are no more resistive to indentation than polymethyl methacrylate denture base resin. The incorporation of an abrasive such as alumina in P. F. does not make the resin significantly harder, but the alumina does make the compound abrasive.

3.12 Adhesion

A rough screening test for adhesion was employed to find out if any of the resin cements or the direct filling resins (posterior type) were actually adhesive to enamel and dentin under conditions of use. A flat surface was ground on one side of the crowns of freshly extracted teeth which were not allowed to dry out. The flat surface of enamel and dentin was swabbed with cotton pellets and dried with warm air as is done in practice. The various resins were then applied to the clean, dried surface. All of the resins showed an initial adhesion to the tooth tissues and if the tooth and resin were kept dry the adhesion was so strong that usually the tooth would be broken if an attempt was made to remove the resin. However, after soaking the tooth with the resin on it in water, this adhesion was lost. There were no exceptions, and zinc phosphate cement adhered as long as the resin cements. After 24 hours soaking in water most of the cements could be easily dislodged; after 1 week soaking, all of them could. Similar tests were performed in the mouth using the buccal surfaces of the lower posterior teeth except, of course, that the surfaces of the teeth were not ground. The teeth were isolated under a rubber dam and the buccal surfaces were cleaned and dried with cotton and warm air blasts and a small amount of resin was applied to every other tooth; zinc phosphate cement was used on the alternate teeth. At the end of 1 week, all were off. The zinc phosphate cement persisted as long as the resin cements.

3.13 Color Stability

Experience over a number of years has shown that the results of laboratory tests using the color stability procedure outlined in American Dental Association Specification No. 12 for Denture Base Resin [16] correlate with service conditions. The denture base resins that discolored under this test discolored in use. The same held for the denture repair resins and the direct filling resins. The procedure was therefore employed to test the color stability of the resin cements. None of the materials (Table 1) complied with the requirements. Some discolored more than others. Methods for making the self-curing resins color stable to ultraviolet light are now available; hence these resin cements will probably be made color stable soon.

As pointed out previously in the discussion of the solubility of the resin cements, those containing carbonate fillers

bleach in the presence of acids such as those present in an incubated glucose-saliva mixture.

3.14 Biological Effects

The authors have not located any literature on the effect of the resin cements upon the tooth pulp. Nor are they acquainted with reports of gross pulp damage after clinical use. The similarity of the resin cements to the direct filling resins (anterior type) would suggest about the same degree of pulp irritation with resin cements as occurs with the direct filling resins. As is well known, there is considerable controversy in the literature dealing with both laboratory and clinical experience on the degree of irritation caused by the self-curing resins. An extensive study by Johnson [17] with one resin cement was on the whole favorable.

4. SUMMARY AND CONCLUSIONS

Data presented deal with the physical and chemical evaluation of nine resin cements and two posterior-type direct-filling resins. All of these resins are somewhat similar to the anterior-type direct-filling resins. None of the resins contained significant amounts of arsenic. The major difference between the resins and the anterior-type direct-filling resins appears to be the use of mineral fillers in the cements which run from 5 to 67 percent by weight of the powders.

All tests on physical properties were conducted on specimens made from standard consistencies using modifications of tests outlined in American Dental Association Specifications for Zinc Phosphate Cement [3], Silicate Cement [2], and Denture Base Resin [16].

The times of setting ranged from 4 to 12 minutes at the standard consistencies. Large deviations from the standard consistencies usually had a surprisingly small effect on the time of setting. The resins were much less sensitive than the zinc phosphate or silicate cements to consistency variations.

The temperature rise on setting of a cylinder having a volume of 200 mm^3 ranged from 10 to 41°C above 37°C which is comparable with the direct filling resins. As the cements are used in much smaller volumes than 200 mm^3, no danger of overheating the pulp is anticipated.

The shrinkage on polymerization ranged from roughly 3 to 8 percent by volume which is far more than reported shrinkages for zinc phosphate cement (0.15 percent) and silicate cement (2 percent). The shrinkage, while being a very objectionable property, is less critical in a cement than in a filling material because the cement is generally used as a thin film in which the shrinkage in its length is localized by the restraint of the surfaces being cemented. The shrinkage of the cement over even a comparatively wide cement margin is not large. Even with a cement having a shrinkage of 8 percent by volume,

the linear shrinkage of a film 100 microns thick would be only about 3 microns.

The resins expanded linearly on sorption of water from 0.2 to 0.6 percent on disks 0.5 mm thick in 1 day. In five resins the expansion decreased with time up to 3 months immersion. In two there was a slight increase, while in four there was no significant change in the 1-day and 3-month values. The expansion caused by water sorption may be responsible for failure of the initial adhesion of the cement to hard tooth tissues.

The resin materials were slightly soluble in distilled water. When subjected to the solubility test used in the American Dental Association Specification for Zinc Phosphate Cements [3], the cements and direct filling resins ranged in solubility from almost zero to 0.4 percent by weight. The resin cements having carbonate fillers were attacked by a glucose-saliva mixture.

Resin cements may be made with optical opacities in the range of human enamel or dentin. These cements would be useful in cementing translucent filling materials such as fused porcelain. The resin cements can be made as radio-opaque as zinc phosphate cement. Such opacities are needed when cementing opaque materials like the gold alloys or when using the cement as a base for other filling materials. The high radio-opacity is needed to distinguish the cement from recurrent or unexcavated decay in interpreting X-ray pictures.

The film thickness of one of the resin cements was as low as 10 microns; this is considerably thinner than the minimum thicknesses obtained with current zinc phosphate cements, which range from 30 to 40 microns. Therefore, resin cements can be formulated that should permit very close seating of inlays and other dental appliances.

The compressive strength of the resins was from two to five times that of zinc oxide-eugenol cement, near that of the zinc phosphate cement, less than half that of silicate cement and from one-third to one-fifth that of amalgam. Clinical experiences based upon the resistance to mastication arrange the foregoing materials in the same order as the compressive strength values.

The indentation hardness (Knoop) number was of the same order as that of other dental resins.

All of the cements and posterior-type direct-filling resins adhered to the tooth tissues if kept dry. No adhesion was retained under oral conditions.

None of the materials was color stable to ultraviolet light as determined by the color stability test employed in the American Dental Association Specification No. 12 for Denture Base Resin [16]. Since self-curing acrylic resins can now be made color stable, undoubtedly the resin cements and direct filling resins presently available will all be made color stable or relatively so to ultraviolet light.

No bioassay of the resin cements has been found in the literature nor are the authors acquainted with reports of gross pulp damage after clinical use. The similarity of the resin cements to the anterior-type direct-filling resins would suggest about the same degree of pulp reaction with the resin cements as occurs with the direct filling resins.

At the present stage of development it might be well to consider the resin cements as experimental materials and not as outright unlimited substitutes for zinc phosphate cement.

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TABLE 1

RESINS INVESTIGATED

	Material	Manufacturer	Date Procured	Color	Batch Numbers Powder		Liquid
RESIN CEMENTS	Acrynamel	American Consolidated Dental Co.	Dec.1953	translucent cream and gray white	none		none
	Dura	Reliance Dental Mfg. Co.	Nov.1953	cream, gray, white, yellow	3EW 3GX	3KR 3JY 3UR	ICB ICU KCA
	Grip	The L.D.Caulk Co.	Feb.1954	gold, gray, ivory,pearl	929 B929 B3-4928	B33228 33728 34928	729
	Justi	H.D.Justi and Son, Inc.	Apr.1954	brown,natural gray and yellow, pink, white	454-A 454-B 454-C 454-D	454G 4-54E 554B 5-54D	354-A
	Smith's	Lee Smith Co.	Mar.1953	brown, gray, white, yellow	253E 253F 253G 253H 553C	6780 6781 6782 6783	7 92-104 9297
	Surgident	Surgident, Ltd.	Oct.1953	dk and lt brown, lt gray and yellow,white	none		103
	Tyton	Lang Dental Mfg. Co.	Dec.1953	gray, lt yellow, white, yellow	none		none
	Vitracril	Fricke Dental Mfg.Co.	Dec.1953	brown, cream, gray, white	none		none

TABLE 1 (cont.)

RESINS INVESTIGATED

	Material	Manufacturer	Date Procured	Color	Batch Numbers Powder		Batch Numbers Liquid
ANTERIOR-TYPE DIRECT-FILLING RESINS	Replica*	Cosmos Dental Products Inc.	Apr.1954	shades 18,22 34,67	R-17 11-121	150931 200521	070731 171231
POSTERIOR-TYPE DIRECT-FILLING RESINS	Dura Kore	Reliance Dental Mfg. Co.	May-Nov.1953	black,copper, incisal white, lt brown and yellow, pale yellow, snowwhite	3EO 3EP 3ES 3ET 3EU 3EV	3FO 3FP 3FS 3FT 3FU 3FV	DKE FKD FKE
	P.F.	American Consolidated Dental Co.	Dec.1953	gingival dk, gingival lt, gingival med., occlusal gray, occlusal translucent, occlusal white	none		none

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* Because the manufacturer also recommends Replica as a resin cement, it is included in this investigation. In succeeding tables Replica is classed as a cement.

TABLE 2

Proportion of Inorganic and Organic Constituents of Resin Powders

Type	Material	Chloroform Soluble (organic) % by wt	Chloroform Insoluble (inorganic) % by wt
Resin Cements	Acrynamel	50	50
	Dura	41	59
	Grip	33	67
	Justi	73	27
	Smith's	42	58
	Surgident	75	25
	Tyton	41	59
	Vitacril	95	5
Posterior-type direct-filling resins	Dura Kore	41	59

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TABLE 3

Some Inorganic Fillers from the Resin Powders

Type	Materials	Major elements determined by spectrographic analysis#	Compounds identified by petrographic analysis
Resin Cements	Acrynamel	Calcium Silicon Aluminum	Calcium carbonate Quartz Mica
	Dura	Calcium Barium Silicon	Calcium carbonate Barium carbonate
	Grip	Calcium Tungsten	* Calcium tungstate**
	Justi	Barium Silicon Titanium	Quartz ***
	Smith's	Calcium Sodium	Calcium carbonate ***
	Surgident	Sodium Zinc	*
	Tyton	Calcium Barium Silicon	Calcium carbonate Barium carbonate Quartz
	Vitacril	Titanium Silicon Zinc	*
Posterior-type Direct-filling Resins	Dura Kore	Calcium Barium Silicon	Calcium carbonate Barium carbonate
	P.F.	Aluminum Sodium Silicon	Aluminum trioxide ***
		A66-135	A82-40, A87-137

\# More than 10 percent
* Particle size too small for petrographic identification.
** Identified by X-ray diffraction.
*** Two unidentified materials.

TABLE 4. Time of Setting of Resins

Type	Material	Consistency	Grams of powder in 0.5 ml of liquid	Time of setting at 37°C (98.6°F)
				min.
Resin Cements	Acrynamel	thin	0.65	7
		standard*	0.85	5
		thick	1.05	4
	Dura	thin	0.75	6
		standard*	0.95	5
		thick	1.15	4
	Grip	thin	0.45	9
		standard**	0.65	8
		thick	0.85	8
	Justi	thin	0.33	10
		standard**	0.38	7
		thick	0.48	5
	Replica	thin	0.35	11
		standard*	0.55	8
		thick	0.75	6
	Smith's	thin	0.85	6
		standard*	1.05	5
		thick	1.25	4
	Surgident	thin	0.45	-
		standard*	0.65	12
		thick	0.85	13
	Tyton	thin	1.20	4
		standard**	1.40	4
		thick	1.60	4
	Vitacril	thin	0.85	6
		standard**	1.05	6
		thick	1.25	6

TABLE 4 (cont.) Time of Setting of Resins

Type	Material	Consistency	Grams of powder in 0.5 ml of liquid	Time of setting at 37°C(98.6°F) min.
Posterior-type Direct-Filling Resins	Dura Kore	thin	0.65	8
		standard*	0.85	6
		thick	1.05	5
	P. F.	thin	1.20	4
		standard*	1.40	4
		thick	1.60	4
Other Dental Materials	ZincPhosphate	Range at standard consistency		4 to 10 (3)
		Thin to thick		over 120 (5)
	Silicate Cement	Range at standard consistency		4 to 10 (2)
		Thin to thick		15 to 30 (6)

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* 30 mm disk (Fig. 2)

** 40 mm disk (Fig. 2)

TABLE 5

Linear Expansion on Sorption of Water
by Resin Disks 0.5 mm Thick

Type	Material	Expansion 1 Day	Expansion 3 Months
		%	%
Resin Cements	Acrynamel	0.2	0.1
	Dura Cement	0.3	0.2
	Grip	0.3	0.5
	Justi	0.5	0.5
	Replica	0.6	0.7
	Smith's	0.3	0.3
	Surgident	0.3	0.2
	Tyton	0.6	0.5
	Vitacril	0.3	0.3
Posterior-type Direct-filling Resins	Dura Kore	0.4	0.4
	P. F.	0.6	0.4

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TABLE 6

Solubility and Disintegration of Resin Cements in Distilled Water

Type	Material	Weight Loss %
Resin Cements	Acrynamel	0.4
	Dura	0.3
	Grip	0.1
	Justi	0.0
	Replica	0.1
	Smith's	0.4
	Surgident	0.1
	Tyton	0.4
	Vitacril	0.2
Posterior-type Direct-filling Resins	Dura Kore	0.4
	P. F.	0.3
Other dental materials	Zinc phosphate cement	0.3*
	Silicate cement	1.4**

A66-180

* Maximum permitted by American Dental Association Specification No. 8 [3].

** Maximum permitted by American Dental Association Specification No. 9 [2].

TABLE 7

Optical Opacity of Resin Cements and Posterior-Type Direct-Filling Resins

Type	Material	Variations with color $C_{0.70}$*
Resin cements	Acrynamel	0.45 - 1.00
	Dura	0.55 - 0.70
	Grip	1.00
	Justi	0.60 - 1.00
	Replica	0.40 - 0.45
	Smith's	0.50 - 0.60
	Surgident	>0.70 - 1.00
	Tyton	>0.70 - 1.00
	Vitacril	0.70 - >0.70
Posterior-type Direct-filling resins	Dura Kore	0.60 - 1.00
	P. F.	0.45 - 0.60
Zinc Phosphate Cements[11]		1.00
Silicate Cements[2]		0.35 - 0.55

A66-35

* The $C_{0.70}$ value represents the daylight apparent reflectance (R_0) of the cement specimen (1 mm thick) when placed over a black glass backing divided by the daylight apparent reflectance ($R_{0.70}$) of the cement specimen when placed against a white backing with an apparent daylight reflectance relative to MgO of 70 percent. When the reflectances are the same, the $C_{0.70}$ value is 1.00 and the cement is 100 percent opaque. If $C_{0.70}$ is equal to 0.50, the cement is said to be 50 percent opaque, etc.

TABLE 8

Radio-opacity of Some Resins, Enamel and Dentin

Type	Material	Film density*
Resin Cements	Acrynamel	2.7
	Dura	1.9
	Grip	0.8
	Justi	2.7
	Replica	2.9
	Smith's	2.4
	Surgident	2.2
	Tyton	1.8
	Vitacril	2.9
Posterior-type Direct-filling Resins	Dura Kore	1.9
	P. F.	2.7
Other Dental Cements	Silicate Cement	1.9
	Zinc Oxide-Eugenol Cement	0.6
	Zinc Phosphate	0.8
Hard Tooth Tissues	Dentin++	1.3
	Enamel++	1.1

A82-113

* Average readings on the 2 mm thick specimens recorded as observed on the zero to three scale. The lower the film dentisty readings the greater the radio-opacity.

++ Data from curve drawn from readings of five molars.

TABLE 9

Film Thickness of Resin Cements

Material	Film Thickness microns
Acrynamel	60
Dura	40
Grip	10
Justi	25
Replica	120
Smith's	25
Surgident	30
Tyton	25
Vitacril	85
Zinc phosphate cements on List of Certified Dental Materials [12]	30 to 40

A66-89

TABLE 10

Compressive Strength of Some Dental Restorative Materials

Type	Material	Age of Specimens 1 hr lb/in²	1 wk lb/in²	Consistency
Resin Cements	Acrynamel	9,500 ± 500	10,000 ± 700	Cementing
	Dura	9,000 ± 300	11,500 ± 200	"
	Grip	10,000 ± 800	12,000 ± 500	"
	Justi	8,000 ± 400	10,500 ± 300	"
	Replica	8,500 ± 200	10,000 ± 200	"
	Smith's	11,000 ± 200	12,500 ± 300	"
	Surgident	6,000 ± 200	7,500 ± 100	"
	Tyton	10,500 ± 100	10,500 ± 300	"
	Vitacril	9,000 ± 300	10,500 ± 200	"
Posterior-type Direct Filling Resins	Dura Kore	8,500 ± 200	11,000 ± 600	Filling or cementing
	P. F.	10,500 ± 100	11,000 ± 100	
Other dental cements and filling materials	Zinc oxide-eugenol cement		2,000 to 5,000 [11]	Filling
	Red copper phosphate cement		14,000 [13]	Cementing
			21,000 [11]	Filling
	Black copper phosphate cement		6,000 to 22,000 [13]	Filling
			9,000 [11]	"
	Zinc Phosphate cement	2,300 to 9,200 [7]	2,000 to 13,800 [4]	Cementing
			19,000 [11]	Filling
	Zinc Silicate cement		22,000 to 25,000 [11]	Filling
	Silicate cement	12,000*	10,500 to 21,500 [8]	Filling
	Amalgam		30,000 to 51,550 [14]	Filling

A66-71

* Unpublished data collected in a former investigation [8].

APPARATUS FOR CONSISTENCY TESTS
ON RESINS

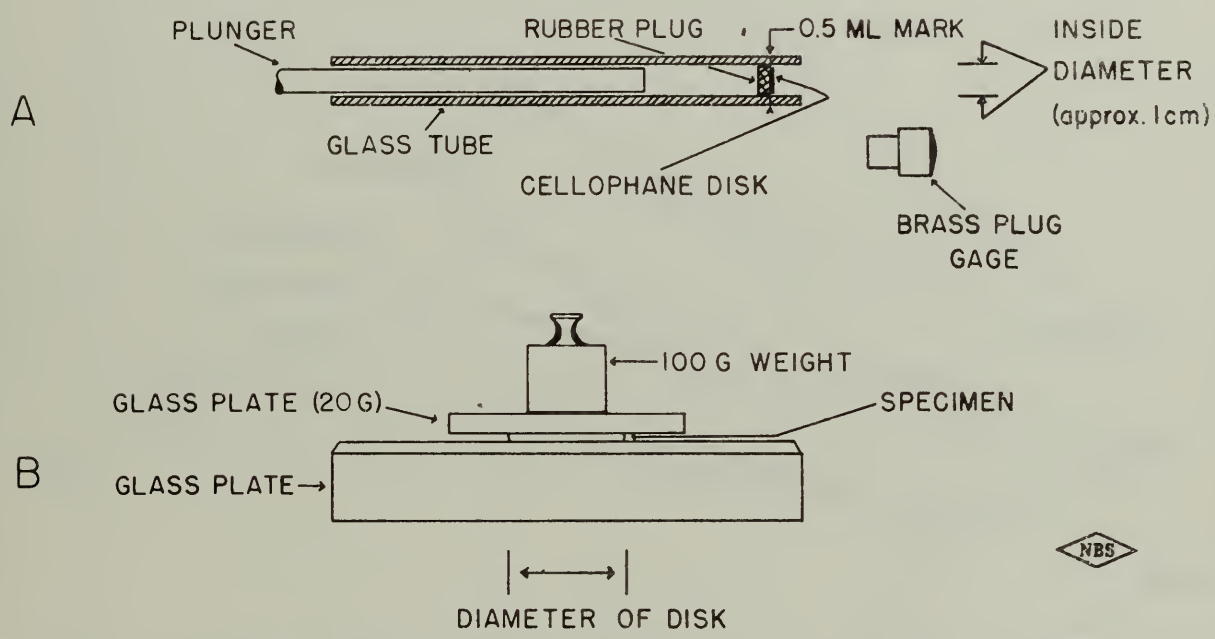

Figure 1. Apparatus used for measuring the consistency of unset resin cements and direct filling resins for posterior teeth:

A. Glass tube used to measure volume of the soft cement.

B. Weight and glass plates which flattened soft cement into a disk.

The diameter of the disk was used as a measure of the consistency of the mix.

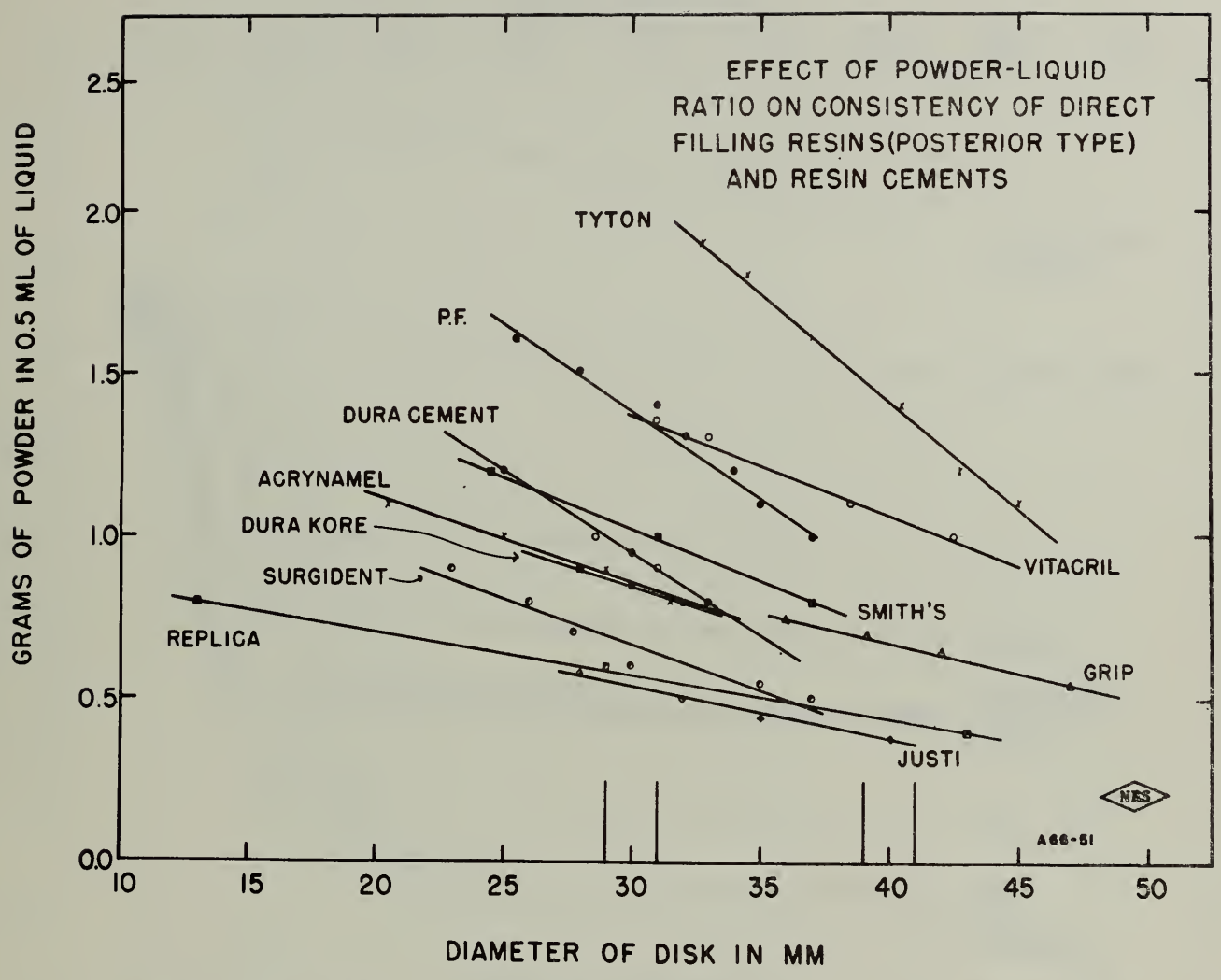

Figure 2. The effect of the powder-liquid ratio upon consistency of some mixed but unhardened dental resins. The 30 ± 1 mm and the 40 ± 1 mm areas as indicated by the extended lines on the bottom of the diagram are the consistencies used in preparing the specimens for the different tests.

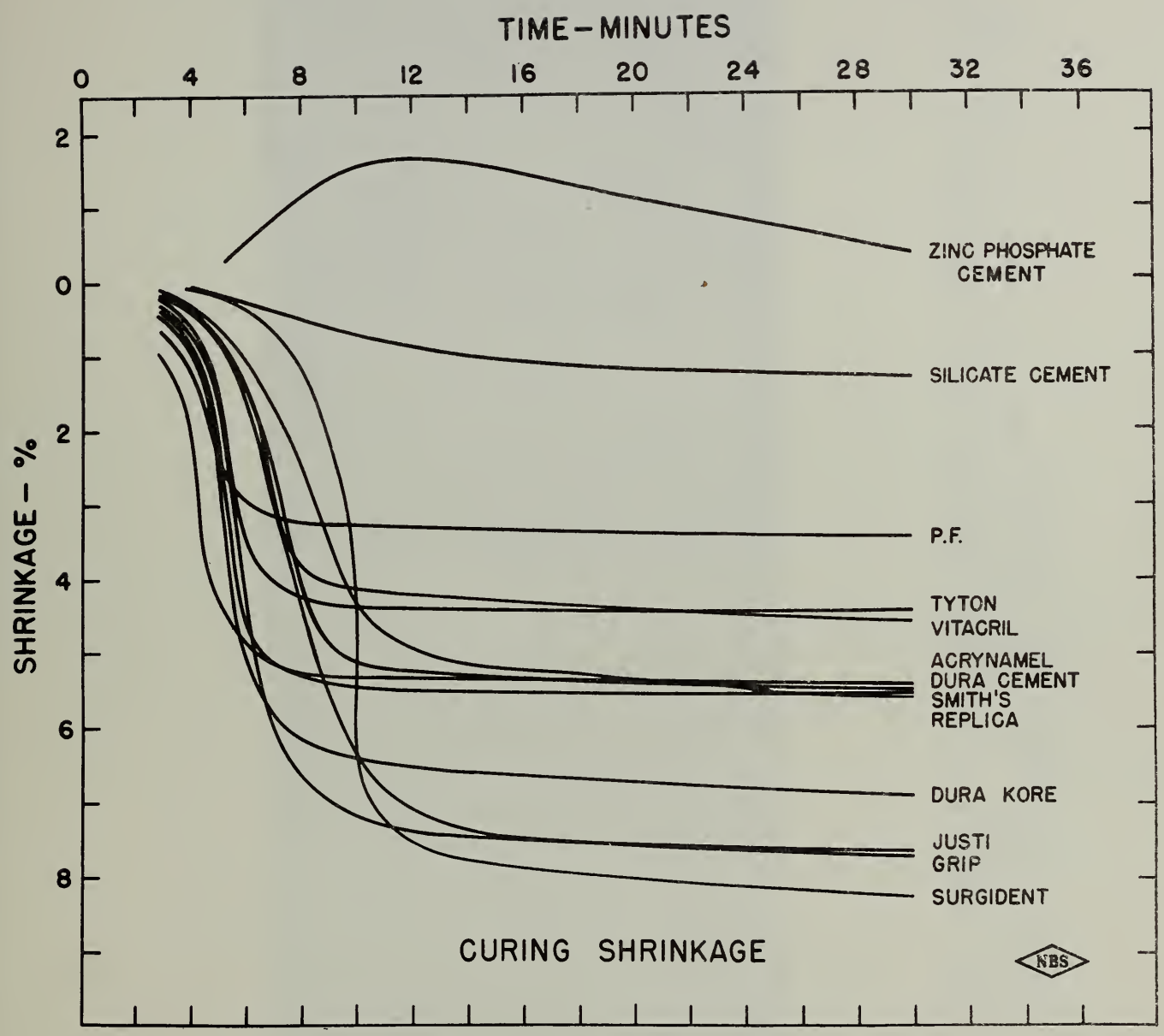

Figure 3. The volumetric shrinkage occurring as various dental resins and cements change from the fluid to the solid state.

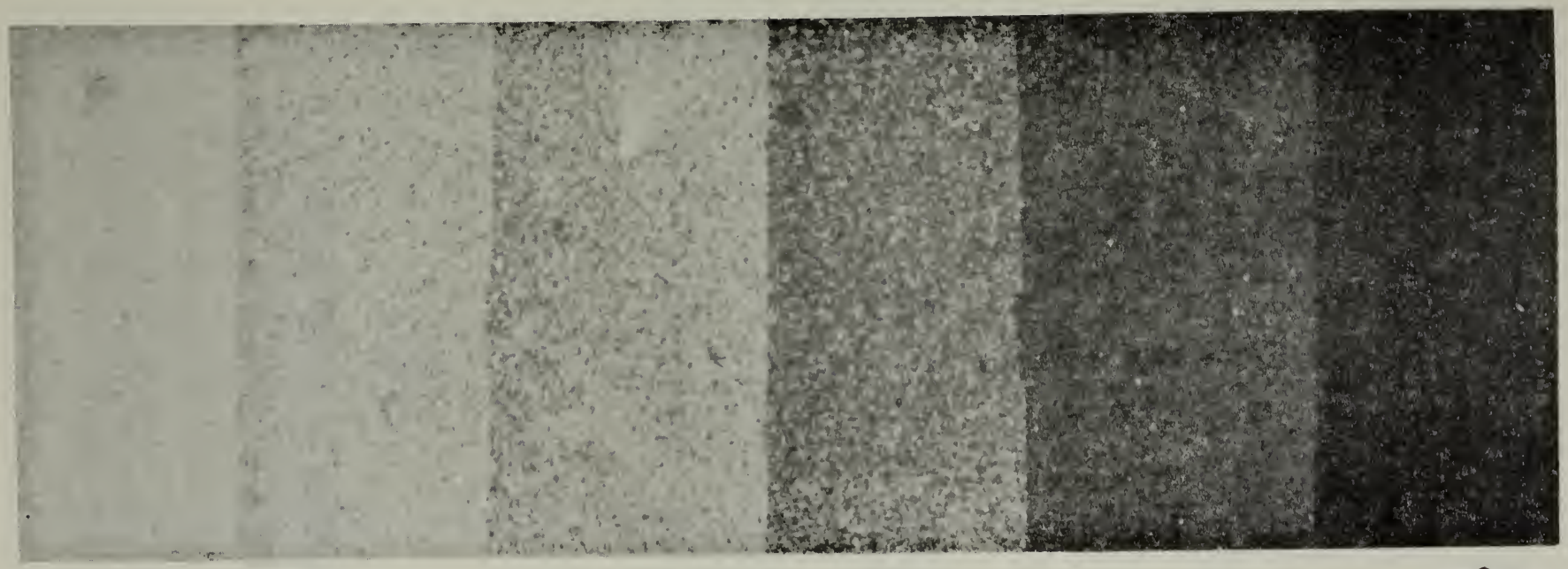

Figure 4. The positive of an X-ray negative of a step-wedge of a dental resin cement. The increasing density of each step is caused by increasing the thickness 0.5 mm. The darkest step was 3.0 mm thick, the lighest 0.5 mm thick.

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Progress Report

PRELIMINARY STUDY: TROPICAL STORAGE
OF
DENTAL MATERIALS

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.

(Task 7756-41 BV No. 55-14)

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PRELIMINARY STUDY: TROPICAL STORAGE OF DENTAL MATERIALS

Abstract

A preliminary survey of some dental materials stored for four years in Puerto Rico by the Armed Services was made to determine changes in properties of dental significance. Comparison was made with duplicates stored at the National Bureau of Standards. Alginate impression materials and investments were found to have deteriorated to an unusable state. Methyl methacrylate monomer (liquid) containing dissolved polymer had polymerized. Some items which had volatile and low melting constituents were shown to be improperly packed and melted. The tests substantiated the present practice of phase buying and preferential storage. The survey indicates the desirability for further study of the effect of storage on many dental items.

1. INTRODUCTION

Deterioration of dental materials during transport and storage is of particular interest to the Armed Services. Long periods of storage, often under extremely adverse conditions, can be a military necessity. Materials which are unusable or in an inferior condition on arrival at the operational level cause a loss of time and money as well as an interruption in

dental service.

In 1951, while a guest worker at the Dental Research Section of the National Bureau of Standards, Col. T. E. Fischer, USAF (DC), planned an investigation to determine critical time limits for the storage of certain dental materials in tropical climates. Although circumstances prevented carrying out the investigation as originally planned, a number of materiel items have been returned to the National Bureau of Standards after four years of storage, and their condition examined by visual observation and applicable specification tests.

2. CONDITIONS OF STORAGE

To avoid variations in composition, date of manufacture, and packaging, samples for storage at three locations were selected with the same batch number.

The dental materials listed under Column A, Table 1 were stored in a constant temperature and humidity room in the Dental Research Laboratory of the National Bureau of Standards. The samples were sealed in a packing case with a moisture-proof liner. The room is maintained at approximately a temperature of 70°F and a relative humidity of 60%.

The items listed in Column B, Table 1 were stored on open shelves in the penthouse of the Rodriguez Army Hospital, San Juan, Puerto Rico. The prevailing temperature at this site was the highest of the three locations.

The materials listed under Column C, Table 1 were stored on open shelves at the Tropical Research Laboratory, San Juan,

Puerto Rico, where they were exposed to year round relative humidities of 75 to 79%.

3. RESULTS AND DISCUSSION

3.1 General Effects of Storage

The appearance of the packaging of individual samples reflected storage conditions. Metal parts of containers showed varying amounts of rusting. Containers stored in the moisture-proof case at the National Bureau of Standards were clean and relatively free of rust; the penthouse containers were spotted with rust; and the seaside samples were very rusty (as may be seen in Figure 1). Cardboard cartons containing materials with volatile or low melting point ingredients were stained by these ingredients. Figure 2 shows cartons of a protective coating material. The penthouse sample, "B", which had been subjected to higher temperatures, is badly discolored.

Materials which were obviously affected by storage or which had become unusable are marked by an asterisk in Table 1. They are discussed in detail below.

3.2 Investment

The investment samples showed no caking or lumping and appeared in usable condition; however, consistency tests, performed according to Federal Specification U-I-546, proved samples from the two tropical locations to be unsatisfactory.

Figure 3 shows typical results of the consistency tests. Samples stored under "A" conditions show normal slumping. Samples stored under "B" and "C" conditions set so rapidly that the test specimens supported their own weight in less

than two minutes, a setting rate too fast for dental use.

Since such behavior is most likely caused by partial hydration [1], samples of investments from "A", "B", and "C" were dried to constant weight at 110°C. The results, as shown in Table 2, show the varying water content and setting times.

Assuming that all water in the sample is in the calcium sulfate and is removed completely by the drying process, calculations on "A" sample of investment indicate that there were approximately 30 grams of calcium sulfate hemihydrate per 100 grams of the investment. This is a reasonable proportion for investments of this type. Comparing the percent weight lost by "B" and "C" samples to that lost by "A" samples, it is readily apparent that partial hydration of the material stored at "B" and "C" had occurred. Further calculations suggest that in "B" samples approximately 9% of the hemihydrate might be considered to be hydrated to the dihydrate form; and in "C", approximately 15%.

The setting rate of the hydrated investment may be slowed, and acceptable consistency obtained, by increasing the ratio of water to investment powder when mixing. This procedure is not recommended because it weakens the investment [2] and changes both the setting and thermal expansion [3]. An inlay cast into a mold made of this partially hydrated material is not likely to fit satisfactorily.

3.3 Resin Materials

Dental resin materials are procured for the Armed Services in powder/liquid form. In addition to samples of the standard supply items, samples of several brands of "filling" resin kits were also stored.

Past experience with resin liquids has indicated the necessity for phase buying and preferential storage of these materials to avoid premature polymerization induced by heat. In this study, "A" samples of denture base resin liquids were found to be still liquid while "B" and "C" samples had polymerized into clear solids, which, of course, are useless in the dental laboratory. Figure 4 shows the effect of four years of storage at "C" on a methyl methacrylate liquid.

It is interesting to note that all of the filling resin liquids were still in the liquid phase. The liquid of one brand had changed in appearance from optically clear to a cloudy pink. The available sample was too small for analysis. However, it is suggested that the change might be due to some chemical reaction involving the tertiary amine initiator. Another brand had not polymerized but the plastic seals on the bottle caps were broken and a large portion of the liquid had evaporated. The remaining samples were unaffected by storage.

These observations substantiate the practice of preferential storage (below 37°C) and phase buying of denture base resin liquids to avoid loss due to short shelf-life. It also

appeared that the self-cured (filling) resin liquids are more resistant to polymerization when stored at elevated temperatures than are the heat-cured resin liquids.

Tests for polymer content were positive for the unpolymerized heat-cured resin liquids and negative for the self-cured resin liquids. Samples giving positive tests for polymer content solidified in less than 23 hours when stored in a constant temperature oven at 85°C. Samples giving a negative test resisted polymerization for more than 168 hours when stored under these same conditions.

Tests for traces of polymer were negative for twelve of fourteen ADA certified denture resin liquids currently on the market. The two brands of resin liquids, which showed polymer content, polymerized into an unusable hard mass in less than 17 hours when stored in the constant temperature oven at 85°C. Two brands of resin liquids, picked at random from the twelve brands without traces of polymers, showed no evidence toward solidification (increased viscosity) after 72 hours in the 85°C oven.

From these results it appears that resin liquids without polymer content can be expected to have a longer shelf-life. A more definitive study of this type might prove the desirability of a change in Federal Specification U-R-179 for Resin, Acrylic, Dental which permits the resin liquid to be "methyl methacrylate monomer or methyl methacrylate monomer which has been partially polymerized."

3.4 Alginate Impression Material

All samples stored had deteriorated to an unusable condition. On mixing at standard temperature and humidity, a gummy, grainy mass was formed in less than one and one-half minutes.

Pfeiffer [4] demonstrated that alginate impression material deteriorates rapidly when stored at temperatures exceeding 37°C. The fact that samples stored under standard temperature and humidity conditions were unusable suggests some factor in addition to temperature affects this material. Procurement and supply agencies now avoid loss of these materials by both phase buying and preferential storage.

3.5 Materials with Volatile Solvents and Low Melting Point Ingredients

This group of materials would be expected to be adversely affected by high temperatures during storage. Some items were stored only in the roof-top location, while others were stored in two or all three locations.

A protective coating material of the theobroma type was stored at all locations, but only the samples stored at "B" were affected to any extent. The metal tube containers had lost approximately one-third of their contents. The remaining portion was easily expressed from the tubes but appeared drier and more grainy than the samples stored at "A" and "C". The material was still usable for protecting restorations. The loss in volume was due to the effect of elevated temperatures

which caused this low melting point material to liquefy and evaporate.

Cellulose acetate cast lacquer samples stored at "A" and "C" had separated into a liquid phase and a gel phase. Samples of this material from "B" had completely lost their solvent (95% chloroform, 5% alcohol, by volume) through evaporation.

Wax shapes and a brand of sheet casting wax from "B" were found to have lost a part of their more volatile ingredients, making the materials unusable for the purposes intended. This deterioration occurred only to the samples where higher temperatures were encountered. Another brand of sheet casting wax and samples of a baseplate wax were unaffected by the higher temperatures.

Two of three brands of preformed plastic patterns were also affected by the higher temperatures met in the roof-top location, but the two brands were affected in different ways. One brand had lost its plasticizer and had become very brittle, whereas samples of the other brand had flowed together and were so sticky and gummy that they could be separated neither from themselves nor their cardboard mounts.

3.6 Cement Filling Materials

Silicate cement stored at "B" and red copper cement stored at "A", "B", and "C" gave no evidence of deterioration. Fischer [5] has shown that deterioration of these materials is due to loss of water from the cement liquid. At the present time, procurement specifications require that cement liquids

be packaged in sealed glass ampoules. This improvement in packaging has been effective in preventing deterioration of these materials during storage.

4. SUMMARY

Deterioration of some materials is avoided only through phase buying and preferential storage, measures which cannot always be utilized. Improved packaging appears to be all that is necessary to insure long shelf-life for other materials. The following recommendations are the result of inspecting and testing dental materials after storage for four years:

1. The condition of investments stored in humid climates shows that the investments are inadequately protected from moisture by the snap-in-lid metal containers in which these materials are now supplied. Better containers should be used.
2. Low melting point materials packaged in screw-cap metal tubes need to be more adequately protected from high temperature by puncture-to-open seals.
3. Specifications for the procurement of preformed plastic patterns should contain a temperature stability requirement.
4. An improvement in the storage stability of denture base resin liquids is desirable.
5. There is a need for a more storage-stable elastic impression material.

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4. Pfeiffer, K. R., Harvey, J. L., and Brauer, G. M., Deterioration during storage of alginate hydrocolloidal dental impression material. U.S.Armed Forces Med. Jnl. 6, 1315-1320 Sept. (1954).

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Table 1. Materials Stored

A	B	C
NBS at 70°F, 60% R.H.	Puerto Rico, Roof-top	Puerto Rico, Seaside
Investment	Investment*	Investment*
Denture Resin Liquid	Denture Resin Liquid*	Denture Resin Liquid*
		Self-cure Resin P/L
Acrylic Resin Powder	Acrylic Resin Powder	Acrylic Resin Powder
Clear Resin Kit P/L	Clear Resin Kit P/L*	Clear Resin Kit P/L*
	3 Brands "Filling" Resin Kits P/L*	
Alginate Material*	Alginate Material*	Alginate Material*
Protective Coating	Protective Coating*	Protective Coating
Baseplate Wax	Baseplate Wax	Baseplate Wax
Wax Shapes	Wax Shapes*	Wax Shapes
3 Brands Casting Wax	2 Brands Casting Wax	3 Brands Casting Wax
	3 Brands Preformed Plastic Patterns*	
Cast Lacquer*	Cast Lacquer*	Cast Lacquer*
Cavity Varnish	Cavity Varnish	Cavity Varnish
	Silicate Cement P/L	
Copper Cement P/L	Copper Cement P/L	Copper Cement P/L

*Items marked by an asterisk were found to have been adversely affected by storage.

Table 2. Water Content and Setting Time of Investment

Sample	Water Content[a] (%)	Setting Time[b] (min)
A	1.8	20
B	2.2	2
C	2.5	1.5

a Average of two determinations of weight loss on heating to constant weight at 110°C.

b On undried samples.

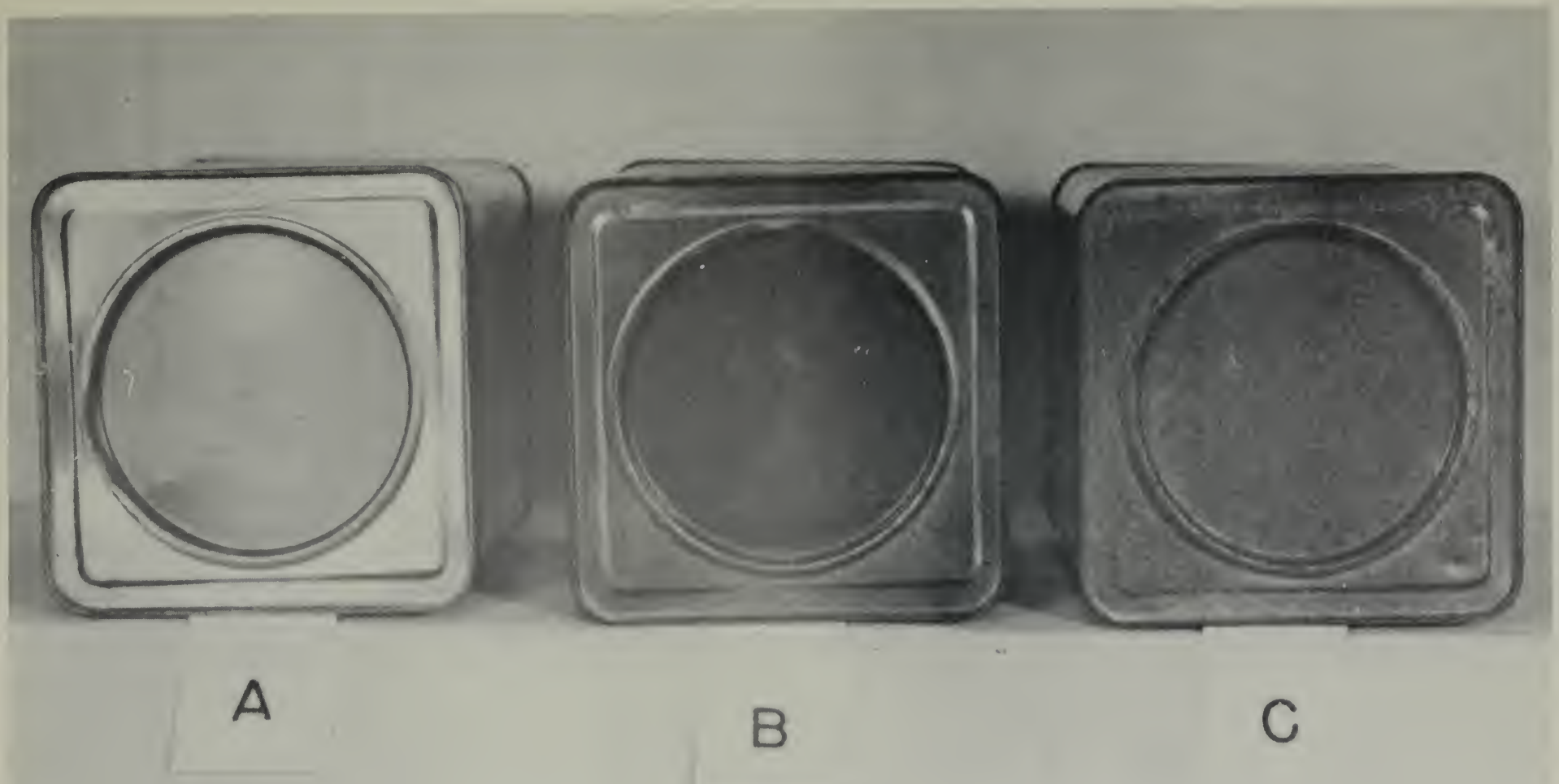

Figure 1. The metal container, "A", stored in a moisture-proof case, is clean and relatively free of rust. Containers "B" and "C", stored on open shelves in the hospital penthouse and pavilion of the Tropical Research Laboratory, are progressively more rusty indicating the effect of the increased humidity at the site of storage.

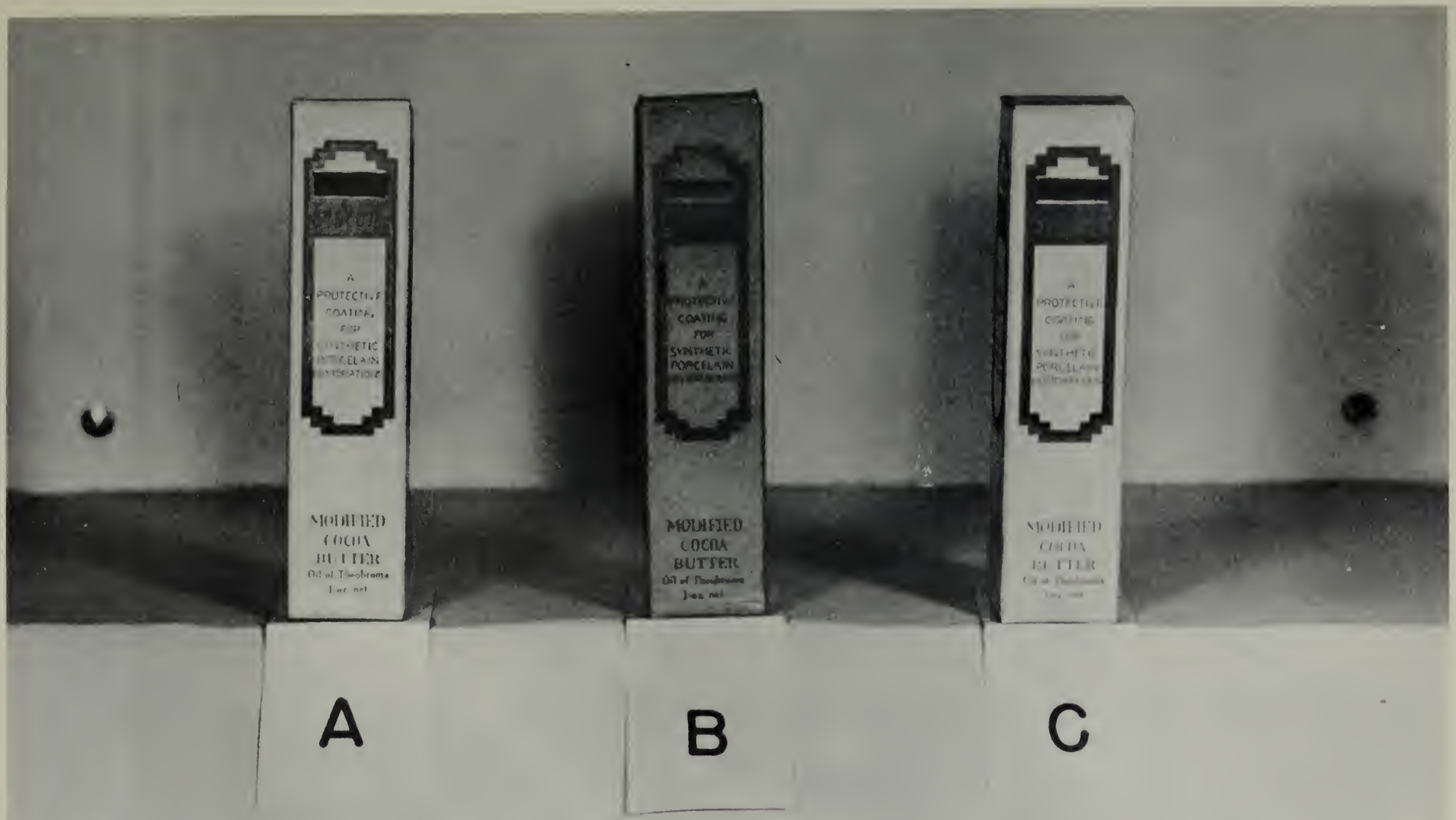

Figure 2. Discoloration of the cardboard carton containing a low melting point material is shown by "B" which was stored in the Rodriguez Army Hospital penthouse. Excessive temperatures during storage reduced the volume of this sample approximately by one-third of its original volume.

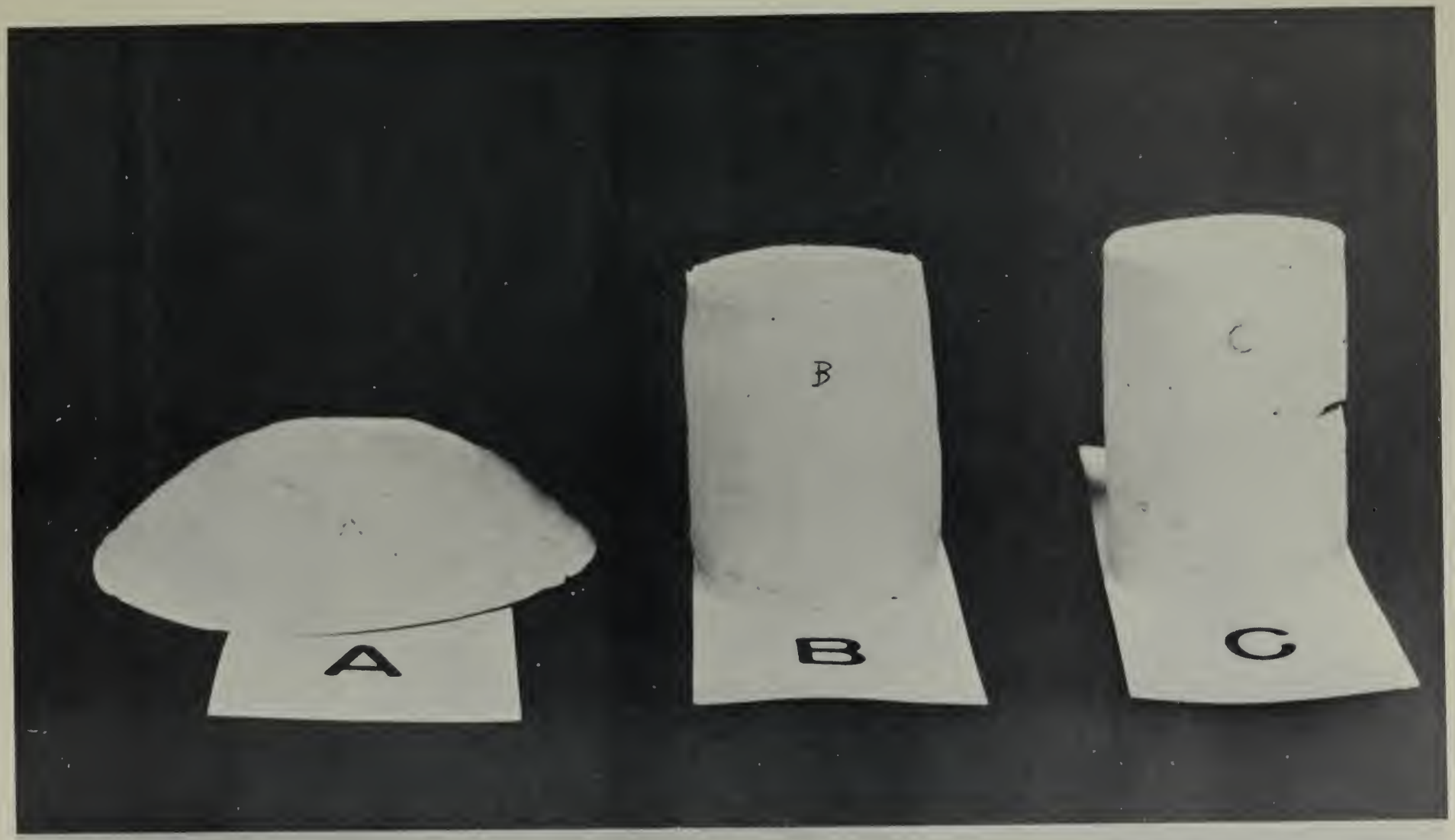

Figure 3. "A" shows normal slumping of investment mixed at the water/powder ratio recommended by the manufacturer for accurate dental castings. "B" and "C" set too rapidly to be of use in the dental laboratory. This behavior is due to moisture contamination.

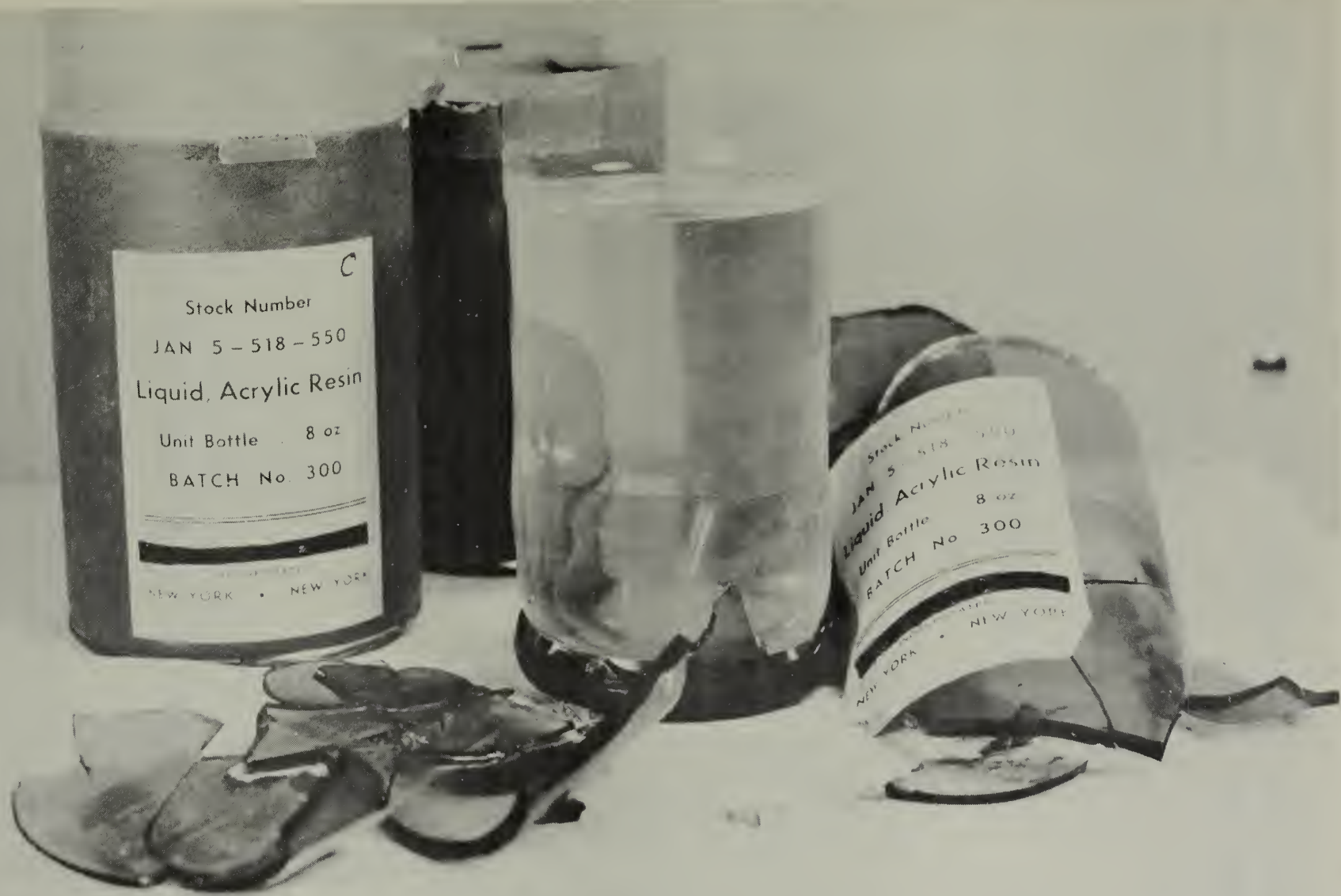

Figure 4. The clear, solid mass which resulted from storage of the denture base resin monomer pictured here is of no value in making dentures. The material, normally a liquid, solified at elevated temperatures reached during four years of storage in Puerto Rico.

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Progress Report

DIMENSIONAL STABILITY OF DENTURE BASE RESINS

by

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This work is 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.

(Task 7756-41 BV No. 55-14)

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

DIMENSIONAL STABILITY OF DENTURE BASE RESINS

Abstract

Dimensional changes during processing and during a period of two years of clinical service were determined on dentures made from heat-curing and self-curing materials. The magnitude of dimensional changes of both heat-cured and self-cured dentures was small, seldom exceeding 0.2 mm. The average processing shrinkage was less and the average expansion during service was slightly greater for self-cured than for heat-cured dentures. During service upper dentures changed less in dimension than did lower dentures and on the average the flange to flange change of upper dentures was negative while all other changes were positive. In general, the greatest service change on all dentures occurred during the first month. After two months very little change occurred.

1. INTRODUCTION

Self-curing denture base resins which polymerize at room temperature are now being used to a considerable extent by the dental profession. These resins are generally similar to the methyl methacrylate denture base materials which have been used for many years with the exception that polymerization of the liquid in the mixture is initiated by an activator present in the polymer powder rather than by the application of heat. Data on some of the properties of self-curing denture resins have been reported previously [1,2]. The present investigation was undertaken to determine the relative dimensional stability of self-cured and heat-cured dentures. For this purpose measurements of the dimensional changes during processing and during a period of two years of clinical service were made on a series of dentures.

In order to supplement the number of dentures which could be made in the National Bureau of Standards laboratory a cooperative program was established with the Veterans Administration. Under this program dentures were processed at the following installations: Veterans Administration Center, Kecoughton, Virginia; Veterans Administration Center, Martinsburg, Virginia; and Veterans Administration Hospital, Perry Point, Maryland.

Materials used in this project were purchased on the open market from the latter part of 1950 to the early part of 1952 and are listed in Table I.

2. PROCEDURE

A total of 91 full dentures of self-curing materials and 28 full dentures of heat-curing materials were processed using routine acceptable techniques. To provide reference points for determination of dimensional changes stainless steel pins, 1/8" long and 1/16" in diameter polished on one end and ruled with fine cross marks, were cemented in the central fossae of the last molars (designated hereafter as the A and B positions) and in the disto-buccal peripheral flanges (designated hereafter as the C and D positions) of the dentures. All measurements were made at 70°F ± 2°F on a toolmaker's microscope and recorded to the nearest 0.0001 in. The average of five readings was taken as the measurement.

On the dentures made at the National Bureau of Standards readings were made on the waxed-up model prior to processing; after removal from the cast; on the denture just prior to insertion; at 30-day intervals for six months after delivery to the patient; and then at 6-month intervals. The dentures fabricated at the Veterans Administration hospitals were first measured just prior to insertion and then on the same schedule as above. Curing shrinkage, therefore, could be determined only on the dentures made at the National Bureau of Standards. The change from the waxed-up measurement to the measurement after removal from the cast of the processed denture was taken as the curing shrinkage.

A series of technique denture blanks with only the last molars in place was made in order to supplement the number of dentures on which curing shrinkage could be determined. Two heat-processing methods were used. One group of the technique dentures was processed for 9 hours at 160°F and another group for 1½ hours at 160°F and ½ hour at 212°F. The self-curing materials were processed according to the directions supplied by the manufacturer. The technique dentures were made of the same materials used for the clinical study.

3. RESULTS

3.1 Curing Shrinkage

The study of curing shrinkage of the clinical and the technique dentures yielded the results given in Table 2.

In both groups of dentures the heat-cured materials had a greater average curing shrinkage but there is overlapping of the ranges. Results obtained on the technique dentures indicate that the type of heat processing did not significantly effect the amount of shrinkage.

3.2 Dimensional Stability

In the study of the dimensional changes of the dentures in use the measurement made just prior to insertion (after immersion in water for at least two days) was taken as the zero reading and all values were calculated with that as a reference point.

Many of the dentures were lost to the project in the course of testing as a result of the unavailability of patients or of wearing away of the cross marks on the pins inserted in the teeth. The number of dentures measured at each interval over the two year period is shown in Table 3.

Dimensional changes of the dentures while in service are shown in Figures 1 to 5 and Table 4. Curves showing the changes in dimension AB (molar to molar) for each of the dentures are plotted in Figures 1 to 4 in order to give an overall picture of the range in dimensional change of the different dentures and an indication of variation with time for individual dentures.

Average curves for both the AB (molar to molar) and CD (flange to flange) dimensions are shown in Figure 5. The values plotted are averages of all values obtained at the time indicated. Since many of the dentures were not available for measurement at later periods, the averages plotted at two years are based on only one-tenth to one-sixth the number of dentures included in the one-month averages (see Table 3). It is obvious from examination of the individual curves in Figures 1 to 4 that deviations from the averages are large compared to the differences between average curves.

A statistical analysis was made of 6 heat-cured dentures and 28 self-cured dentures on which data were complete through the first 180 days, Table 4. The results are summarized as follows:

The standard deviation characterizing the variability of replicate measurements made on the same denture is about 0.00015 inch. However, the experimental errors involved in the study are higher than indicated by the precision of measurement. This is due to variability in behaviour between different dentures and variations with time of individual dentures (possibly resulting from uncontrollable factors in the clinical use of the dentures). The differences between dentures are of two types: (1) systematic, in which one rate of change of dimensions of one denture is consistently higher or lower than that of another denture and (2) random, in which the rate of change of one denture is sometimes higher and sometimes lower than that of another. The latter variability is characterized by a standard deviation of approximately 0.0014 inch or about 10 times the standard deviation of replicate measurements. The standard deviations of the systematic differences between self-curing dentures varied between 0.003 and 0.0017 inch. No

systematic variations between heat-cured dentures were observed.

The upper heat-cured dentures as a group showed no significant changes in dimensions throughout the 180 first days of test. Lower heat-cured dentures increased, on the average, by about 0.00044 inch per 30 days over the AB dimension and about 0.00073 inch over the CD dimension.

Both upper and lower dentures made with self-curing resins showed significant dimensional changes during the first 180 days. A gradual slowing down in the rate of change occurred during this period. The observed rates of change are shown in Table 4.

3.3 Clinical Evaluation

According to patient reaction all but one of the dentures, regardless of the type of resin used, have given comfortable and satisfactory service. The one report of loss of fit occurred after the denture had been in service a little over a year. Measurements made after the complaint revealed no excessive changes. The case history of the patient showed that he had previously worn another denture for one year but that the oral tissue was still not firm. It seems probable, therefore, that the failure in this case was a result of tissue change rather than change in dimension of the denture.

4. DISCUSSION

The results obtained show that with the precision of measurement employed in this study variations in dimensional changes during processing and during service can be demonstrated for both heat-cured and self-cured dentures. However, it should be pointed out that the magnitude of these variations is not large; in most cases the changes are within the range of -0.1 to 0.4% (approximately -0.05 to +0.2 mm). According to patient reaction these changes do not significantly affect the serviceability of the dentures.

On the average the processing shrinkage of self-cured dentures was less than that of heat-cured dentures. Such an effect would be expected since the lower polymerization temperature of the self-curing materials should tend to give less thermal contraction after polymerization.

The average expansion of the self-cured resins during service was slightly greater than that of heat-cured materials. This might be the result of a lower sorption of water by the self-cured denture during processing and a subsequent higher sorption and expansion during service.

There appears to be a greater increase in dimension during service in the lower than in the upper dentures. Also the change in dimension from molar to molar (A to B) is greater percentage-wise in most cases than is the change from flange to flange (C to D) indicating that the change is not a uniform enlargement but involves some distortion of the dentures. The average flange to flange change during service on upper dentures was negative while all other average changes during service were positive.

In general, individual dentures showed the greatest dimensional changes during the first month and after two months almost no significant changes took place. It has been demonstrated [3] that dimensional changes of approximately 1% can be produced in dentures by changes in water content. It is possible, therefore, that the variations observed during service may be dependent to a considerable extent upon changes in water content resulting from conditions under which the dentures are used in service.

5. SUMMARY

The magnitude of dimensional changes of both heat-cured and self-cured resins was small, seldom exceeding 0.2 mm. Patient reaction indicated that changes of this amount did not significantly affect the fit of the dentures.

The average processing shrinkage of self-cured dentures was less than that of heat-cured dentures and the average of expansion of self-cured dentures during service was slightly greater than that of the heat-cured dentures.

During service upper dentures changed less in dimension than did lower dentures and on the average the flange to flange change on upper dentures was negative while all other changes were positive.

On the average the greatest change on all dentures occurred during the first month. After two months very little significant change occurred.

6. BIBLIOGRAPHY

1. Caul, H. J., Stanford, J. W. and Serio, A. F. Properties of self-curing denture base resins, J.A.D.A. 44:295 (1952).

2. Swaney, Aubrey C., Paffenbarger, G. C., Caul, H. J., and Sweeney, W. T. American Dental Association Specification No. 12 for denture base resin: second revision. J.A.D.A. 46:54 (1953).

3. Sweeney, W. T., Paffenbarger, G. C. and Beall, John R. Acrylic resins for dentures. J.A.D.A. 29: 7 (1942).

Table 1

DENTURE BASE MATERIALS USED

Brand Name	Manufacturer	Date Received at NBS
	Self-Curing Resins	
Acralite 88	Acralite Co., Inc.	6/50
Isodent	Precision Dental Mfg. Co.	12/50
Duz-All	Coralite Dental Products Co.	12/50
Cold Cure	Perfected Dental Products Co.	1/51
Cur-O-Matic	Acri-Lux Dental Mfg. Co., Inc.	1/51
Coldpac	The Motloid Co., Inc.	12/50
Bio-Therm	B. L. Dental Co. Inc.	12/50
Nu-Set	J. Yates Dental Mfg. Co.	2/51
	Heat-Curing Resins	
Certified Acrylic	Lee S. Smith and Son Mfg. Co.	3/52
Crystolex Formula 102	Kerr Mfg. Co.	8/52
Densene 33	Cosmos Dental Products, Inc.	2/52

Table 2

CURING SHRINKAGE OF DENTURE BASE RESINS

Specimen	Material	Cure	No. of Dentures	Shrinkage
				%
Dentures	Self-curing	Mfr's directions	21	0.27 ± 0.15*
	Heat-curing	Mfr's directions	8	0.43 ± 0.12
Technique Dentures	Self-curing	Mfr's directions	5	0.25 ± 0.03
	Heat-curing	9 hrs at 160°F	5	0.35 ± 0.09
	Heat-curing	$1\frac{1}{2}$ hrs at 160°F $\frac{1}{2}$ hr at 212°F	5	0.34 ± 0.07

* Plus or minus values indicate average deviation.

Table 3

NUMBER OF DENTURES MEASURED AT EACH TIME PERIOD

Denture	Dimension	Time - Days								
		30	60	90	120	150	180	360	540	720
Self-cured										
Upper	AB	36	36	35	35	30	30	23	10	4
Upper	CD	35	35	35	35	30	24	15	11	6
Lower	AB	32	32	32	32	25	19	12	8	5
Lower	CD	30	30	30	30	25	21	11	8	4
Heat-cured										
Upper	AB	10	10	9	9	8	6	5	3	1
Upper	CD	9	9	8	8	8	5	4	3	1
Lower	AB	10	10	9	9	8	6	4	2	1
Lower	CD	9	9	8	8	8	6	4	2	1

Table 4

RATE OF DIMENSIONAL CHANGE OF DENTURES

Type of Material	Period (Days)	Dimensional Change AB Upper in.	AB Lower in.	CD Upper in.	CD Lower in.
Self-cured	0-30	0.0021	0.0022	0.0009	0.0017
	30-60	0.0012	0.0015	0.0000	0.0014
	60-90	0.0006	0.0009	-0.0005	0.0004
	90-120	0.0002	0.0004	-0.0003	0.0000
	120-150	0.0000	-0.0001	-0.0003	-0.0005
	150-180	-0.0001	0.0001	-0.0003	-0.0004
Heat-cured	0-30	0.0007	0.0003	-0.0002	0.0013
	30-60	0.0004	0.0008	+0.0002	0.0010
	60-90	0.0003	0.0006	-0.0001	0.0012
	90-120	0.0002	0.0005	+0.0002	0.0006
	120-150	-0.0005	0.0004	-0.0003	0.0003
	150-180	-0.0001	-0.0000	-0.0004	0.0000

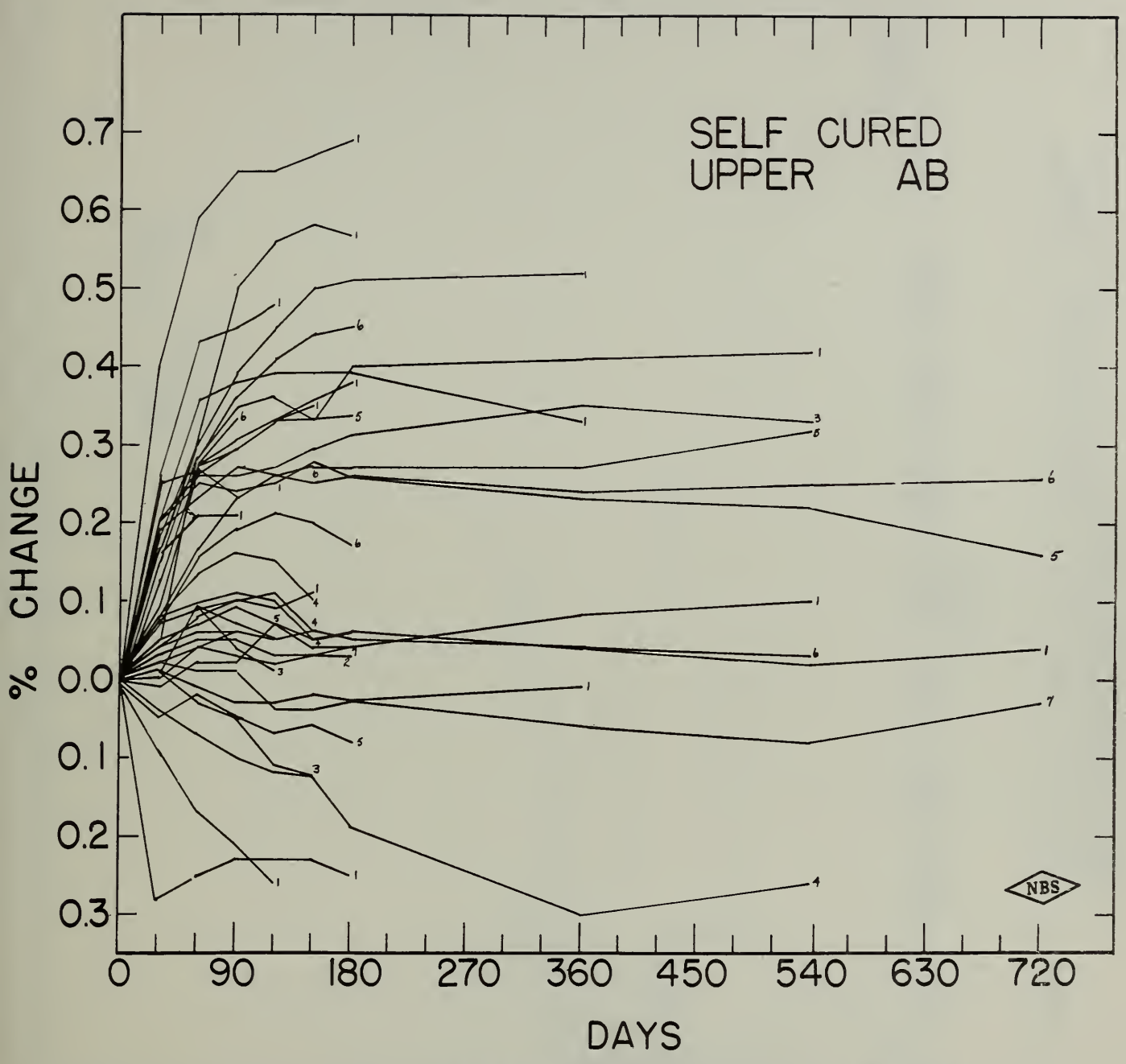

Figure 1. Dimensional changes during service of self-cured upper dentures over AB (molar to molar) dimension. Curves for all dentures made from same brand of material are designated with same number.

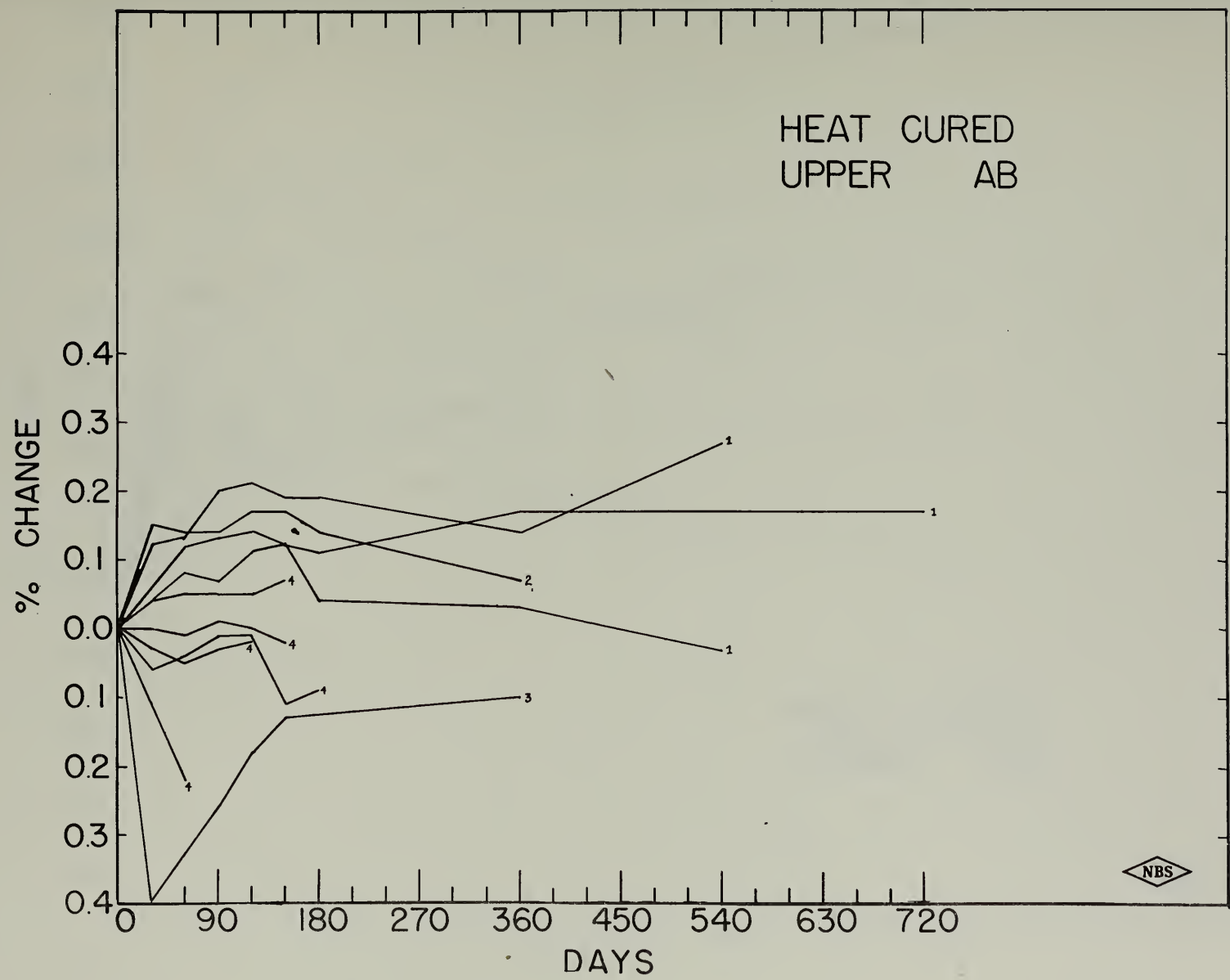

Figure 2. Dimensional changes during service of heat-cured upper dentures over AB (molar to molar) dimension. Curves for all dentures made from same brand of material are designated with same number.

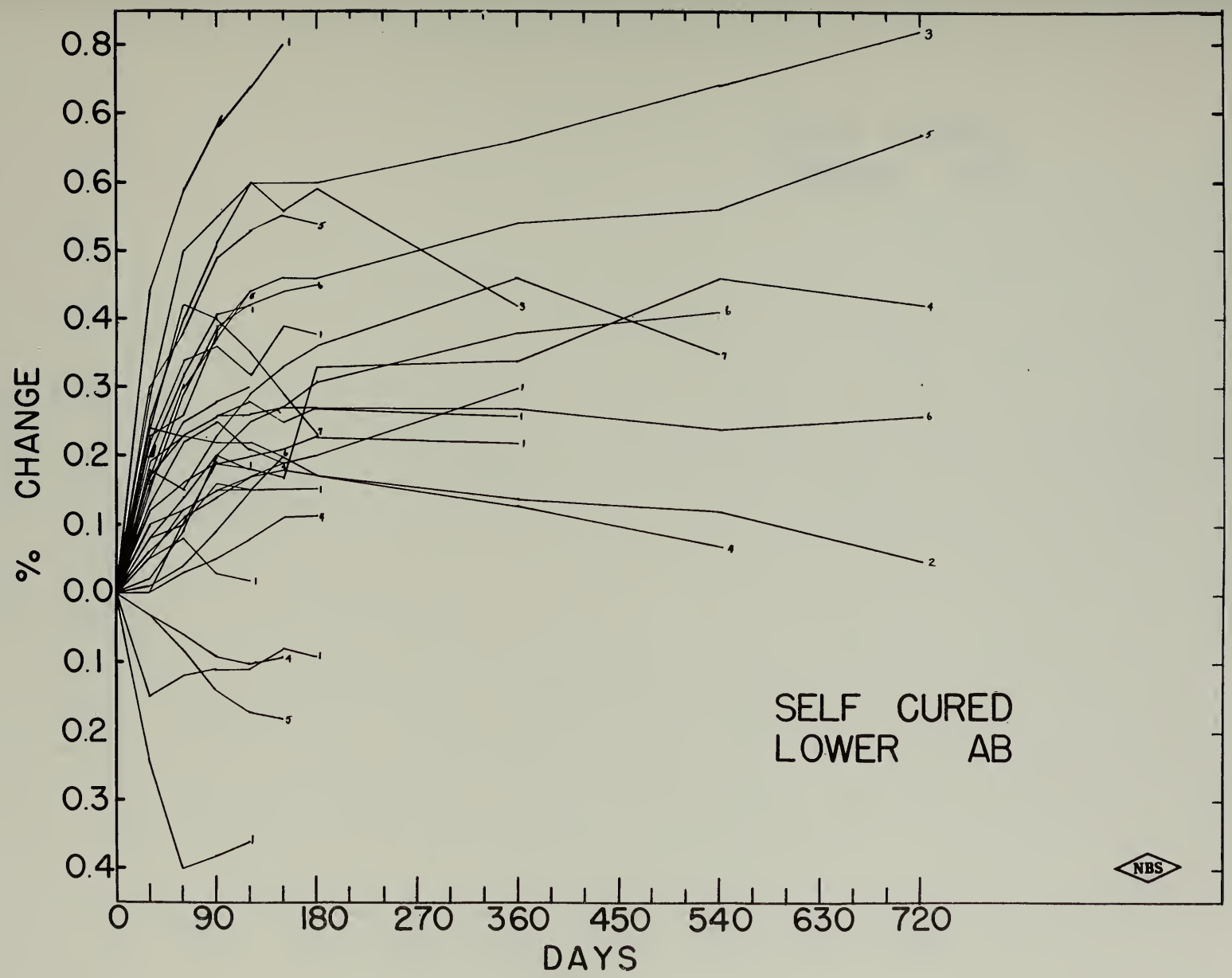

Figure 3. Dimensional changes during service of self-cured lower dentures over AB (molar to molar) dimension. Curves for all dentures made from same brand of material are designated with same number.

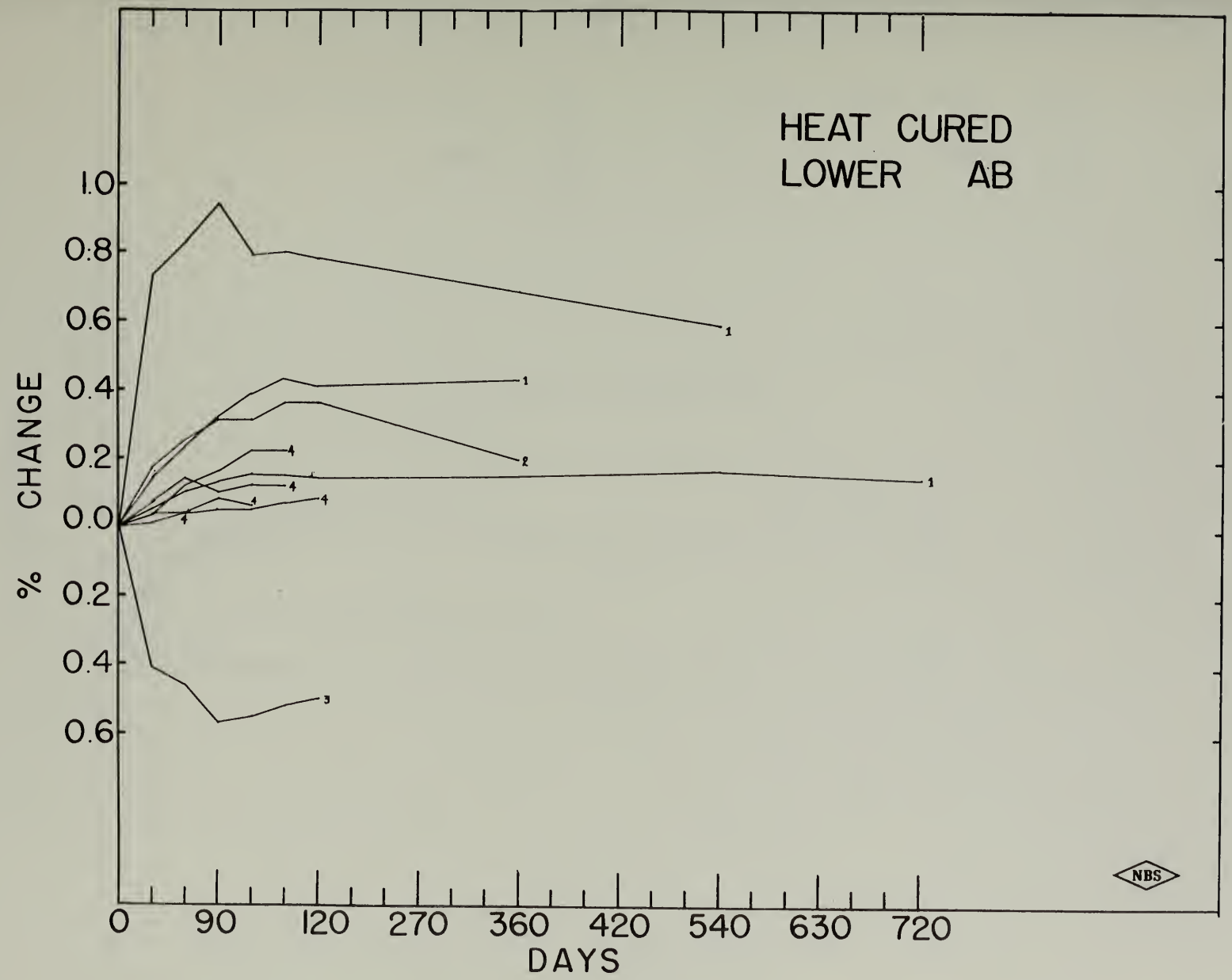

Figure 4. Dimensional changes during service of heat-cured lower dentures over AB (molar to molar) dimension. Curves for all dentures made from same brand of material are designated with same number.

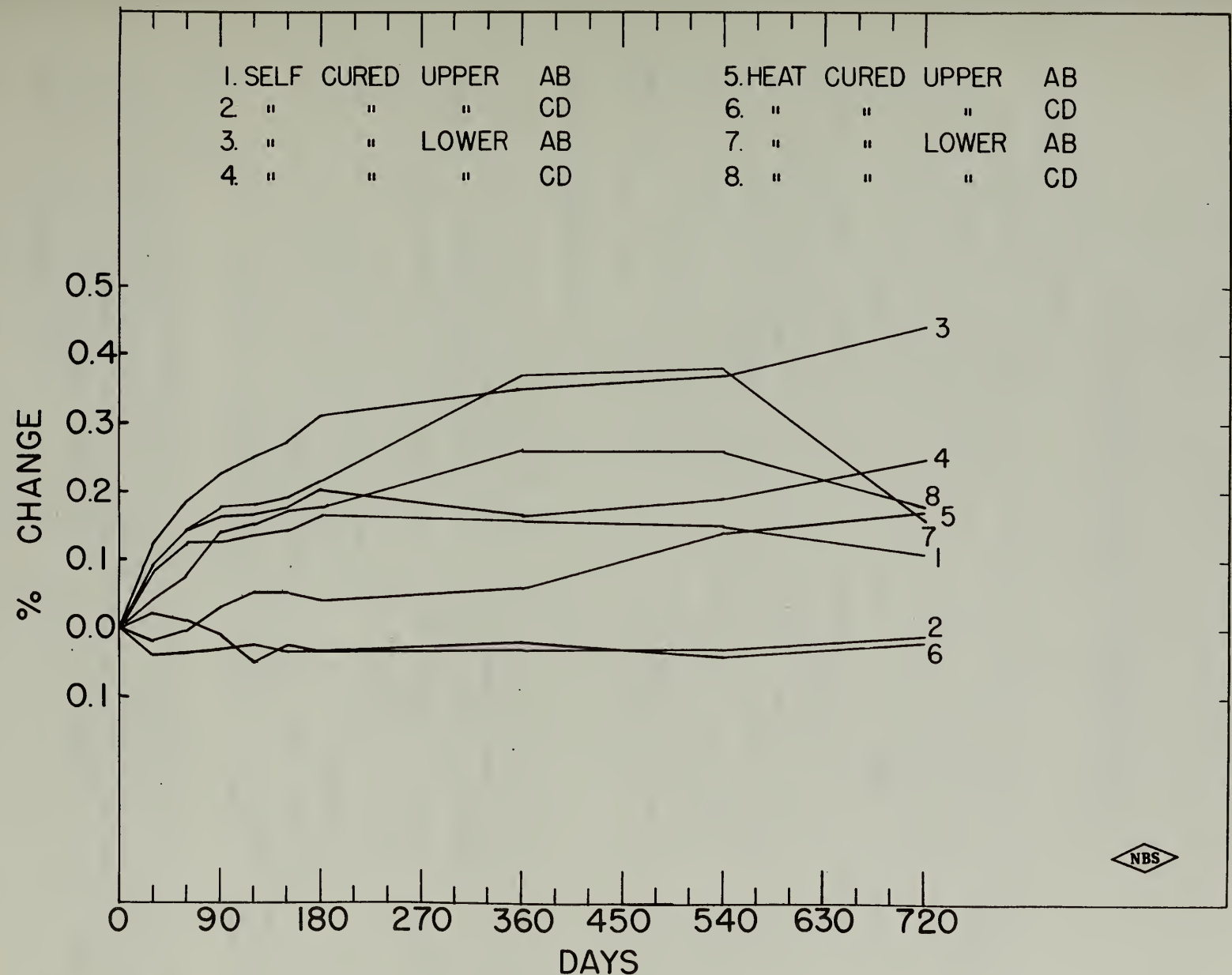

Figure 5. Average dimensional change during service of self-cured and heat-cured dentures over AB (molar to molar) and CD (flange to flange) dimensions.

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