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Geo. C. Paffenbarger

NATIONAL BUREAU OF STANDARDS REPORT

2718

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1953

Dental Research Laboratory



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

U. S. DEPARTMENT OF COMMERCE

Sinclair Weeks, *Secretary*

NATIONAL BUREAU OF STANDARDS

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THE NATIONAL BUREAU OF STANDARDS

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

Heat and Power. Temperature Measurements. Thermodynamics. Cryogenics. Engines and Lubrication. Engine Fuels. Cryogenic Engineering.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Measurements. Infrared Spectroscopy. Nuclear Physics. Radioactivity. X-Rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. Atomic Energy Commission Instruments Branch.

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Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion.

Mineral Products. Porcelain and Pottery. Glass. Refractories. Enameled Metals. Concrete Materials. Constitution and Microstructure. Chemistry of Mineral Products.

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. Machine Development.

Electronics. Engineering Electronics. Electron Tubes. Electronic Computers. Electronic Instrumentation.

Radio Propagation. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Frequency Utilization Research. Tropospheric Propagation Research. High Frequency Standards. Microwave Standards.

Ordnance Development. These three divisions are engaged in a broad program of research and development in advanced ordnance. Activities include basic and applied research, engineering, pilot production, field testing, and evaluation of a wide variety of ordnance matériel. Special skills and facilities of other NBS divisions also contribute to this program. The activity is sponsored by the Department of Defense.

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● Office of Basic Instrumentation

● Office of Weights and Measures.

NATIONAL BUREAU OF STANDARDS REPORT

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0708-10-0724
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July 31, 1953

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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1953

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.



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REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

The activities of the Dental Research Laboratory at the National Bureau of Standards during the half year ending June 30, 1953 have included investigations of a wide variety of dental materials and equipment and studies of natural tooth structures. Summaries of the results obtained on work now in progress are given below. In addition, copies of reports issued on completed phases of the investigations are included.

2. REPORTS ISSUED

- NBS No. 2384 Deterioration of Alginate Hydrocolloidal Dental Impression Material on Storage
- NBS No. 2566 A Transverse Strength Testing Machine
- NBS No. 2628 Some Factors Affecting the Dimensional Stability of Ag-Sn-(Cu-Zn) Amalgams
- NBS No. 2647 Direct Filling Resins: Mechanical Properties

3. WORK IN PROGRESS

3.1 Structure of Human Tooth Enamel and Dentin

Investigation of the fundamental structural characteristics of human tooth enamel and dentin - - -

- (a) Fluorescence Investigation. In the investigation of tooth structure by means of fluorescence two lines of approach were used (1) the application of the previously developed fluorophotomicrographic method for histological studies (2) the development of equipment for obtaining additional fundamental information on tooth structures through studies of the nature of the fluorescence emitted.

Fluorophotomicrographs of tooth sections of known history and special histological interest were made in collaboration with Dr. B. M. Bhussry of the Eastman Dental Clinic. Since work at the Eastman Clinic has indicated that there may be a relationship between some types of surface pigmentation, age and caries susceptibility of teeth, the fluorescence studies are being undertaken to obtain information on the characteristics of the pigmentation present.

In response to a request from the Fish and Wildlife Service, sea otter teeth were examined to investigate the possibility of using fluorescence methods, developed for the study of human teeth, to determine the age of the sea otter. Although definite lines of growth were revealed by ultraviolet excitation, no correlation with age will be possible until teeth of known ages can be obtained.

Since the decay time of the fluorescence emitted by a substance is characteristic of the nature of the material, plans are being drawn up for the construction of a decay fluorometer capable of measuring extremely short periods of decay (from 10^{-6} to 10^{-9} seconds). Construction of a depolarization fluorometer has also been started. From measurements of the decay time and the depolarization it is hoped that some idea of the molecular weight of the fluorescing material in tooth structure can be obtained.

- (b) Crystallographic Investigation. Through a Fourier analysis of the x-ray diffraction maxima of the apatite reflections from a sample of steamed bone, it was demonstrated that the apatite particles ranged from about 10 to 1000A in size. This indicates that the 50A particles found by low angle scattering were probably apatite rather than carbonate as previously suggested.

An attempt was made to determine whether or not carbonate containing apatites (bone, teeth, etc.) changed in any physically perceptible manner when the carbonate was leached out with lactic acid. Employing x-ray diffraction as well as electron diffraction, it was impossible to detect any change in a series of diffraction patterns of samples taken before and after the acid leach. This points to the probability that the carbonate is not a part of the apatite structure but is possibly admixed in some manner.

3.2 Surface Crazeing of Acrylic Resins

Determination of the mechanism involved in the surface crazeing of acrylic resins - - -

Investigations of the effect of temperature and molecular weight on the water sorption of methyl methacrylate were completed. Specimens of varying molecular weight showed approximately the same weight increase on storage in water below the second-order transition temperature T_g . Within a few degrees centigrade of T_g water sorption increased markedly. On storage at $10-20^{\circ}\text{C}$ above T_g the disks of highest molecular weight decomposed into the original granules. This indicates that on molding the specimens at 150°C fusion of the individual particles to a homogeneous material is not accomplished for high molecular weight, straight chain polymer. On the other hand, molding at higher temperatures will increase the degree of depolymerization.

Specimens molded at 150°C and used in the water sorption measurements over a 4° to 85°C range showed a decrease in molecular weight from 1,600,000 to 830,000. Similar degradation was observed for samples of lower molecular weight.

No hysteresis effect was found for the water sorption of finely powdered polymethyl methacrylate. Larger granules showed a slight hysteresis effect over the 10 to 50% relative humidity range.

The waterproofing of SR_4 strain gages embedded in resin for measurements of internal strain has been done effectively by surrounding the gage with a .001" brass shim envelope. There is, however, some doubt as to the adherence of the brass to the cured methylacrylate. The effectiveness of another method of waterproofing, curing of neoprene around the gage, will be determined.

3.3 Polymerization of Acrylic Resins

Investigation of the chemical reactions which are responsible for the induction period of the polymerization of methyl methacrylate - - -

Since study of the decomposition rate of α, α diphenyl β picryl hydrazyl (D.P.P.H.) appears to offer a convenient approach to measurements of rate of free radical formation, reactivity and efficiency of inhibitors, the apparent decomposition rate of D.P.P.H. in the presence of 2:2-azo-bis (isobutyronitrile) (A.I.B.N.) was determined in the presence of over 25 typical inhibitors containing various functional groups. The half time decomposition of inhibitors containing phenolic groups is shortened due to the oxidation of the inhibitors. Diphenylamine, benzidine and phenylene also showed a shortened half time decomposition. The presence of oxygen, sulfur, di- and tri-nitroaromatic compounds, triphenylmethyl chloride, stilbene maleic anhydride and 0.01% styrene or methyl methacrylate had no effect on the decomposition rate of D.P.P.H. Iodine and p-nitroaniline react preferentially with radicals formed from A.I.B.N. Thus in the presence of 0.007% iodine the apparent half time decomposition of D.P.P.H. is changed from 138 min to 233 min.

An attempt was made to measure the thermal formation of free radicals from methyl methacrylate and styrene. The D.P.P.H. decomposition rate is rapidly increased on increase of the styrene concentration and does not follow any clear-cut kinetics.

On the other hand, free radical formation from methyl methacrylate is much smaller than that for styrene and follows second-order kinetics. This is indicative of the formation of a biradical from monomer, probably through a bimolecular collision. The reaction order and rate are not appreciably changed over a limited concentration range. Comparison with previously reported values of the rate constants shows that the results obtained by this method are much too large. This can be accounted for by side reactions which take place between D.P.P.H. and the double bond of the monomer.

An investigation was initiated to follow the kinetics of polymerization of methyl methacrylate in the presence of 2% benzoyl peroxide and varying concentrations of different accelerators. The course of the polymerization is followed by means of an ultrasonic viscometer.

3.4 Physical, Chemical and Engineering Properties of Dental Materials

Determination of the properties and processing characteristics and development of more satisfactory techniques for the use of materials employed in the practice of restorative dentistry - - -

- (a) Metallurgical Investigations. Additional gallium alloys have been made and investigated as possible replacements for dental amalgam. Gallium-gold in certain concentrations was found to react exothermically to form AuGa_2 . An apparent correlation between the crystal type of the alloying metal and



ease of alloying near room temperature was observed. Gallium alloyed more readily with face centered cubic metals than with body centered cubic metals. Data so far obtained indicate that the hardness and the strength of certain gallium alloys are approximately 20 to 30% greater than those of the dental amalgams now in use.

- (b) Chrome Alloys for Dental Castings. Tensile properties of the three most widely used brands of chrome cobalt casting alloys were determined under a variety of casting conditions and specimen shapes. Threaded specimens appear to be more suitable for specification testing than do the straight rods now specified for testing of other dental alloys. The data obtained indicate also that it may be desirable for testing purposes to specify a definite casting procedure. Other properties including chemical composition, hardness and corrosion resistance of the alloys will be determined to obtain the necessary data for writing a specification for dental chrome alloys.
- (c) Rotating Dental Cutting Instruments. Studies were made comparing the behavior of diamond abrasive instruments when cutting pyrex glass with their behavior when cutting human tooth enamel. It is hoped, thereby, that diamond abrasive instrument tests using pyrex glass, can be related more accurately to clinical performance in the practice of dentistry.

A program of high-speed photography is also under way, in which the basic cutting behavior of dental burs is being studied. Burs of steel and carbide of conventional design and number of blades, and burs having fewer than the standard number of blades, will be photographed at speeds of rotation of from 5000 to 15000 rpm as they cut human tooth enamel and dentin and other materials. The information obtained from this study should be of great value in the development of more efficient rotary cutting instruments.

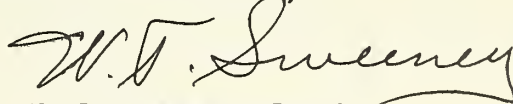
- (d) Dental Resin Cements. Modified methyl methacrylate resins are being advocated as replacements for zinc phosphate cements for fastening appliances and restorations to teeth. Various properties of these resins were therefore measured for comparison with the properties of zinc phosphate materials. The standard consistency tests used for silicate and zinc phosphate cements were modified and adapted for testing the resins. It was found that the setting time of the resin cements is much less sensitive to differences in consistency than is that of the zinc phosphate cements. The compressive strength of the resins was $12,000 \pm 1000$ psi, approximately the same as that of the zinc phosphate. The opacities of the resin cements varied from $C_{0.70}$ values of 0.50 to 1.00 and were thus more satisfactory than the 1.00 (completely opaque) value for the zinc phosphate cement. Temperature rise on hardening of the various resin cements varied from 13 to 29°C while that of the zinc phosphates varied from 4 to 13°C.
- (e) Zinc Oxide-Eugenol Impression Paste. Empirically developed zinc oxide-eugenol materials are widely used as impression pastes, tooth treatment cements and in certain gingivo-alveolar therapeutic materials. Since there is very little published information on the mechanism of the hardening of these materials and since numerous instances of failure are observed, an investigation of the materials was undertaken. Results obtained so far show



that more than 80% of the eugenol in a mixture of the paste can be extracted from the hardening material with chloroform. Thus only 4 mole % of eugenol could have reacted with the zinc oxide. This suggests that the setting mechanism is either a gel formation or a surface reaction. It was found that the water content of the zinc oxide greatly affects setting time. Carefully dried zinc oxide mixed with eugenol in a dry atmosphere did not set within a period of several days.

- (f) Porcelain Teeth. A method was developed for determining and specifying porosity of porcelain teeth. The method developed consists of sectioning, mounting and polishing the teeth. A cover glass with a square 0.5 mm on a side ruled on its surface is then placed on the polished tooth sample. The bubbles in the square are counted and the four largest bubbles measured. This procedure is repeated on five different areas of the tooth. The average number of bubbles per square millimeter is determined and the average diameter of the four largest bubbles is determined. These two values give a satisfactory indication of the over-all porosity of the tooth.
- (g) Ampules. An instrument for testing the strength of glass anesthetic ampules was designed for the Armed Forces. Examination of a large number of ampules for strain under polarized light and subsequent breaking of the ampules in the test instrument indicated that annealing of the glass was desirable.
- (h) Evaluation of Materials. Materials evaluated for the cooperating Federal dental services and the American Dental Association by specification or special test methods included amalgams, mercuries, gold alloys, silicate cements, denture base repair resins, alginate impression materials, waxes, filling lubricants, cavity liners, impression compounds, glass ampules, plastic teeth and solders.

For the Director,



W. T. Sweeney, Chief
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NATIONAL BUREAU OF STANDARDS REPORT

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2384

Progress Report on DETERIORATION OF ALGINATE HYDROCOLLOIDAL DENTAL IMPRESSION MATERIAL ON STORAGE

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the Army Dental Corps, the Air Force Dental Service, the Navy
Dental Corps and the Veterans Administration Dental Service.



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DETERIORATION OF ALGINATE HYDROCOLLOIDAL DENTAL IMPRESSION MATERIAL ON STORAGE

Abstract

Numerous instances of deterioration of alginate dental impression materials have been reported. Investigation of samples of these materials stored at controlled temperatures has shown that deterioration occurs very rapidly (complete failure in one month) at 65°C, slowly at 50°C and extremely slowly if at all at 37°C or lower. Data obtained indicate that the deterioration is a result of degradation, probably by depolymerization, of the alginate constituent of the impression material. To prevent deterioration it is recommended that alginate impression materials be stored at temperatures of 37°C or lower.

1. INTRODUCTION

The alginate type materials for taking dental impressions were introduced during World War II as a substitute for the then scarce agar-agar. They have gained increasing favor because of their ease of handling and accuracy of reproduction.

The physical properties and clinical behavior of these materials have been studied by, Skinner and Pomes [1, 2], Cresson [3], Worner [4], and Schoonover and Dickson [5]. One of the serious difficulties encountered in their use has been their tendency to deteriorate during storage. Two distinct types of aging failure have been observed. In some cases the material, after storage for a short time at ordinary temperatures, will not form an insoluble elastic gel. Schoonover and Dickson [5] showed that this was caused by the removal of the retarding agent by premature reaction with the compounds added to convert the soluble gel into the insoluble form. This type of difficulty is readily overcome by proper compounding of the mixture and is no longer a serious factor. The second type of failure is observed most

often when the materials are stored at elevated temperatures and has been particularly noticeable when these materials are shipped to and stored in tropical areas. Materials subjected to these conditions often have inferior physical properties, the strength of the gels is greatly reduced, their setting time is altered, and the accuracy of the reproduction is inadequate for dental use. Experimental data obtained in this investigation show that this type of deterioration results from degradation of the alginate polymer at elevated temperatures.

2. EFFECT OF TEMPERATURE-ON DETERIORATION OF ALGINATE IMPRESSION MATERIALS

Samples of five commercial brands of alginate impression materials were stored in the packages as received, at temperatures of 21°C, 37°C, 50°C and 65°C for one month. At the end of one month samples of each material were removed and their setting times, permanent deformation, compressive strength, ease of manipulation and gel-forming characteristics were determined. This procedure was repeated on other samples stored at 50°C for 3-1/2 months. The method described in American Dental Association Specification No. 11 for hydrocolloidal impression materials [6] was used to determine setting time. The permanent deformation was determined by the method described by Cresson [3]. The compressive strength was determined on cylindrical specimens approximately 0.5 inch in diameter and 0.75 inch in height loaded at a head speed of 0.20 inch per minute on the testing machine until rupture occurred. These specimens prior to crushing were stored for one hour at $21 \pm 1^\circ\text{C}$ under conditions approximating 100% relative humidity. The gel-forming properties and ease of manipulation were determined by making mixes of the material and observing the general characteristics of the mix. The data obtained are given in Tables 1 and 2. It will be observed from these data that no appreciable change occurred in any of the materials stored at 37°C (as compared with those stored at 21°C) for one month. However, in general the properties of most of the brands were markedly altered after one month's storage at 50°C, as indicated in a reduction in their compressive strengths. The deterioration was more pronounced after storage for 3-1/2 months at 50°C and resulted in a loss of strength of from 25 to 45%. Storage at 65°C produced such rapid deterioration that all the products were unsatisfactory after one month's storage at this temperature.

Another series of specimens was stored for 30 months in an unheated storage room (temperature range approximately (5 - 50° C). Properties of two brands changed little (Table 2) and these materials were considered satisfactory for general use after storage. A third impression compound did not set after storage under the same conditions. This material did not change appreciably on storage at 21°C for the same length of time.

It was observed that the impression materials stored at 65°C exhibited an irreversible loss in weight even after being dried to constant weight over Drierite at room temperature. The cause of this loss was not clearly established but is related to the extent of degeneration. The results are shown in Figure 1 where ultimate compressive strength is plotted against weight loss.

Any decrease in weight on oven drying (of the samples previously dried over Drierite) was extremely critical; a loss in weight of as little as 0.25% of the impression compound (corresponding to about 1% of the algin) rendered the material unsatisfactory for clinical use.

This loss in weight and the resulting loss in strength do not appear to be caused by oxidation of the organic alginate, since impression materials stored under nitrogen and heated deteriorated in a similar manner and at approximately the same rate as the materials exposed to air during heating.

The possibility of microbiological action was rejected owing to the highly alkaline nature of some ingredients of the impression compounds and to the fact that no microscopic evidence of such action was ever apparent in the deteriorated powders.

Since the inorganic salts and fillers used in compounding these materials are usually heat stable at the temperatures of storage, loss of the gel-forming properties during storage is more likely to be associated with a change in the alginate component of the impression material.

Sodium alginate is a linear polymer of the sodium salt of anhydro- β -d-mannuronic acid of colloidal dimensions [7, 8, 9, 10, 11] having recurring units of the formula $C_6H_8O_6$ and containing one carboxy and two hydroxy groups.

The structure of alginic acid contains acid groups which decarboxylate (decompose with loss of carbon dioxide) almost completely at temperatures above 200°C [12]. No evolution of carbon dioxide was observed on storage of samples at 65°C, although the samples showed the usual deterioration. Hence, decarboxylation is not a likely cause for this change.

Extensive reduction in molecular weight, which is normally about 15,000, has been reported under a number of conditions, [13] indicating that the polymer will depolymerize at elevated temperatures. Storage of alginate impression materials at elevated temperature would therefore account for the deterioration often observed.

To investigate further the depolymerization reaction, samples of a sodium alginate were carefully dried to constant weight over Drierite and then stored at approximately 50° and 65°C for 7 weeks. At the beginning and periodically throughout the storage period samples of the alginate powder were removed, dissolved in water and the viscosity of the solution determined. The solutions were made by adding 0.25 gram of alginate to 100 ml of distilled water. The viscosity measurements were made at $37 \pm .05^\circ\text{C}$ in an Ostwald-Fenske viscometer. It was observed that the viscosity decreased with increased time of storage at 65°C (Fig. 2). After 3-1/2 months of storage at this temperature, the viscosity was reduced by approximately 30%. This decrease in viscosity was attributed to degradation of the alginate polymer. The depolymerization appears to be a chain reaction, since Diaz [13] observed that it is inhibited by phenol, a typical chain terminator. The depolymerization may take place by an exclusive breaking of terminal links or a random scission (i.e. all bonds are split with equal ease). Either mechanism leads to products of lower molecular weight. It is believed that this depolymerization of the alginate is the primary cause for the deterioration of alginate impression materials during storage at elevated temperatures.

3. CONCLUSIONS AND RECOMMENDATION

1. Alginate hydrocolloidal impression materials deteriorate rapidly at elevated temperatures. Materials stored for one month at 65°C were unsuitable for dental use and either failed to set or showed increased setting time and greatly decreased compressive strength. At 50°C these materials also deteriorated but at a much slower rate. No appreciable change was observed in materials stored at 37°C.

2. Deterioration of the alginate impression materials is caused by degradation of the alginate constituent, which probably depolymerizes.

3. Alginate impression materials should not be stored for prolonged periods at temperatures above 37°C.

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Table 1. Effects of Storage Temperature on the Properties of Alginate Materials

MATERIAL	SETTING TIME						PERMANENT DEFORMATION ϵ (After 12% strain)						CRUSHING STRENGTH σ (One hour after mix)						REDUCTION IN STRENGTH AF- TER 3-1/2 MOS. AT 50°C				
	Storage						Storage						Storage										
	1 month						1 month						1 month										
	21°C	37°C	50°C	65°C	min	min	3-1/2 mos.	21°C	37°C	50°C	65°C	%	21°C	37°C	50°C	65°C	3-1/2 mos.	21°C		37°C	50°C	65°C	psi
Coe-Loid	5	5	5	fs*	7	min	%	1.8	1.7	2.0	--	%	2.1	45	43	34	--	27	40				
D-P Elastic Impression Cream	5	5	5	8	5	min	%	2.3	2.3	2.3	3.8	2.1	151	134	130	12	114	25					
Kalginate	5	5	5	fs	6.5	min	%	3.0	3.4	3.7	--	4.1	76	69	56	--	42	45					
Moyco	4	4	4.5	fs	6	min	%	2.1	2.2	2.7	--	2.2	26	26	19	--	16	38					
Zelex	4.5	4	4	fs	3	min	%	1.5	1.3	1.6	--	1.9	50	48	46	--	35	30					

†Values considered accurate within 10 percent.

*Failed to set.

Note: Specimens of Coe-Loid, Kalginate and Moyco changed color when stored at 65°C (149°F).

Table 2. Deterioration of Alginate Impression
Materials after Storage for 30 Months

Material	Laboratory Storage Conditions	Setting Time	Permanent Deformation (after 12% strain) [‡]	Crushing Strength (1 hour after mix) [‡]
		min	%	psi
D-P Elastic Impression Cream	Tested on arrival 30 mos. at 5-50°C [‡]	3-2/3	2.3	121
		4	2.8	123
Kalginate	Tested on arrival 30 mos. at 5-50°C [‡]	2-1/2	2.2	80
		2-1/2	2.3	86
Zelex	Tested on arrival 30 mos. at 5-50°C [‡] 30 mos. at 21°C*	3-1/2	1.3	61
		Did not set 3-1/2	1.8	56

[‡] Kept in unheated storage room.

^{*} Values considered accurate within 10 percent.

* Kept in constant temperature room.

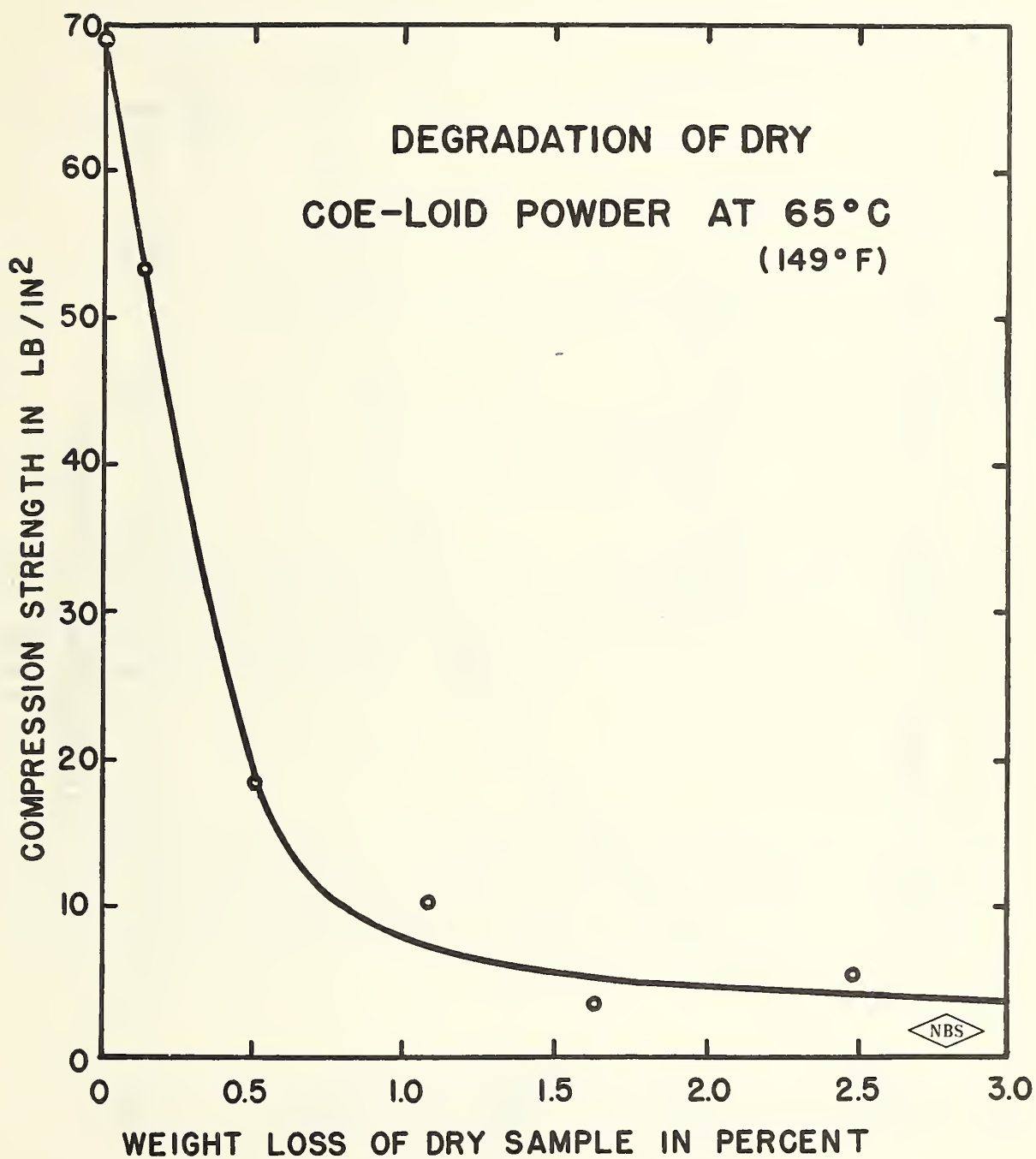


FIG. 1

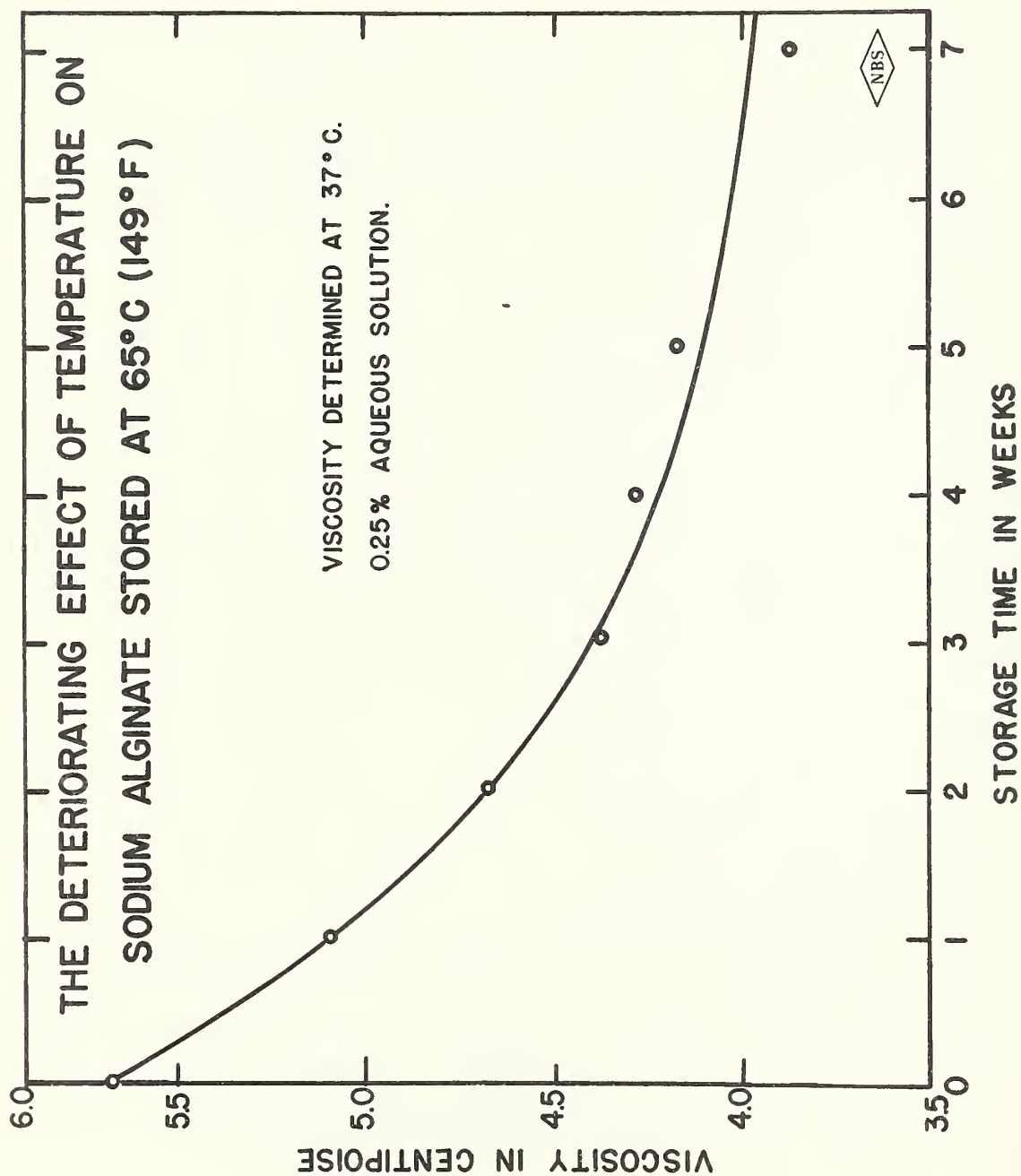


FIG. 2

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2566

A TRANSVERSE STRENGTH TESTING MACHINE

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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 Corps, the Navy Dental Corps and the Veterans Administration.



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A TRANSVERSE STRENGTH TESTING MACHINE*

W. T. Sweeney, Harold J. Caul, and Willy Gneug

Abstract

This paper describes a transverse strength testing machine for use in determining the stress-strain relation on small specimens of denture resin. The machine was designed to replace an older type and has several added features, such as automatic loading rate, lower initial load, control of the medium in which the specimen is held during the test (air or liquid), and thermostatic temperature control. The primary objectives in developing this new machine were to obtain more precise placement of the load and greater efficiency in operation than were possible with the type of machine previously used.

1. Introduction

An improved instrument for testing transverse strength has been developed to replace a machine of older design [1] that has been in service for some twelve years. The new instrument provides for applying specific loads to the center of a specimen 2.5 x 10.0 x 65 mm in size, supported on bars 50 mm apart, and for measuring the deflection produced in the specimen.

The significance of this type of equipment is evident from the fact that practically all of the denture base materials used by the dental profession in this country are evaluated on the basis of transverse strength. Although the older instrument was adequate, there were several difficulties encountered in its use. The specimen holder and specimen had to be positioned by the operator without the assistance of stops. It was necessary to align the plunger so that the load contact surface was perpendicular to the sides of the specimen. The loading rate was controlled manually, and it was very difficult for one person to operate the instrument and record data, since readings were made at practically the same time as the load increments were added. Also, this instrument permitted testing in air only, a serious drawback since the application of stress to acrylic resin produces different amounts of strain, depending upon whether the specimens are stressed in water or air, making it desirable to be able to test them in either medium. These difficulties have been overcome with the new design.

* Detail drawings of this instrument are available and can be obtained from the Dental Research Laboratory, National Bureau of Standards, Washington 25, D. C.

2. Description of Instrument

The instrument is constructed of rust-resistant metals with a base of 9 x 9 in. and an over-all height of 17 in. (Fig. 1). The design provides for the application of a load in 500 gm increments of lead shot from the 24 cells of drum A. The load is gradually and uniformly delivered over a period of 30 ± 5 seconds. The operator positions the ring D to which the lift E is attached in order to open each cell to deliver the load increment. The ring D is held in the same relative position for each cell by a spring finger which fits in the grooves on the ring. Successive units of 500 gm can be applied as desired. The shot rolls down an inclined plane to symmetrically load the pan or holder over the piston C through which the load is applied to the specimen B.

The balancing weight F may be adjusted so that the total weight of the shot pan, dial pressure, and piston is counter-balanced. This makes it possible to read deflections of the specimen from an initial zero load.

The resin specimen B, 10.00 ± 0.03 by 2.50 ± 0.03 mm and approximately 65 mm long, is placed over a 50 mm span of the specimen holder G. The bearing surfaces which contact the specimen are 3.2 mm in diameter. The specimen holder is positioned by pins in the base so that the load is applied at the middle of the span.

The sensitive dial gage H has a 25 mm travel and is accurate to 0.01 mm. The gage spring is removed in order to avoid variable pressure at different positions. The deflection of the specimen is measured at predetermined time intervals by reading the dial gage. Thus, by observing the deflection and the load at the middle of the span, the necessary data for determining the stress-strain relationship in transverse loading can be obtained. Stop I, which consists of a metal plug with a rubber top, is provided to prevent the end of the plunger from contacting the bottom of the specimen holder when the specimen fails. A closed spout J is provided for emptying the shot after the test is completed.

Fig. 2 shows a drawing of the instrument with a thermostatically controlled liquid bath in position. The bath fits inside the base supports and is provided with suitable centering pins to properly align it with the loading mechanism. The temperature is controlled by a flexible resistance heater and a mercury thermostat to about 0.1°C . This makes it possible to determine the transverse strength of the resin at any desired temperature in water or other liquids. For the most precise control of specimen temperatures in liquids it would probably be desirable to insert a section of heat-insulating material in the plunger to reduce conduction from or to the specimen at the point of contact with the plunger.

The instrument is designed so that the load is applied through the square piston normal to the long axis of the specimen and at the mid-point of the span. When a cylindrical plunger was used, the operator adjusted the position of the curved surface contact visually. This led to uncertainty of the positioning of stress concentration in the specimen under test. On the new specimen holder lines have been scribed so that the maximum stress applied will be 25 mm from these lines. Thus, by placing an index line on the specimen, the position of the applied load can be accurately determined. This facilitates the positioning of the specimen at a specific point such as a repair joint or union of two types of resin in the specimen.

The accuracy of loading the specimen is dependent upon the low friction roller bearing on the one-inch-square piston and the low friction roller bearing supports for the counterbalancing mechanism. The applied load is considered accurate to 25 gm. A maximum load of 12 kg can be applied without refilling the loading pan with shot.

3. Summary

This instrument is designed to determine the transverse strength of materials under controlled rates of loading. It is especially useful for testing resins using the standard specimen (2.5 x 10.0 x 65 mm) required by the American Dental Association and Federal specifications for denture base resins.

The gravity feed of lead shot provides a more nearly constant rate of loading than manual loading methods.

The strength of the resin can be determined in air or in a thermostatically controlled liquid bath.

The instrument provides for accurate positioning of the specimen and load.

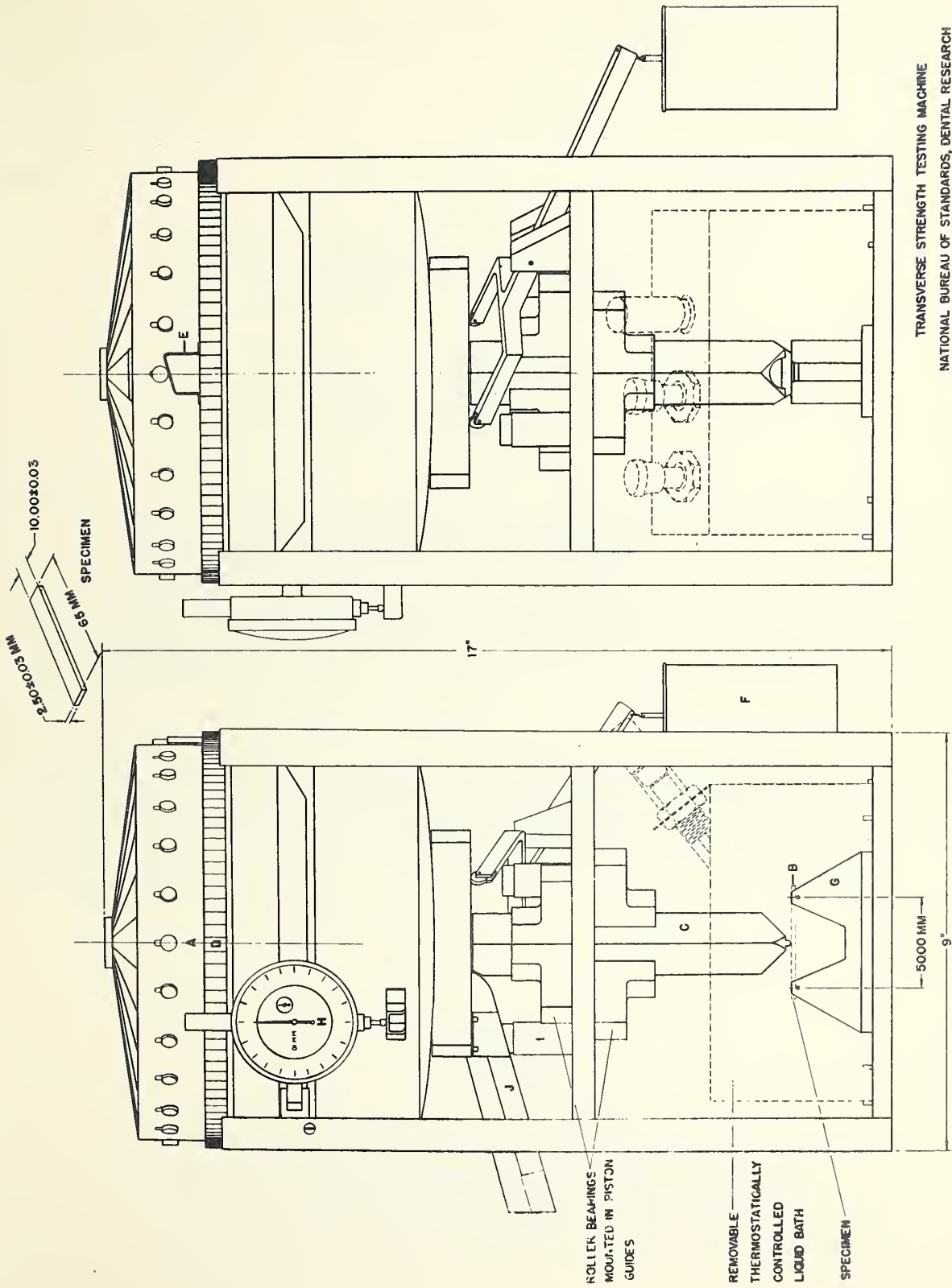
The automatic loading and ease of positioning of the specimen make it possible for one operator to conduct transverse tests efficiently.

Reference

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Figure 1. Transverse strength testing machine.



TRANSVERSE STRENGTH TESTING MACHINE
NATIONAL BUREAU OF STANDARDS, DENTAL RESEARCH
JANUARY 1953
SCALE



Figure 2.

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Some Factors Affecting the Dimensional Stability of the Ag-Sn-(Cu-Zn) Amalgams

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SOME FACTORS AFFECTING THE DIMENSIONAL STABILITY
OF THE AG-SN-(CU-ZN) AMALGAMS

Abstract

An investigation of the X-ray diffraction characteristics and of the dimensional changes of Ag-Sn (Cu-Zn) amalgams during and after their hardening period indicated that uncombined mercury was present in the amalgams after the initial solidification and that this uncombined mercury disappeared during the period when greatest dimensional changes occur. On the basis of the data obtained it is postulated that the expansion during the hardening of amalgam results from diffusion of uncombined mercury throughout the material; the subsequent shrinkage then results from combination of this mercury with existing phases or with residual alloy.

1. Introduction

Although an enormous amount of experimental work has been done on the Ag-Sn-(Cu-Zn)* amalgams [1,2,3,4,5,6], no mechanism has been proposed which will satisfactorily explain the initial contraction, subsequent expansion, and final contraction which occur during the first twenty-four hours after amalgamation. Various investigators have attempted to explain these changes in terms of mercury content of the amalgam system. Their difficulty may have resulted from the failure to differentiate between total mercury and combined mercury in this system. It is probable that in the hardening of the heterogeneous mass not all the mercury is in the combined form. Chemical analysis of the amalgam would not distinguish between combined and uncombined mercury. Furthermore, photomicrographic evidence [7] indicates that the rate of attack on the alloy particles by mercury may vary widely depending upon the conditions under which the specimen was prepared. The possible diffusion of this mercury if it is present, and its subsequent reactions with the alloy may account for the dimensional changes observed in the hardened amalgam.

* Cu-Zn is placed in parentheses because these elements are not always present in the above mentioned amalgams.

With this in mind this investigation was undertaken to determine (1) whether uncombined mercury was present after the amalgam had hardened; (2) whether the uncombined mercury, if present, continued to take part in any reaction; and (3) whether the dimensional changes which occur in hardened amalgam could be correlated with this reaction.

2. Experimental Approach and Procedures

X-ray diffraction methods can not be used to detect the presence of free or uncombined mercury in an amalgam at room temperature since the mercury, being a liquid at this temperature, does not have a crystalline structure and does not give an X-ray diffraction pattern. However, if the mercury is chilled below its solidification point, typical lines representing mercury are detected by diffraction methods. Therefore, if uncombined mercury is present in amalgam immediately after hardening, it should be possible to determine its presence by X-ray investigation of amalgam specimens held below the freezing temperature of mercury. Furthermore, it should be possible to study the rate of disappearance of the uncombined mercury with time by periodic examination of the specimen at temperatures below the freezing point of mercury.

There is the possibility that the intermediate phases in the Ag-Sn-(Cu-Zn) amalgams might have a higher mercury solubility at room temperature than at temperatures below the freezing point of mercury. Such being the case, crystalline mercury at low temperatures might be formed by rejection from a solid solution which existed at room temperature. Evidence will be given later in this paper to support the contention that if this does occur, the amount of mercury involved is insignificant.

In order to investigate the X-ray diffraction patterns of amalgam at reduced temperatures, specimens were manually condensed employing standard dental procedures in a stainless steel mold constructed so that it could be cooled with liquid nitrogen during the period of observation. The amalgam specimens were frozen immediately upon completion of condensation by introduction of liquid nitrogen into the mold. An iron-constantan thermocouple was used to measure the temperature of the specimens.

The compositions of the three commercial amalgam alloys used in the investigation are given in Table 1. The amalgams were triturated in a mechanical amalgamator (Wig-L-Bug) using the mercury-alloy ratio of 2 to 3 for Alloys 1 and 2, and a ratio of 2 to 3.6 for Alloy 3.

A Philips high-angle spectrometer goniometer [8] was used to obtain chart records of the copper K alpha diffraction. The diffraction unit was operated at 35 KVP and a tube current of 20 milliamperes. The scanning speed was $1^{\circ} 20'$ per minute and the chart speed was 1/2 inch per minute.

Dimensional changes of amalgam specimens were measured by means of dental interferometers [9] in an air bath at the temperatures indicated.

3. Results

1. X-ray Diffraction Examination of the Ag-Sn-(Cu-Zn) Amalgams

X-ray diffraction charts of the amalgam alloys at 25°C prior to amalgamation, of pure mercury at -125°C, and of amalgams at -125°C are shown in Figures 1 to 4. The data show that uncombined mercury was present in the amalgam and that this mercury disappeared with time, as indicated by the reduction in the height of the mercury lines. Simultaneously with this reduction in uncombined mercury there is also a disappearance of the lines representing the original alloy particles and an increase in the γ_1 and γ_2 phases*. This indicates that the disappearance of the mercury lines was through combination of the mercury with the alloy to form mercury compounds. The disappearance of the mercury lines also indicates that these lines represent uncombined mercury rather than mercury rejected from a solid solution as a result of the reduced temperature.

The data also show that the almost complete disappearance of the mercury lines within six hours corresponds generally to the period of time during which expansion and contraction of the amalgams are commonly observed.

To determine the effect of addition of mercury to fully hardened amalgam, seven-day-old specimens which had been placed in mercury for 12 hours were cooled to -125°C and examined by X-ray diffraction periodically for a period of 24 hours after removal from the mercury. Intense mercury lines were observed in the specimens immediately after removal from the mercury bath, Figure 4. These mercury lines were not detected after the specimens had been held at 37°C for 24 hours or at 21°C for 3 days.

* γ -original alloy ($\text{Ag}_3\text{Sn} + \text{Cu, Zn}$)

γ_1 - Ag_2Hg_3

γ_2 - Sn_7Hg

β_1 - AgHg not observed

2. Dimensional Change Determinations of the Ag-Sn-(Cu-Zn) Amalgams

To examine the effect of uncombined mercury on dimensional changes of hardened amalgam, mercury was added both externally and internally to hardened amalgam specimens and their dimensional changes were observed by means of interferometers. Hardened specimens of amalgam in iron cups were positioned in interferometers; mercury was added to the cups and the dimensional changes were observed over a period of 15 days on two series of specimens held at 21°C and 37°C respectively. In other experiments a small hole was drilled in the specimen and mercury injected into the hole in the amalgam by means of a hypodermic syringe after the specimens had been positioned in the interferometer. Dimensional changes were observed as in the above case. Large expansions were observed in all cases, Figure 5.

In two experiments the supply of mercury was removed from contact with the specimens after a period of 15 days and dimensional changes were observed for an additional period of 26 days, Figure 6. No further expansion occurred in these specimens. A slight shrinkage was observed immediately after removal of the mercury supply.

To obtain information on the effect of temperature on the reactions occurring during the hardening of dental amalgam, dimensional changes of amalgams prepared and observed at various temperatures were determined.

Amalgams prepared and maintained at 37°C expanded less than specimens prepared and observed at 21°C (Figures 7, 8, 9 and Table 2). Furthermore, an over-all shrinkage occurred in all amalgams maintained at 37°C regardless of the temperature at which they were prepared. Specimens prepared at 37°C and maintained at 21°C shrank less than specimens prepared and maintained at 37°C.

Discussion of Results

The observations of dimensional changes, along with the X-ray diffraction evidence that uncombined mercury is present in the amalgam, tend to substantiate the theory that the mechanism of dimensional change is associated with the presence of the uncombined mercury.

The following mechanism is postulated to explain the physical phenomena observed. The initial shrinkage always observed results from the formation of compounds of mercury and alloy having a smaller volume than the sum of the original volumes of the alloy and mercury. The subsequent expansion which is observed results from the diffusion into new areas of uncombined mercury entrapped in spaces throughout the amalgam. The reaction of this uncombined mercury with existing phases or with residual alloy to form compounds of lesser volume would then account for the contraction which follows the expansion of the amalgam.

This mechanism would account for the dimensional changes which occurred on the addition of mercury to hardened amalgam. When mercury is added to hardened amalgam the diffusion of this mercury throughout the specimen would produce the large expansion observed. The slight shrinkage observed immediately after the removal of the supply of mercury could result from the combination of free mercury in the specimen with existing phases or with residual alloy.

The greater shrinkage of amalgam mixed and maintained at 37°C rather than at 21°C may result from a more rapid chemical combination and disappearance of the uncombined mercury at elevated temperatures.

The proposed mechanism would also account for the shrinkage of amalgam which occurs from overtrituration or excessive working during condensation in that either of these treatments would tend to reduce the amount of uncombined mercury by either furnishing new surfaces for reaction with the mercury or by actual mechanical removal of the mercury. These treatments would also tend to distribute the uncombined mercury present more uniformly throughout the amalgam so that there would be fewer mercury-rich areas from which diffusion could take place. On the basis of this explanation, a reduction in size of the alloy particle or a heat treatment which would make the particles more reactive would tend to cause a reduced expansion or a shrinkage of the amalgam.

The possibility that the dimensional changes could also result from phase changes which can take place more readily in the presence of uncombined mercury should not be excluded as a possible mechanism.

Summary

1. Residual or uncombined mercury has been demonstrated by X-ray diffraction studies to be present in amalgams after their initial solidification.
2. This uncombined mercury disappears during the period when greatest dimensional changes occur in the hardening of the amalgam system.
3. A possible mechanism for the dimensional changes based on the presence and disappearance of the uncombined mercury is presented.

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Table 1

Chemical Composition of Alloys Investigated

Elements	No. 1	No. 2	No. 3
Ag	74.5	70.2	70.1
Sn	25.0	25.6	26.5
Cu	0.0	2.4	3.4
Zn	0.5	1.8	0.0



Table 2

Comparison of Dimensional Changes of the Ag-Sn-(Cu-Zn) Amalgams at 21°C and 37°C

Alloy No.	Temp. of Obs.*	No. of Specimens Observed	Fiducial Obs. 15 Min. after Start of Mix					Fiducial Obs. 10 Min. after Start of Mix		Typical Curves (Fig. 9)
			Initial Contraction	Max. Expansion	24 hr			24 day		
					Avg.	Range	Avg.	Range	Avg.	
1	°C		μ/cm	μ/cm	μ/cm	μ/cm	μ/cm	μ/cm	μ/cm	
	21	7	-1.3	+7.0	+6.2	+5.5 to +7.7			+4.3	
	37	8	-4.1	0.0	-2.1	-0.4 to -5.0			-6.2	
	Difference		2.8	7.0	8.3				10.5	
2	21	4	-0.3	+2.1	-0.9	-0.4 to -1.2	-3.0	-2.9 to -3.2		
	37**	4	-4.2	-3.4	-7.0	-6.0 to -8.2	-9.9	-9.5 to -11.0		
	Difference		3.9	5.5	6.1		6.9			
2	21	15	-0.3	+2.0	-1.0	-0.2 to -1.6			-2.6	Curves A and D
	37	7	-2.6	-2.0	-8.6	-8.2 to -9.6			-12.6	
	Difference		2.3	4.0	7.6				10.0	
2	21	15	-0.3	+2.0	-1.0	-0.2 to -1.6				Curves A and B
	21 changed to 37	4	Not observed	+1.3	-3.4	-2.0 to -5.3				
	Difference			0.7	2.4					

Continued on next page

2	37	7	-2.6	-2.0	-8.6	-8.2 to -9.6				Curves C and D
	37 changed to 21	4	Not observed	-1.7	-4.6	-4.2 to -4.9				
	Difference			0.3	4.0					
3 Δ	21	10	-0.3	+3.6	+2.4	+1.6 to +3.9			+1.2	
	37	7	-1.8	+1.4	-2.1	-0.8 to -3.9			-5.2	
	Difference		1.5	2.2	4.5				6.4	

* Equipment, materials, mixing and condensing procedures at 21°C unless otherwise noted.

** Equipment, materials, mixing and condensing procedures at 37°C.

Δ Not comparable with Alloys Nos. 1 and 2 because of differences in alloy-mercury ratio and mixing time.

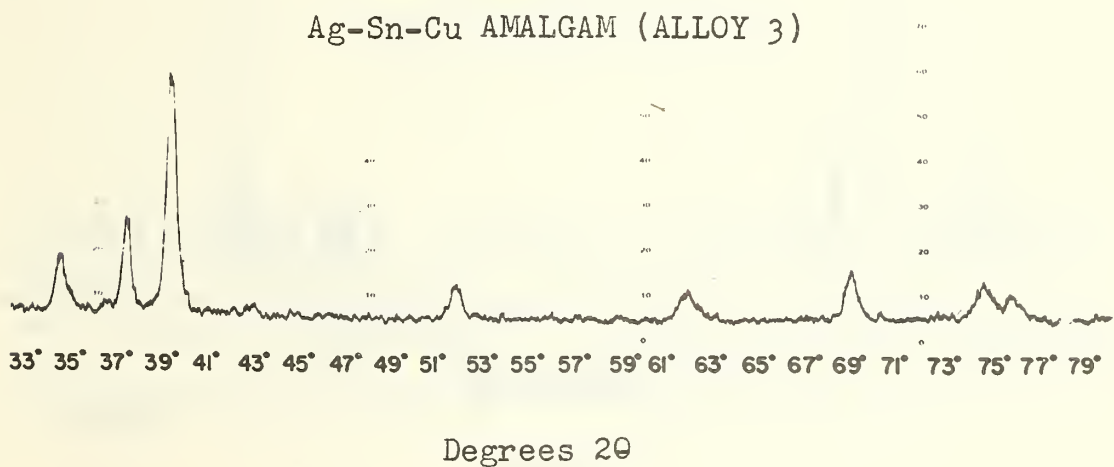
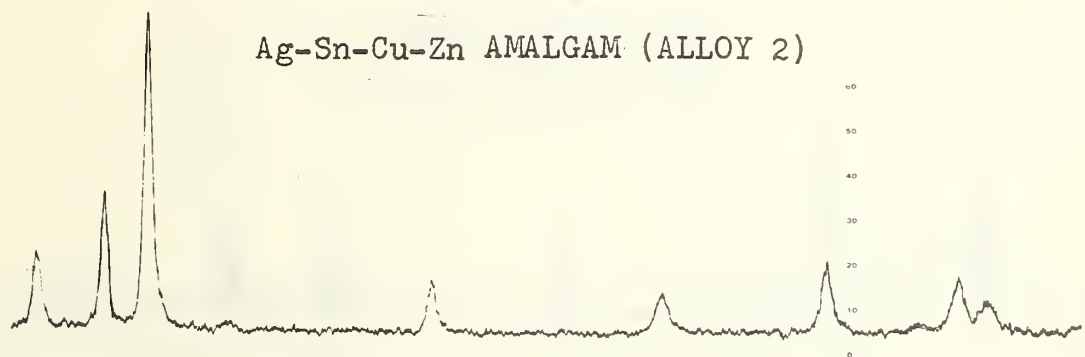
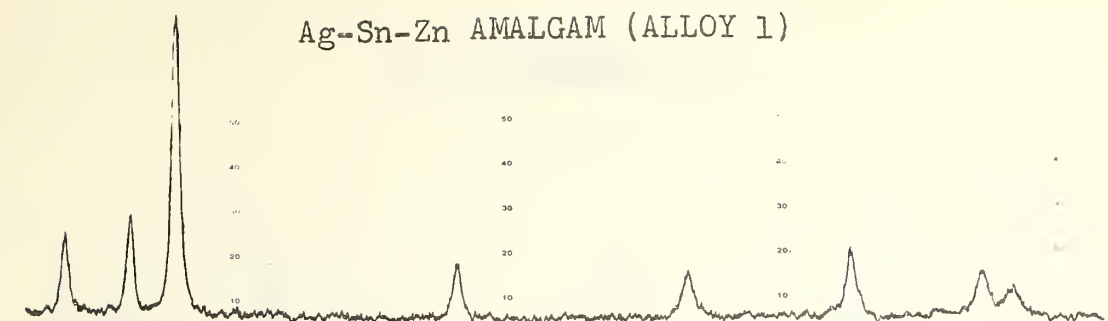


Figure 1. X-ray diffraction charts (with a scale factor of 4) made at 25°C.

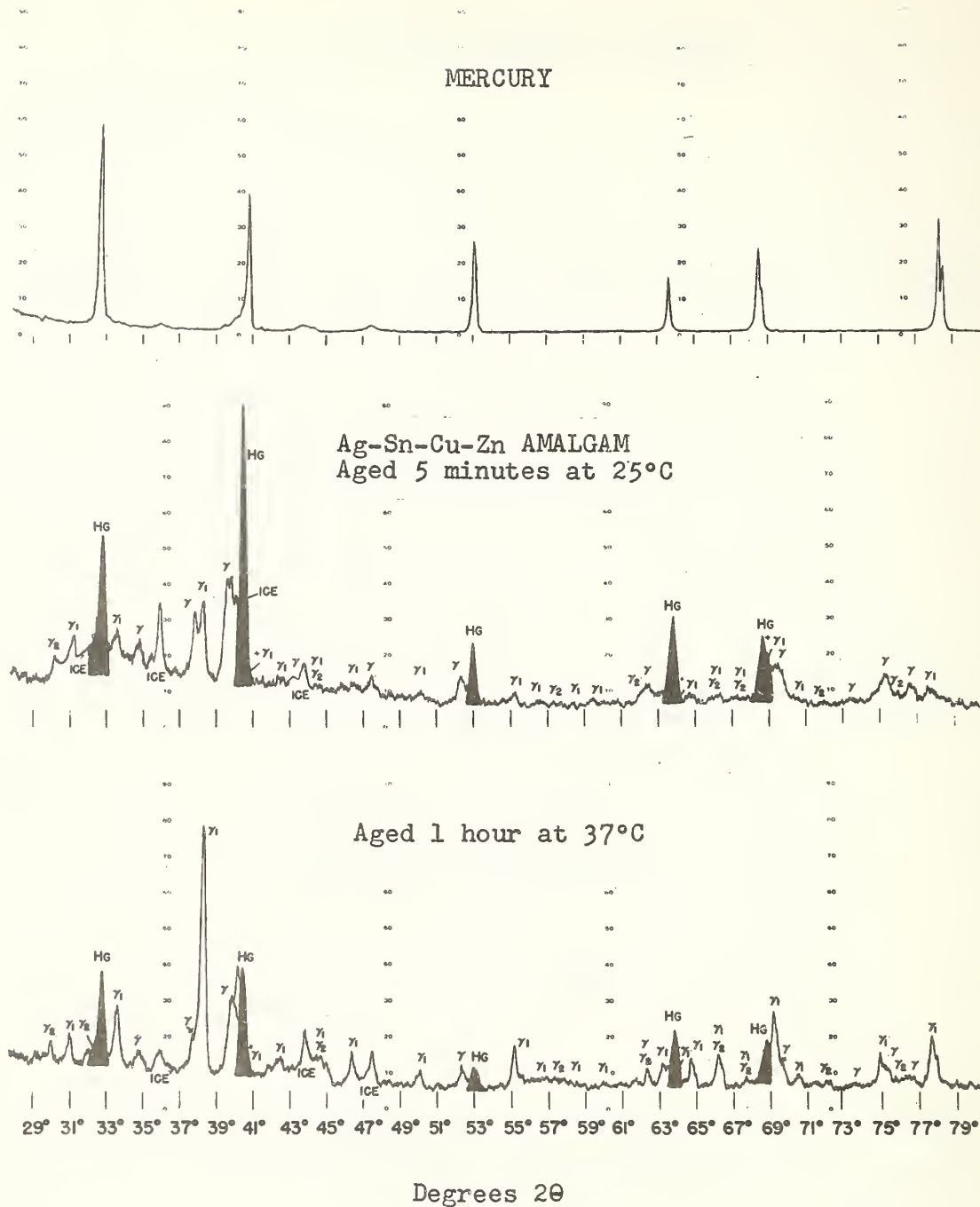


Figure 2. X-ray diffraction charts made at -125°C . Scale factor of 32 used for obtaining the tracings of mercury. Scale factor of 4 used for the remainder of the procedures.

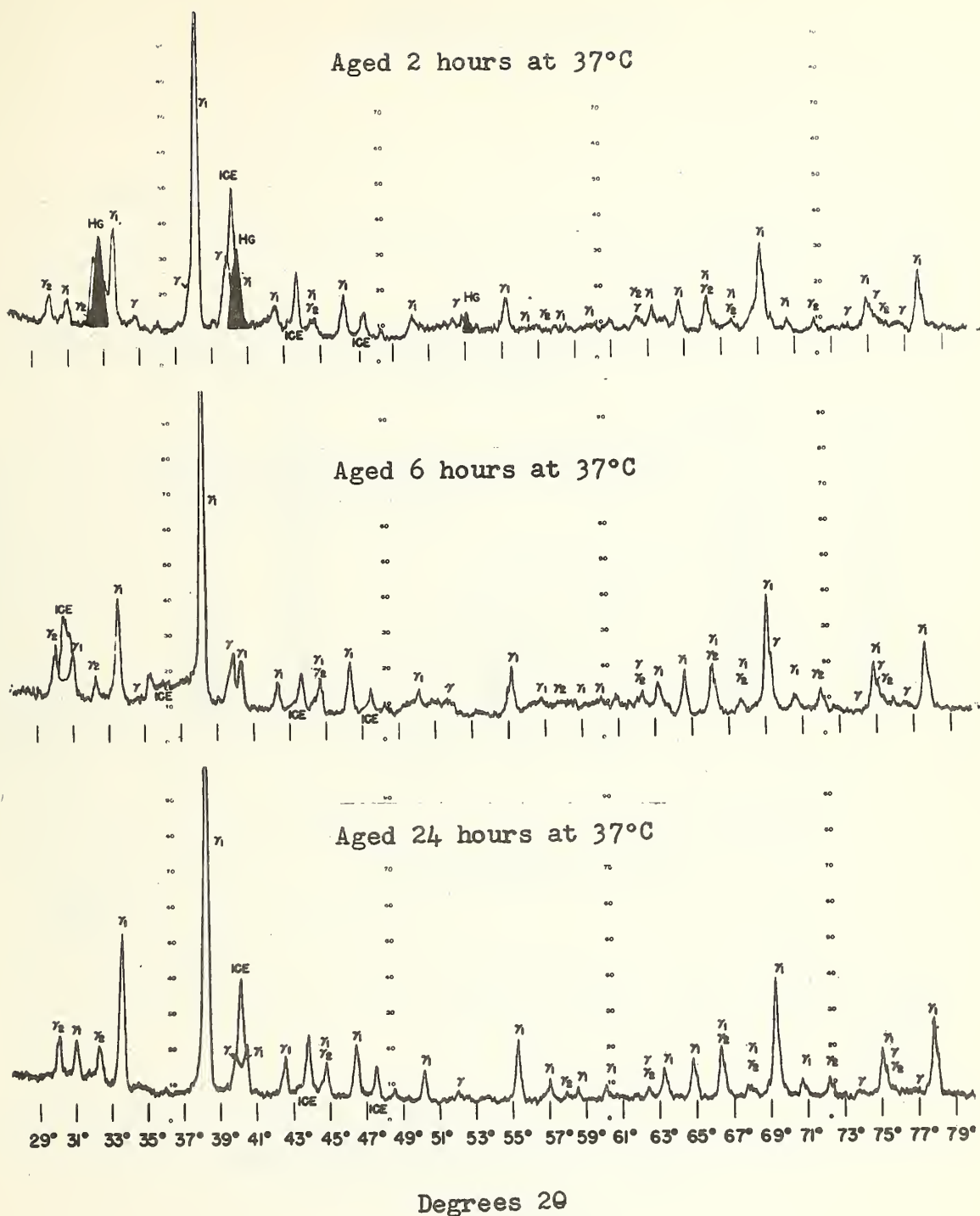
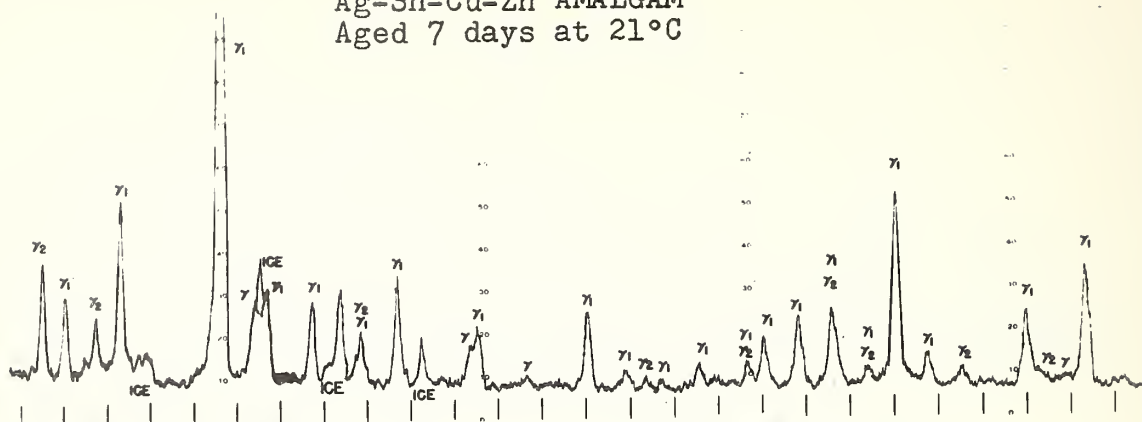
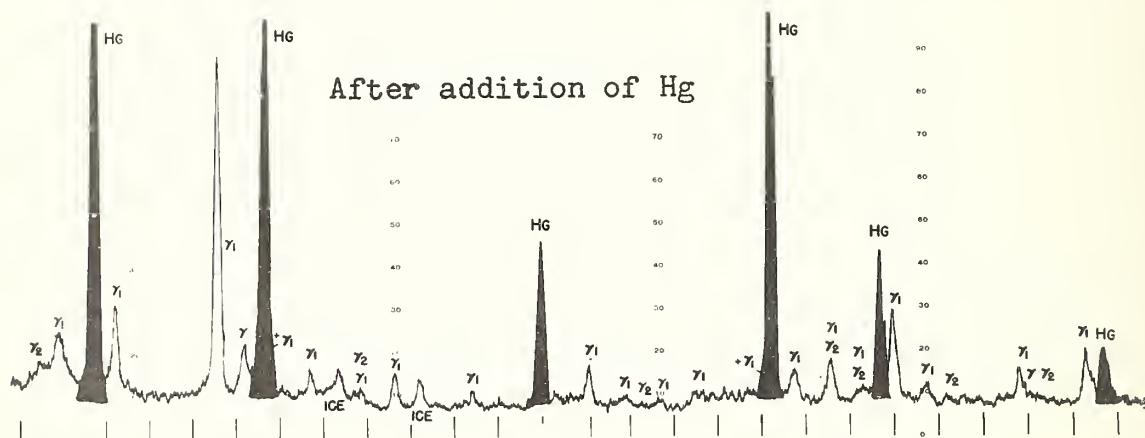


Figure 3. X-ray diffraction charts, a continuation of Figure 2.

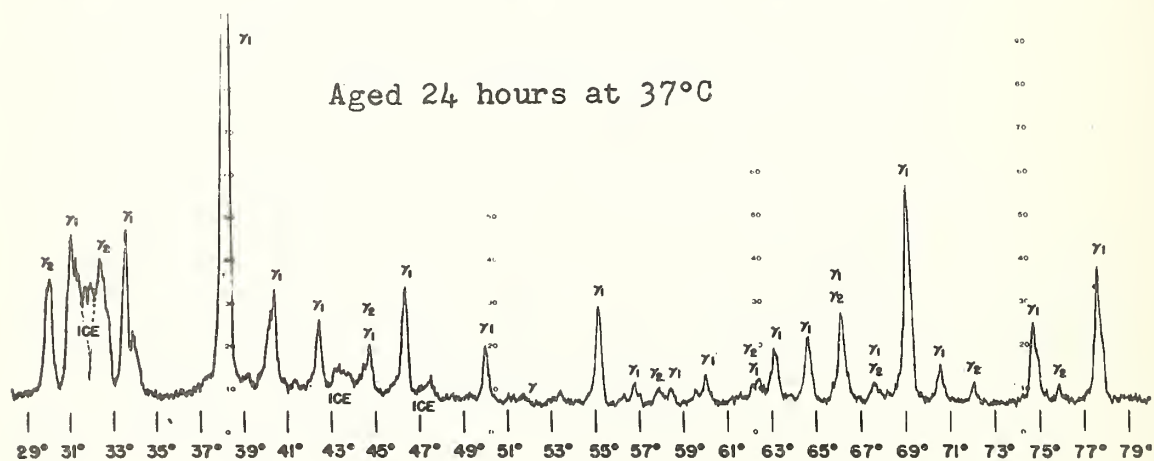
Ag-Sn-Cu-Zn AMALGAM
Aged 7 days at 21°C



After addition of Hg



Aged 24 hours at 37°C



Degrees 2θ



Figure 4. X-ray diffraction charts made at -125°C.

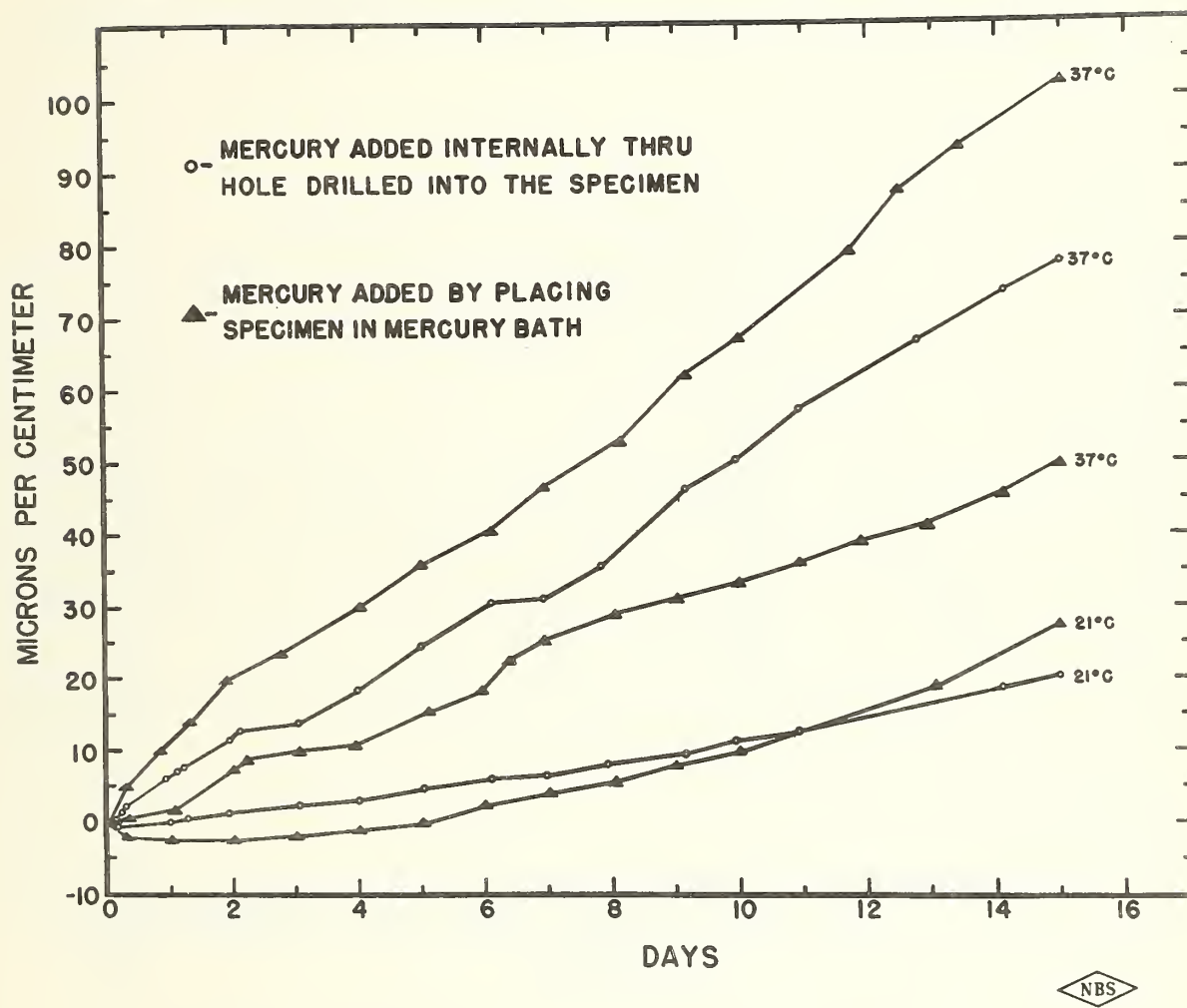


Figure 5. Dimensional changes in Ag-Sn-Cu-Zn amalgam (Alloy 2) resulting from addition of mercury.

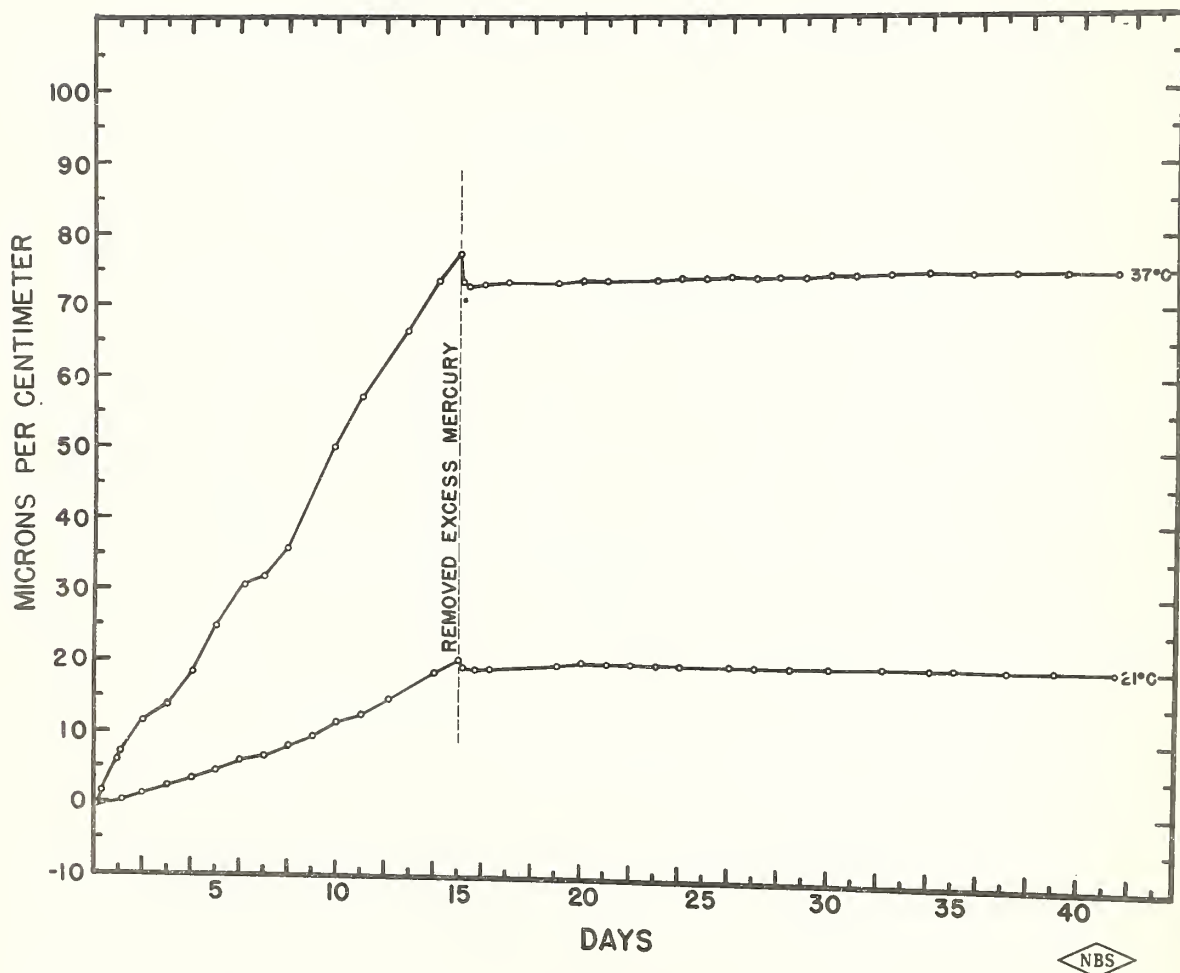
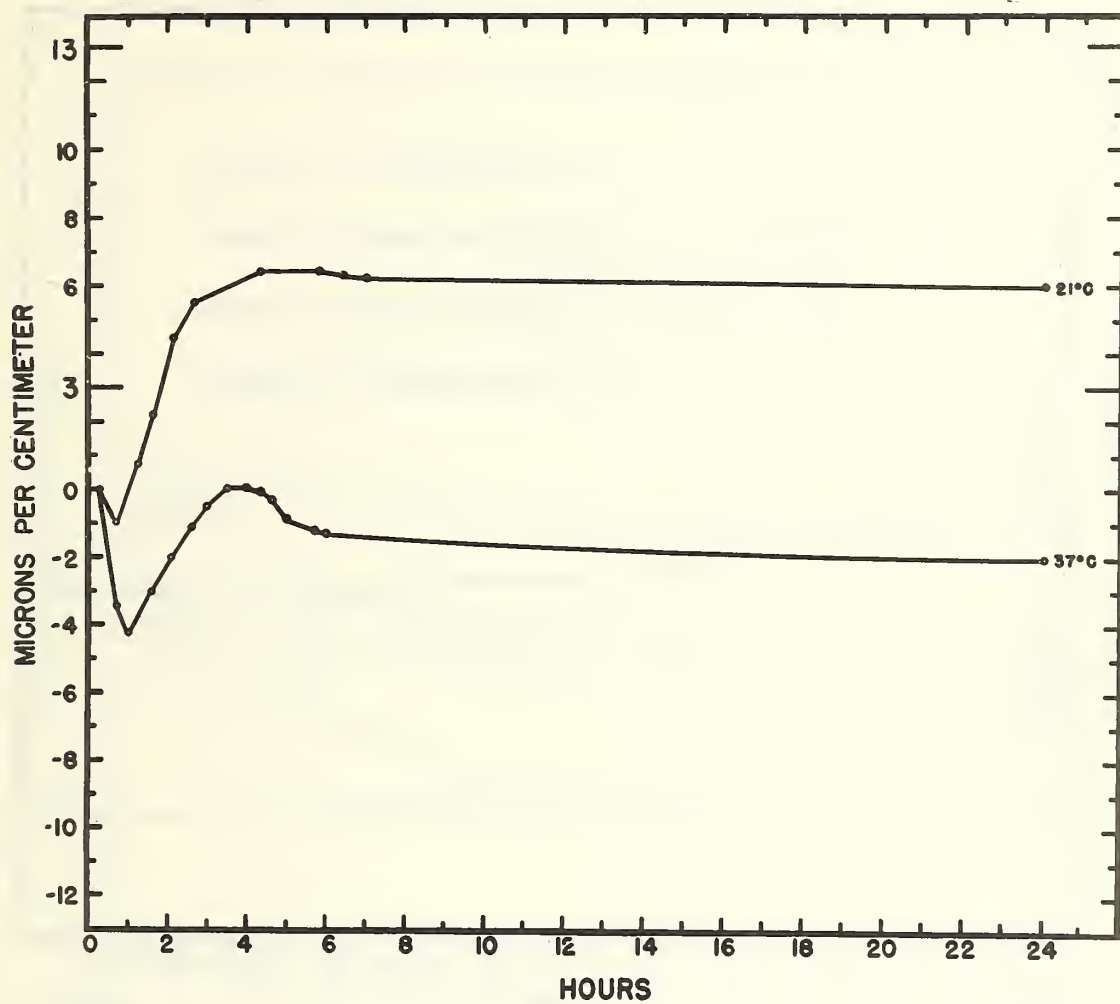


Figure 6. Dimensional changes of Ag-Sn-Cu-Zn amalgam (Alloy 2) resulting from addition and removal of mercury. 0 days - mercury added internally through hole drilled into specimen. 15 days - excess mercury removed from hole drilled into specimen.



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Figure 7. Comparison of dimensional changes of Ag-Sn-Zn amalgam (Alloy 1) at 21°C and at 37°C. Equipment, materials, mixing-condensing procedures at 21°C.

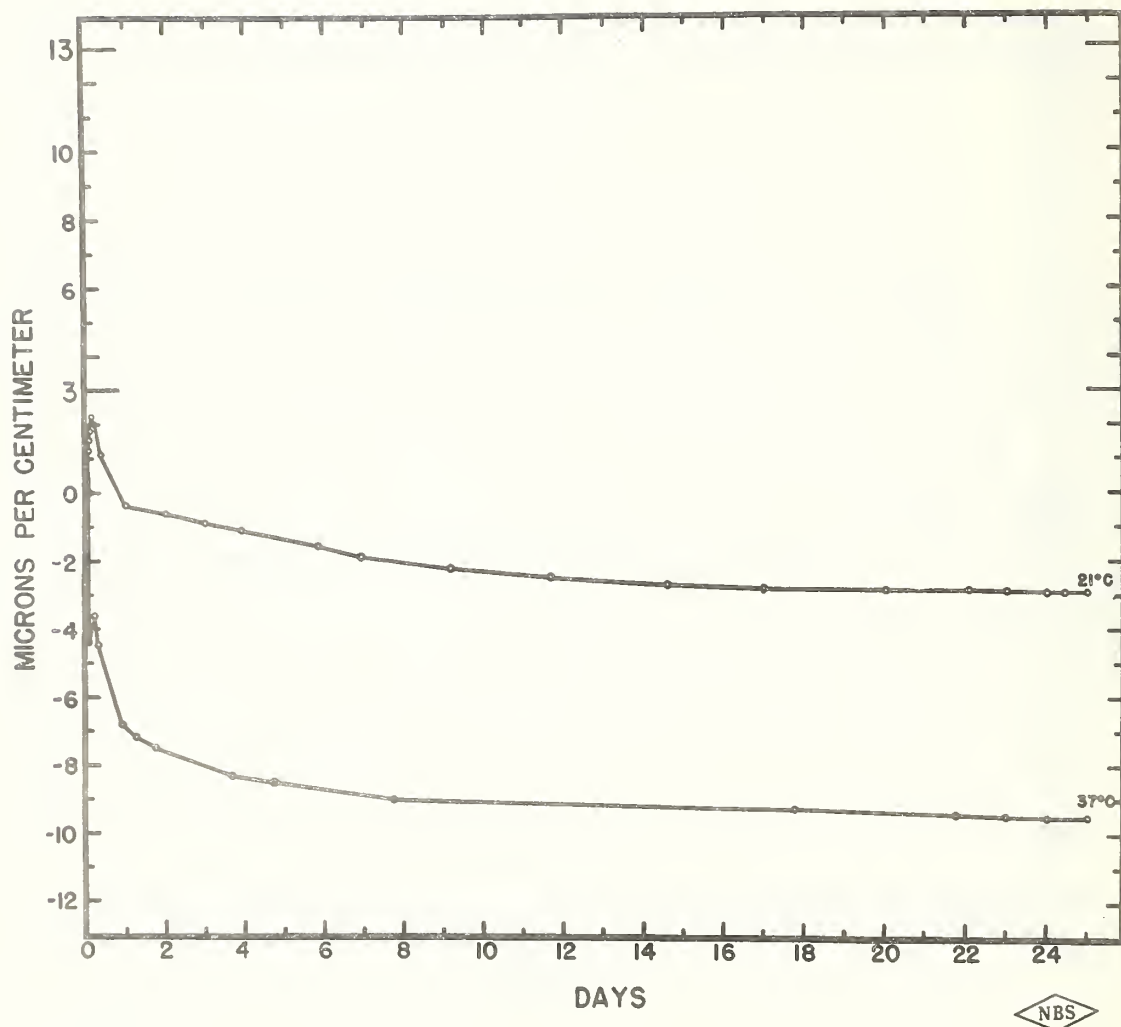


Figure 8. Comparison of dimensional changes of Ag-Sn-Cu-Zn amalgam (Alloy 2) at 21°C and at 37°C. Equipment, materials, mixing-condensing procedures, and observations were made at the respective temperatures.

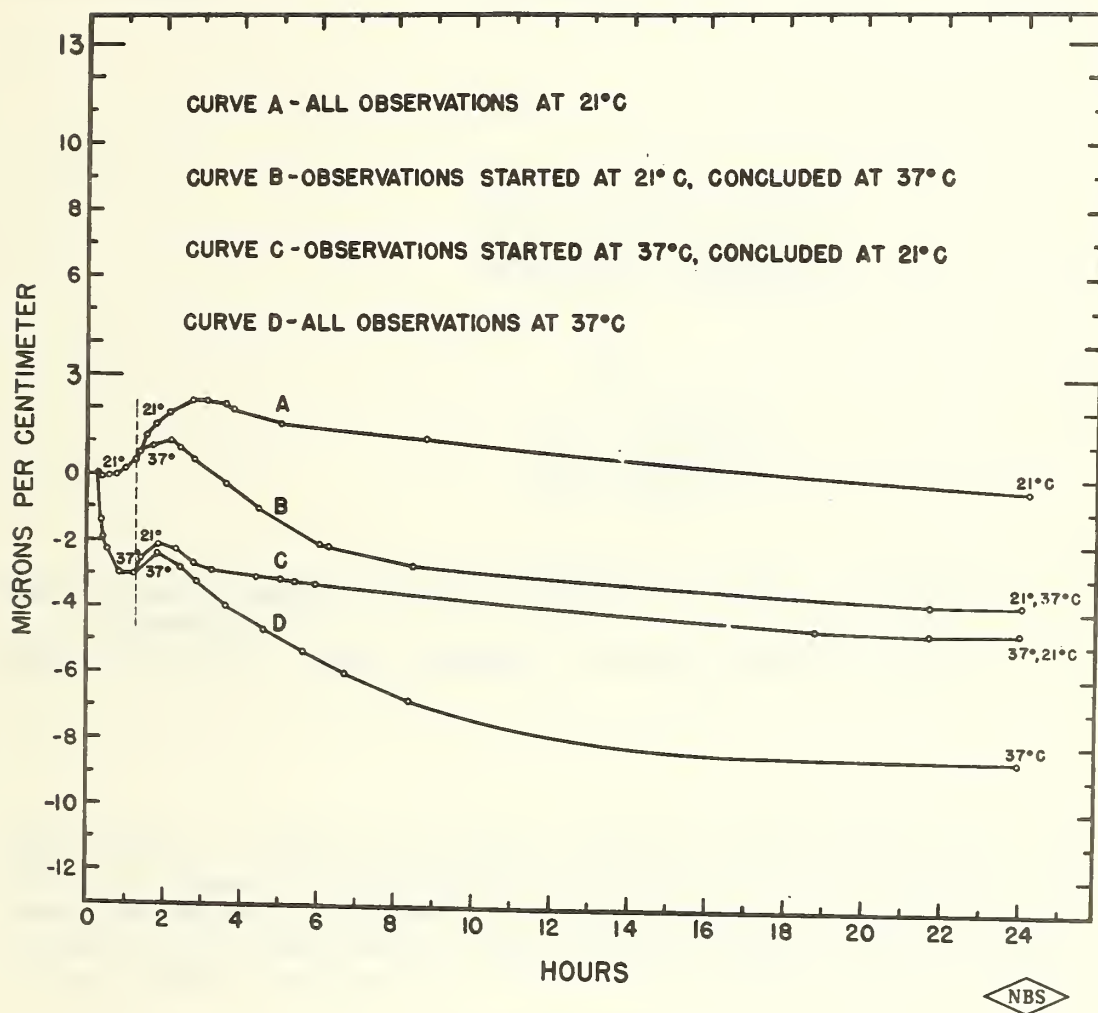


Figure 9. Comparison of dimensional changes of Ag-Sn-Cu-Zn amalgam₁ (Alloy 2) at 21°C and at 37°C.

NATIONAL BUREAU OF STANDARDS REPORT

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DIRECT FILLING RESINS:

MECHANICAL PROPERTIES

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DIRECT FILLING RESINS: MECHANICAL PROPERTIES

Abstract

The use of acrylic type resins for direct filling of cavities in ~~the~~ teeth has been recently developed to such an extent that a large percentage of the dental profession use this type of material. This paper reports the results on the mechanical properties of ten trade brands of materials, as well as the methods developed for obtaining data on small specimens, comparable to dental applications. A new test is included which is based on rate of indentation of a sphere under constant load.

The ~~obtained~~ data show that the mechanical properties improve for approximately 24 hours after mixing. Moduli of elasticity varied from 1.51 to 3.09 psi and compressive strength from 4,000 to 7,400 psi.

DIRECT FILLING RESINS: MECHANICAL PROPERTIES

1. INTRODUCTION

The success of any material used to restore lost tooth structure depends to a large extent upon its physical and chemical properties. This applies to all types of filling materials, whether they are metallic, ceramic or resinous. The development of direct filling resins and their widespread use as restorative materials where esthetics must be considered, make it desirable to know more about their mechanical properties. A knowledge of these properties will aid in determining the type of restorations for which resins are most suitable and in determining the techniques which should be used to obtain optimum results with these materials.

The mechanical properties reported are of special interest in the evaluation of resinous filling materials. The modulus of elasticity of the resin is an index to its stiffness and to the amount of movement of the restoration at the margin or walls of the cavity as a result of forces encountered in the mouth. The yield strength is a measure of the forces required to cause a permanent deformation in the restoration. The resistance of the resin to indentation under a continuous load is an indication of its ability to resist deformation in the mouth in locations where forces are applied repeatedly on occlusal surfaces or constantly at contact points.

The investigation of the properties of direct filling resins was somewhat complicated by the fact that these resins polymerize in the tooth and that the temperature rise on polymerization [1], the rate of hardening and the completeness of polymerization depend on the size of the restoration. For these reasons measurements of mechanical properties were made on specimens comparable in size to restorations used in practice. Since change in mechanical properties continues for some hours, a series of determinations were made on specimens of different ages. Determinations of the modulus of elasticity, yield strength and resistance to indentation of ten brands of direct resin filling materials (Table 1) are reported in this paper.

2. EXPERIMENTAL PROCEDURE

Modulus of Elasticity and Yield Strength

To determine the modulus of elasticity and yield strength of the resins, loads were applied to specimens 3 mm in diameter and 6 mm in length in a Tinius Olsen Testing Machine, and the deformation of the specimens was measured with Tuckerman strain gages.

All specimens were prepared and tested in a constant temperature room at $22 \pm 1^\circ \text{C}$ ($71 \pm 2^\circ \text{F}$) to insure uniformity of specimens and of testing procedure. Mixing was done according to the manufacturers'

directions insofar as details were available. Approximately 0.75 g of polymer with the recommended ratio of liquid was employed for each mix. Specimens were molded in a stainless steel split-mold, Fig. 1, consisting of six cavities, each accurately machined to 3 mm in diameter and 6 mm in length. The mold was assembled and slightly overfilled with the resin at the time the material would normally be placed in the tooth cavity. A steel plate was placed on top of the mold and pressure was applied by two screw-clamps. Immediately after it was clamped, the mold was placed in an oven regulated to $37 \pm 1^\circ \text{C}$ ($98 \pm 2^\circ \text{F}$). After thirty minutes the mold was removed from the oven and disassembled. The specimens were removed and allowed to stand at room temperature (22°C) (72°F) for 3 to 5 days before testing.

The procedure used for measuring the modulus of elasticity was as follows. Because of the shortness of the specimens, the 1-inch Tuckerman strain gages used to measure deformations were attached to steel pins placed above and below the specimens in the testing machine as shown in Fig. 2. The error due to this pin arrangement was found to be negligible because of the size of the pins ($1/2$ inch diameter) and the relatively low modulus of the plastic.

A continuous load was applied with the testing machine, using a head speed of 0.20 in. per minute, and the strain was read from the Tuckerman strain gages by means of an Autocollimator [2] at 2.5 lb load increments. Loads were recorded from 5 to approximately 100 lbs depending upon the strain produced in the material. Six specimens of each brand were used to obtain an average value. Fig. 3 shows that the variation obtained in six specimens of a typical material for the stress-strain relationship was of the order of 6 percent. The variations are caused mainly by differences in individual specimens.

The average moduli of elasticity of the direct filling materials investigated varied from 1.51 to 3.09×10^5 psi, Table 2. The stress-strain curves of the materials are shown in Figs. 4 and 5. The modulus of elasticity was computed over the stress range of 1,000 to 6,000 psi.

The "yield strength" for the purposes of this paper is defined as the stress (load per unit cross-sectional area) at which the deformation produced by a unit stress equals or exceeds 1.25 times that observed in the first few increments of stress [3]. The calculated yield strengths (Table 2), which represent an approximation of the stress that can be applied to the resin without permanent deformation, ranged from 4,000 to 7,400 psi.

Resistance to Indentation

The resistance of the resins to indentation was observed by applying loads to specimens with the Rockwell Superficial Hardness Tester. By observing the change in the depth of indentation while the load remained on the resin for ten minutes, flow properties were

determined. Recovery after flow was determined by measurements made after removal of the load. The relationship between degree of polymerization and resistance to indentation was determined by loading specimens at various lengths of time after preparation.

The specimens were prepared in accordance with the standard mixing procedure and formed at a temperature of $22 \pm 1^\circ \text{C}$ ($71 \pm 2^\circ \text{F}$) in tinfoil lined brass molds 34mm long by 12 mm wide by 1.5 deep. A load of 2 kg was placed on the top plate of the mold immediately after the insertion of the resin. Specimens to be tested 10 minutes after the start of the mix were removed from the mold at 8 1/2 minutes and stored at room temperature until placed in the testing equipment. All other specimens were removed from the mold 25 minutes after the start of the mix and stored at $37 \pm 1^\circ \text{C}$ ($98 \pm 2^\circ \text{F}$) until five minutes before testing, at which time they were allowed to come to room temperature.

In measuring the resistance to indentation in the Rockwell Superficial Hardness Tester the Y-30 scale employing a minor load of 3 kg, a major load of 30 kg and 1/2 inch steel ball was used. The minor load was used for the fiducial reading and the major load applied for 10 minutes was used to indent the material. Observations were taken at frequent intervals in order to determine the relationship between depth of indentation and time of load application. Indentation was observed to ± 0.001 mm by a dial indicator.

The uniformity of the data obtained in measuring indentation is shown in Fig. 6. The variation obtained when testing five specimens of an individual brand was within plus or minus 3 percent. The calculated probable error is of the magnitude of ± 0.004 mm. As in the stress-strain testing, it is felt that deviations in individual determinations are caused chiefly by unavoidable differences in individual specimens rather than by inherent errors in the apparatus and techniques.

Data for a typical indentation and recovery curve are shown in Fig. 7.

Table 3 and Figs. 8 and 9 give the indentation values for a 10-minute application of the major load for specimens of various ages up to 120 hours. As shown in the table, the average depth of indentation at 10 minutes was more than twice the depth of indentation at 120 hours, and the average depth at 30 minutes was more than 1.1/2 times that at 120 hours. Also included in Table 3 are values for "indentation strength." These figures ranging from 4100 psi at 10 minutes to 9300 psi at 120 hours were obtained by dividing the load on the indenting tool by the projected area of the indentation, a

method commonly used for calculating hardness as determined by indentation. In determining the projected area of the indentation from the depth of indentation a correction was applied to include the slight indentation produced by the minor load. *

* The corrected equations for projected area were derived as follows:

$$\frac{L}{A} = \frac{L'}{A'} = \text{Indentation strength} \quad (1)$$

$$A' = \pi (2 R y' - y'^2) \quad (2)$$

$$A = \pi [2 R (y + y') - (y + y')^2] \quad (3)$$

where

L = major load on indenter

L' = $\frac{L}{10}$ = minor load on indenter

A = projected area of indentation produced with major load

A' = $\frac{A}{10}$ = projected area of indentation produced with minor load

R = radius of indenter sphere

y' = depth of indentation produced with minor load

y = instrument reading

y + y' = depth of indentation produced with major load

If in the above equations the small y^2 , y'^2 and $(y + y')^2$ terms are neglected it can be seen that $A' = \frac{2\pi R}{9} y$ (4)

or substituting the value 0.25 inch for R and including the factor for converting y in millimeters to inches.

$$A' = 0.00687y \quad (5)$$

A more accurate approximation in which fewer terms are neglected gives

$$A' = \frac{2\pi R}{9} y - \frac{11}{81} y^2 \quad (6)$$

or substituting as above

$$A' = 0.00687y - 0.00066y^2 \quad (7)$$

Indentation strength values obtained from equation 7 differ from those obtained from equation 5 by less than 2.5 percent if the indentation reading is less than 0.25 mm and by less than 1 percent if the indentation reading is less than 0.1 mm.

The percentage of recovery after indentation of the various brands of material increased from values of approximately 40 ± 10 percent at 30 minutes to values of 70 ± 10 percent at 120 hours, Table 4. Recovery was computed by dividing the measured depth caused by 10 minutes of application of the major load by the amount of recovery during 10 minutes of application of the minor load.

3. DISCUSSION OF RESULTS

One important characteristic of the direct resin filling materials demonstrated by the data is their change in properties during the first few hours after mixing of the monomer and polymer. This change is evident in the results showing the relationship between depth of indentation and age of specimen, Figs. 8 and 9 and Table 3. The resistance to indentation increases rapidly for approximately six hours. Following this there is slight increase in resistance during the period from 6 to 24 hours, after which this property remains essentially constant. Table 4 shows that the extent to which the resins recover after being deformed is also related to age. Recovery under the conditions used in this test was approximately 30 to 50 percent when the specimens were 1/2 hour old, but was of the order of 75 percent after 24 hours.

That the change in mechanical properties is related to completeness of polymerization is illustrated by Fig. 10. The depth of indentation obtained at 10 minute application of the major load is plotted against age of the specimen. Monomer content of the same specimens, determined by a modified form of the method employed by Lewis and Mayo [4], is also plotted against age of the specimen. These data demonstrate the importance of the presence in the direct filling resins of the proper catalysts and accelerators to cause the polymerization of the resins to be as complete as possible.

There is some indication that those resins which cure most rapidly, as evidenced by early peak temperatures, have higher moduli of elasticity and yield strengths.

The data on modulus of elasticity point out one of the greatest weaknesses of the resins. The values obtained were approximately 60 percent of the value obtained for a well cured denture base resin. Gold alloys used for inlays have a modulus of 15 million psi, while that of the resins is of the order of 0.3 million psi. This means that equal forces on similar specimens of resin and gold will produce approximately 50 times as much deformation in the resins as in the gold. Clinically this indicates that these resins should be used in restorations where they will be well supported by tooth structure. Forces applied to unsupported resin restorations will result in

deformation with resultant movement at the margins of the restoration.

The relatively low yield strength and low resistance to indentation of the direct filling resins limit their usefulness to some extent. The resistance to indentation is approximately one-half that of amalgam. The average yield strength was found to be 6400 psi. Since biting forces of over 100 lbs are not uncommon, [5] it can be seen that stresses of over 6400 psi could occur on occlusal surfaces and that plastic flow would occur on direct resins in such locations.

The data presented in the report evaluate the mechanical properties of the ten brands of direct resin filling material investigated. The superiority of one brand over another, however, cannot be judged by mechanical properties alone. To make an overall evaluation it would be necessary to consider in addition such factors as porosity, curing shrinkage, dimensional stability, color stability and clinical behavior.

4. CONCLUSIONS

1. Methods were developed for measuring mechanical properties of small specimens of resin comparable in size to tooth restorations by use of two standard testing machines, the Tinius Olsen compression machine and the Rockwell Superficial Hardness Tester.
2. The direct filling resins tested were found to improve in mechanical properties during a period of approximately 24 hours after mixing. This improvement coincided with a decrease in monomer content during the same period.
3. The moduli of elasticity of the resins tested varied from 1.51 to 3.09×10^5 psi, indicating that, compared with other restorative materials, the resins are low in stiffness.
4. The yield strength in compression of the direct filling resins varied from 4,000 to 7,400 psi. This low value would permit plastic flow to occur under stresses which might be encountered on occlusal surfaces.
5. The values obtained on the resins for resistance to indentation were approximately one-half of the values obtained on dental amalgam.
6. In general the mechanical properties of the direct filling resins are low in comparison with the properties of dental golds, amalgam or denture base materials.

5. REFERENCES

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2. Tuckerman, L. B., Optical Strain Gages and Extensometers, Proc. Am. Soc. Test. Mats. 23, 1017 (1923)
3. Paffenbarger, G. C., Sweeney, W. T., and Isaacs, A., Wrought Gold Wire Alloys, J. Am. Dent. Assn. 19, 2061 (1932)
4. Lewis, F. M. and Mayo, F. R., Precise Method for Isolation of High Polymers, Analytical Edition of Ind. and Eng. Chem. 17, 134 (1945)
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Table 1. Direct Filling Resins Investigated

Trade Brand	Manufacturer
Ames	The W. V-B Ames Co.
A-thermoplast V-10	Athermoplast Products, Inc.
Dentafil	Dental Fillings, Ltd.
Duz-all	Coralite Dental Products Co.
Fastcrown	Acralite Co., Inc.
Kadon	The L. D. Caulk Co.
Plasto-filling pf3	Plastodent, Inc.
Replica	Cosmos Dental Products, Inc.
Texton	S. S. White Dental Mfg. Co.
Vitafilling	Vitaliner Co.

Table 2. Modulus of Elasticity and Yield Strength
(ages - 3 - 5 days)

Material	Modulus Elasticity (average)	Probable Error	Yield Strength
	psi	psi	psi
Ames	2.60×10^5	$\pm 0.10 \times 10^5$	5,400
A-thermoplast V-10	1.51×10^5	$\pm 0.37 \times 10^5$	4,000
Dentafil	2.63×10^5	$\pm 0.29 \times 10^5$	6,600
Duz-all	2.71×10^5	$\pm 0.14 \times 10^5$	6,400
Fastcrown	2.61×10^5	$\pm 0.06 \times 10^5$	6,400
Kadon	3.09×10^5	$\pm 0.23 \times 10^5$	7,400
Plasto-filling pf3	2.94×10^5	$\pm 0.17 \times 10^5$	7,400
Replica	2.91×10^5	$\pm 0.29 \times 10^5$	7,200
Texton	2.74×10^5	$\pm 0.12 \times 10^5$	—
Vitafilling	2.57×10^5	$\pm 0.10 \times 10^5$	6,400

Table 3. Indentation and Indentation Strength versus Age of Specimen

Material	10 min	30 min	1 hr	2 hr	4 hr	6 hr	24 hr	120 hr
Depth of Indentation*								
	mm	mm	mm	mm	mm	mm	mm	mm
A-thermoplast V-10	0.277	0.210	0.202	0.181	0.150	0.146	1. 0.137	0.115 1
Dentafil	0.227	0.173	0.136	0.126	0.117	0.114	2. 0.111	0.109 2
Duz-all	0.217	0.139	0.122	0.111	0.104	0.101	0.095	0.096 3
Fastcrown	0.264	0.165	0.146	0.136	0.112	0.115	4 0.104	0.101 4
Kadon	0.219	0.165	0.142	0.135	0.122	0.115	5 0.102	0.105 5
Plastofilling pf3	0.235	0.146	0.122	0.116	0.112	0.110	3 0.110	0.102 3
Replica	0.228	0.153	0.142	0.131	0.121	0.116	4 0.104	0.106 4
Texton	0.224	0.167	0.160	0.144	0.127	0.118	-	0.104 5
Vitafilling	-	-	-	-	-	-	-	0.103 6
Average Indentation	0.236	0.165	0.146	0.135	0.121	0.117	0.109	0.104
Indentation Strength								
	psi	psi	psi	psi	psi	psi	psi	psi
Average Indentation Strength	4,100	5,900	6,700	7,200	8,000	8,300	8,900	9,300

* Indentations are accurate to approximately 0.005 mm. Major load applied for 10 minutes.



Table 4. Recovery of Direct Filling Resins

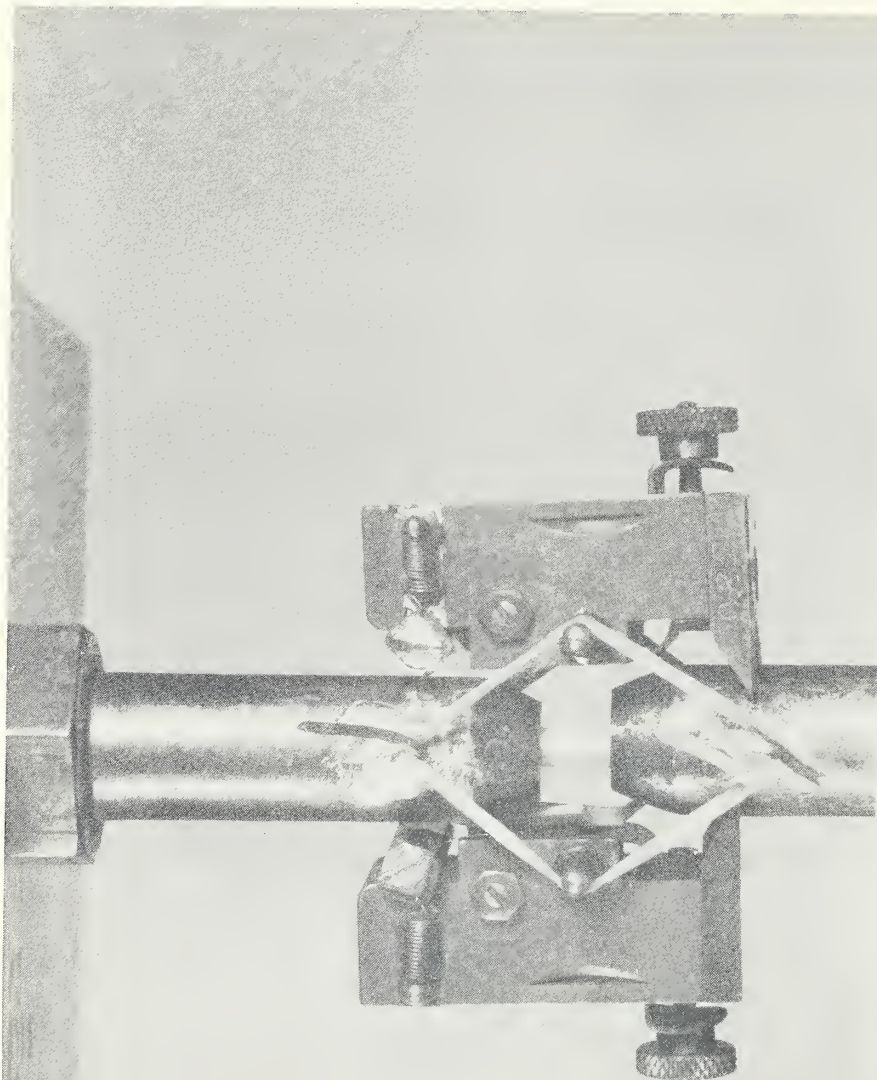
Material	Age of Specimen							
	10 min	30 min	1 hr	2 hr	4 hr	6 hr	24 hr	120 hr
	%	%	%	%	%	%	%	%
A-thermoplast V-10	*	30	36	45	50	55	55	10 60
Dentafil	4	38	46	58	56	64	68	9 69
Duz-all	21	53	61	61	74	75	81	1 80 (10)
Fastcrown	1	42	49	53	55	64	69	8 71 (5)
Kadon	29	41	49	64	63	64	73	3 79 (2)
Plastofilling pf3	14	45	60	68	73	68	77	5 76 (3) + 76 (5)
Replica	17	42	49	53	55	64	69	7 71 (4)
Texton	27	42	43	50	58	64	-	2 80 (1)
Vitafilling	-	-	-	-	-	-	-	6 75 (2)

* Too soft to measure.

NOTE: Recovery computed as percent indentation depth recovered after major load 30 kg was released and minor load 3 kg remained.



Fig. 1. Apparatus used to mold specimens for stress-strain measurements. Part B fits into part "A" and is fastened by screws. The cavities are then packed, steel plate is applied, and pressure is obtained by screw-clamps.



0 1 2

INCHES



Fig. 2. Specimen and gages in position between the platens of the testing machine used to record stress-strain relationships.

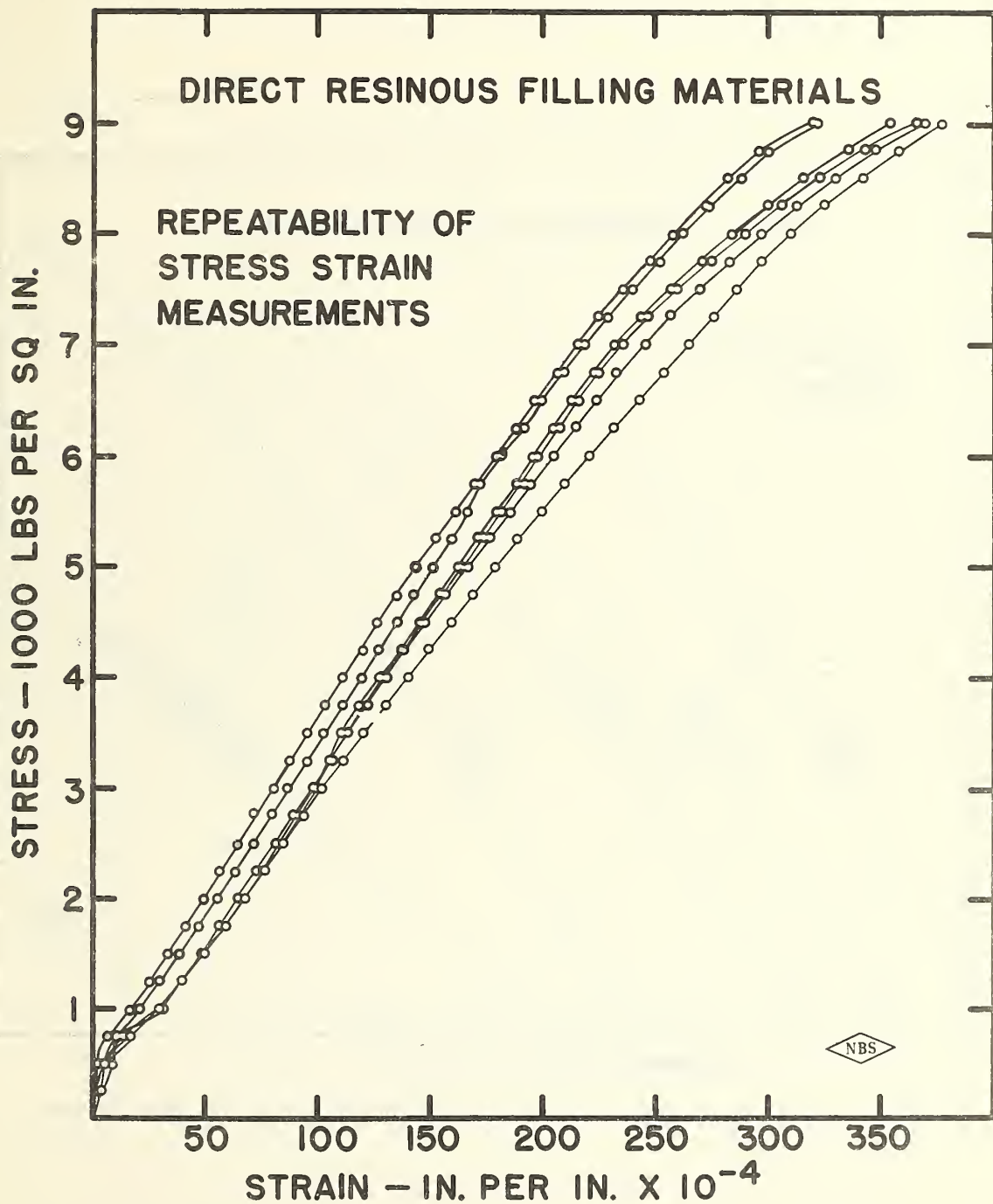


Fig. 3. Stress-Strain data on six samples of a particular brand of direct filling resin showing variations caused by unavoidable differences in the samples.

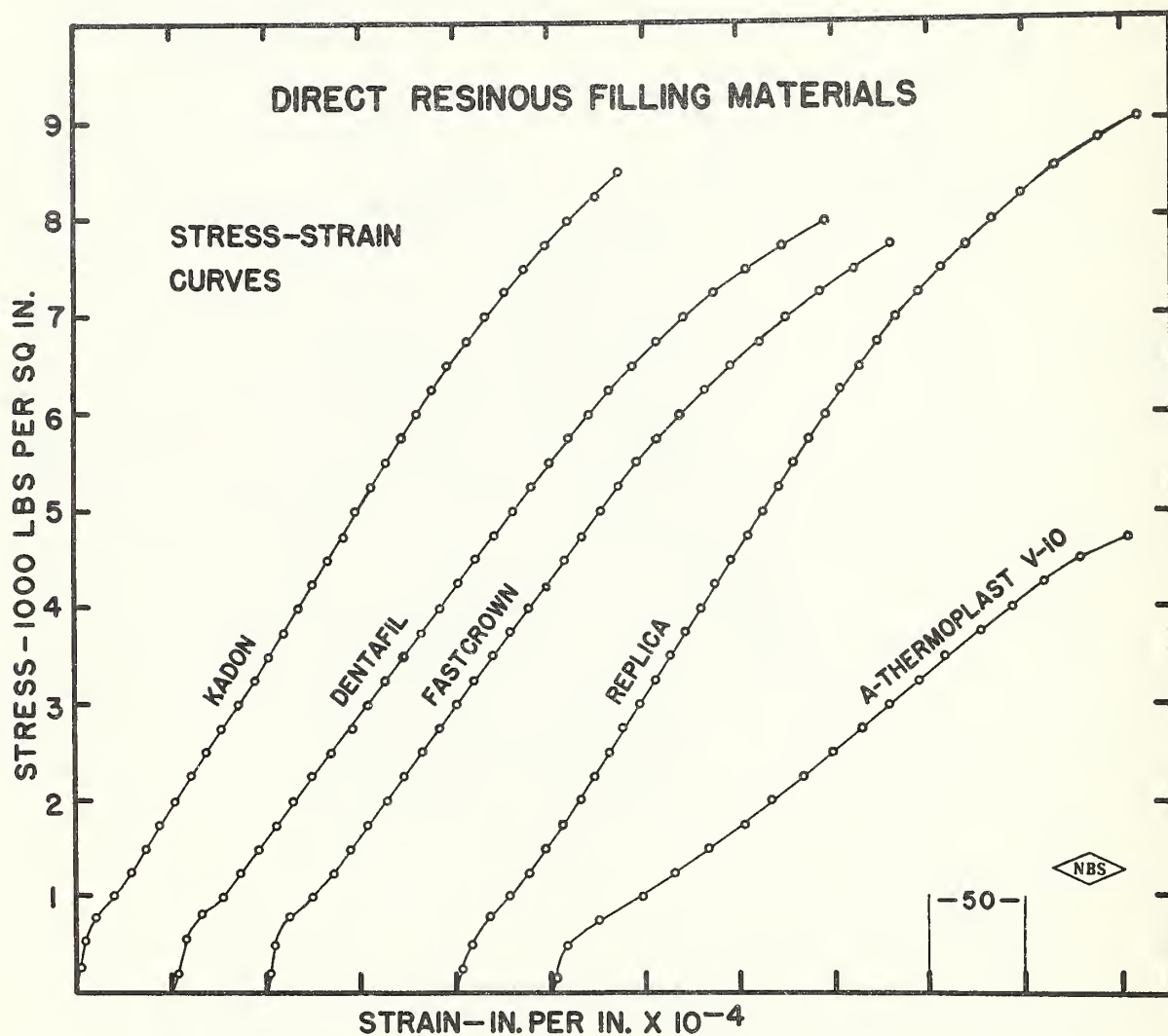


Fig. 4, Stress-Strain curves for five different brands of direct filling resins.

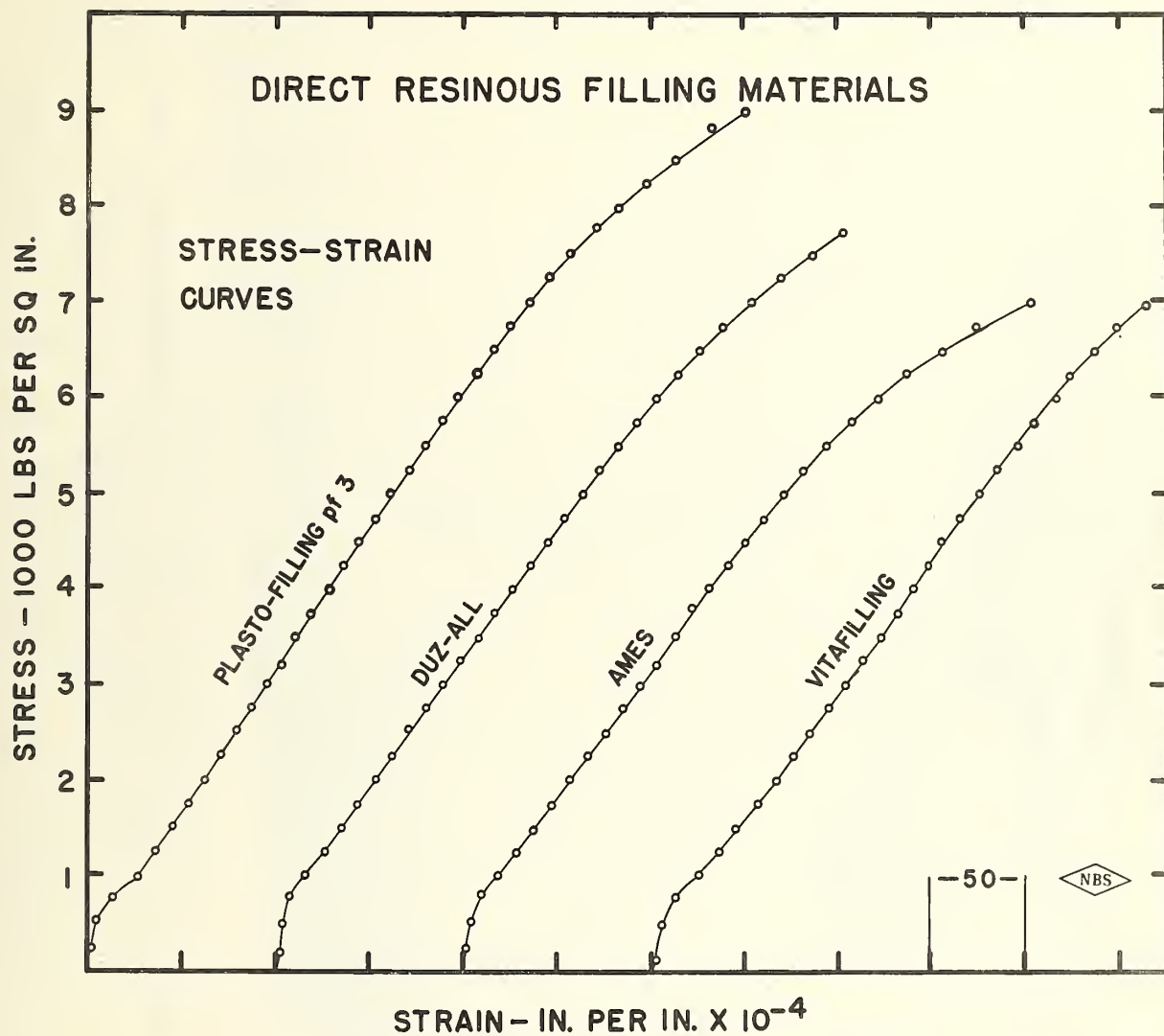


Fig. 5. Stress-Strain curves for four different brands of direct filling resins.

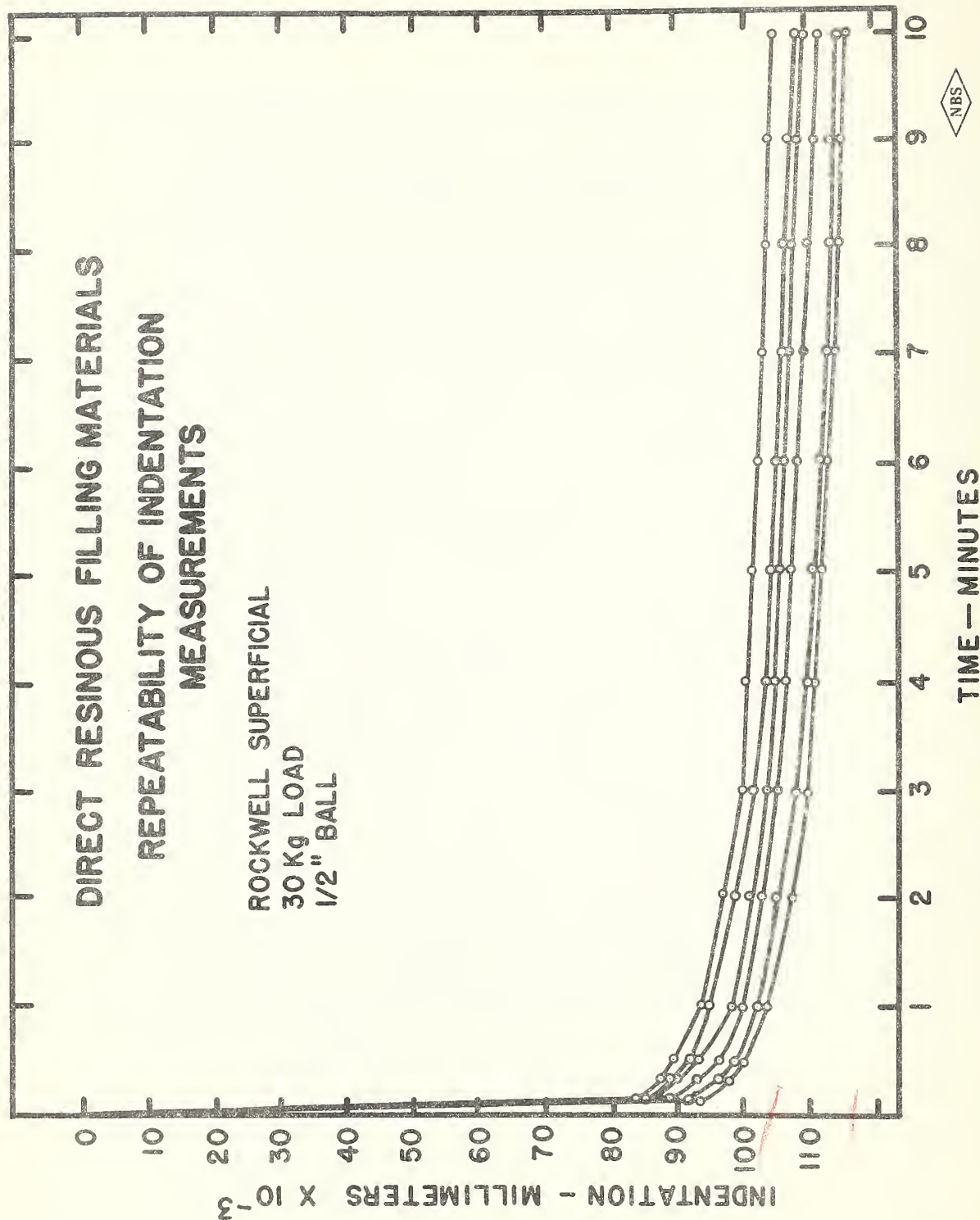


Fig. 6. The variations of six samples are shown when tested by the Rockwell Superficial Hardness Tester.

DIRECT RESINOUS FILLING MATERIALS INDENTATION AND RECOVERY

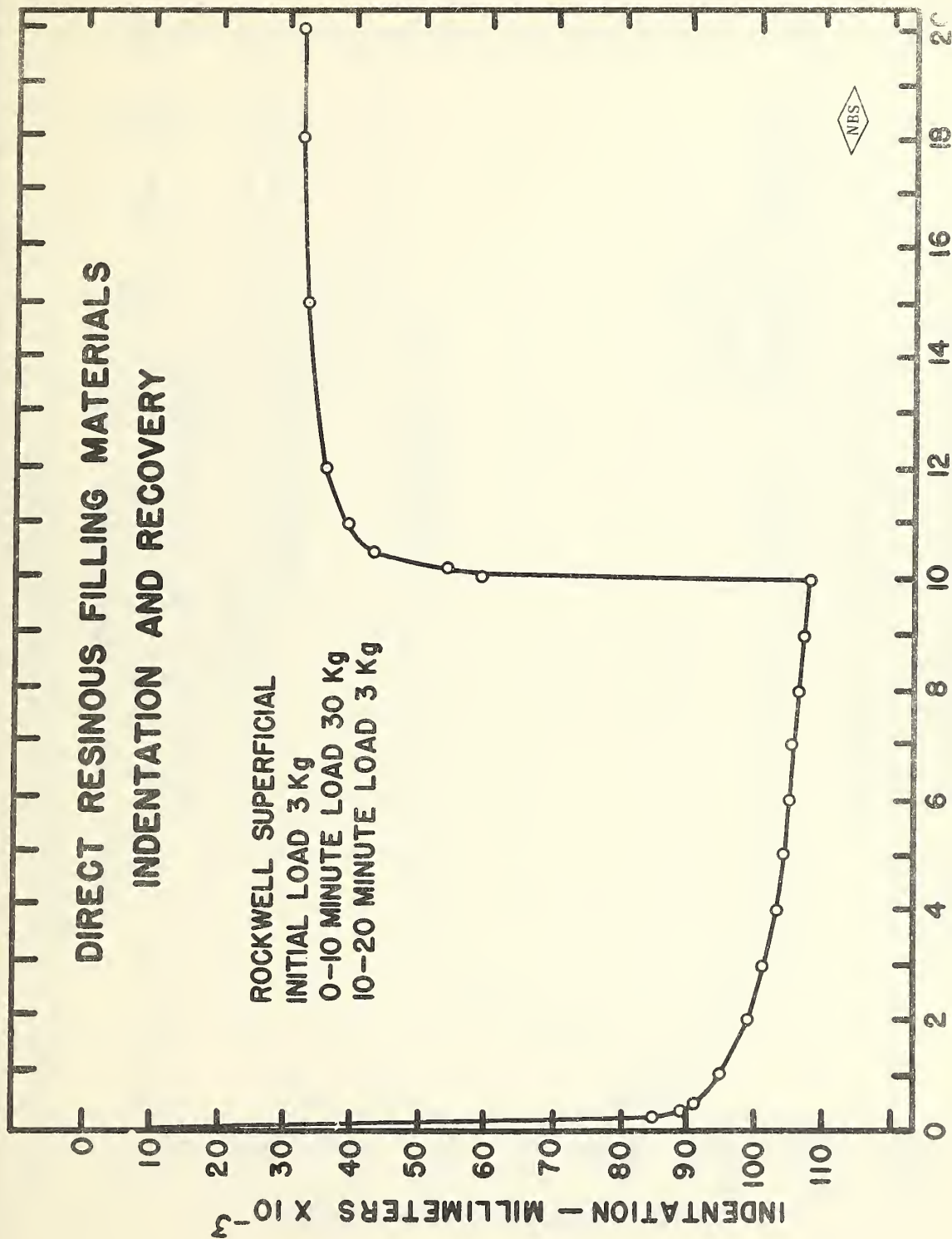
ROCKWELL SUPERFICIAL
INITIAL LOAD 3 Kg
0-10 MINUTE LOAD 30 Kg
10-20 MINUTE LOAD 3 Kg

INDENTATION - MILLIMETERS $\times 10^{-3}$

TIME - MINUTES



Fig. 7. Indentation is plotted against time for a typical indentation and recovery curve.



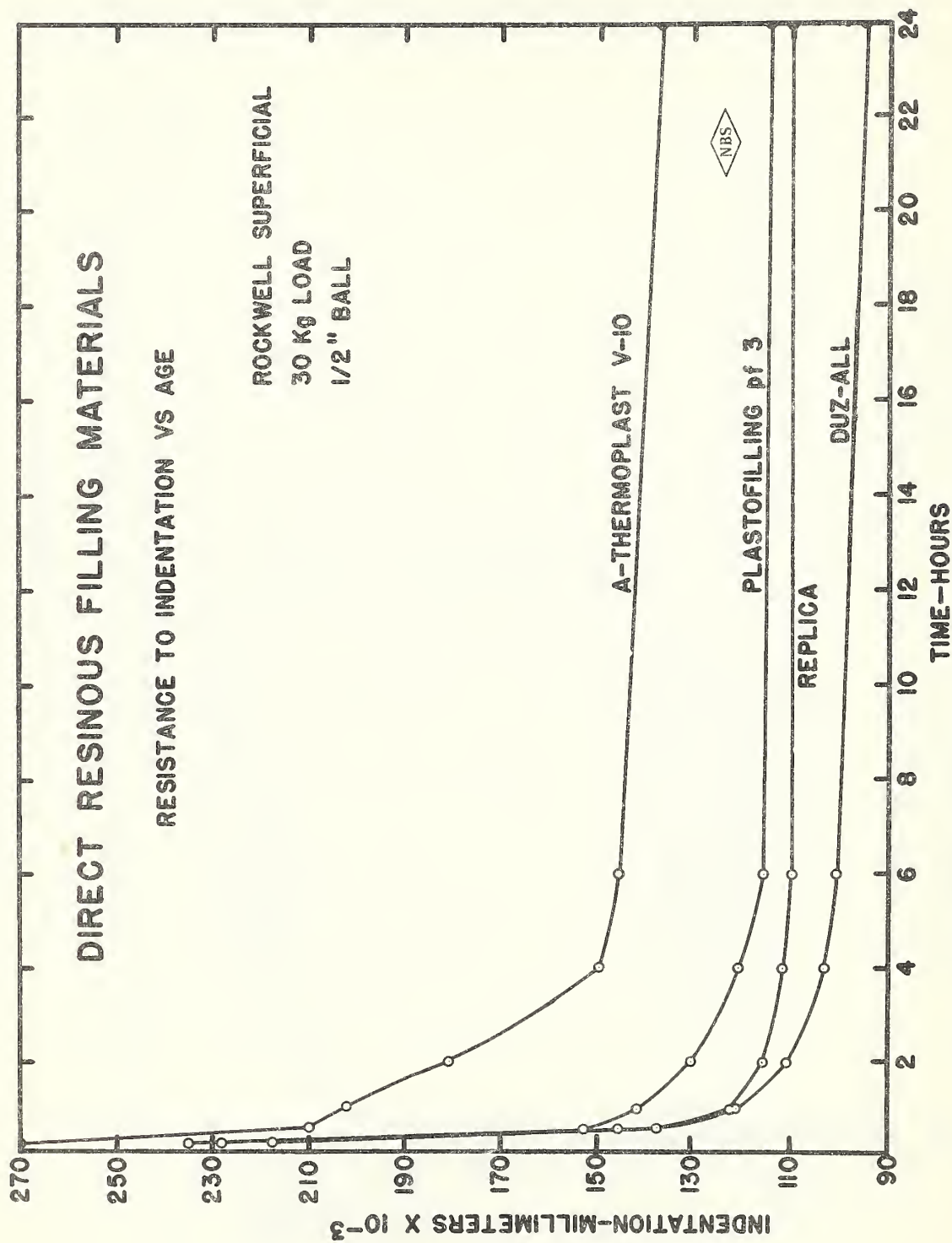


Fig. 8. Hardness increases with age as shown by the plotting of indentation against the age of four different specimens.

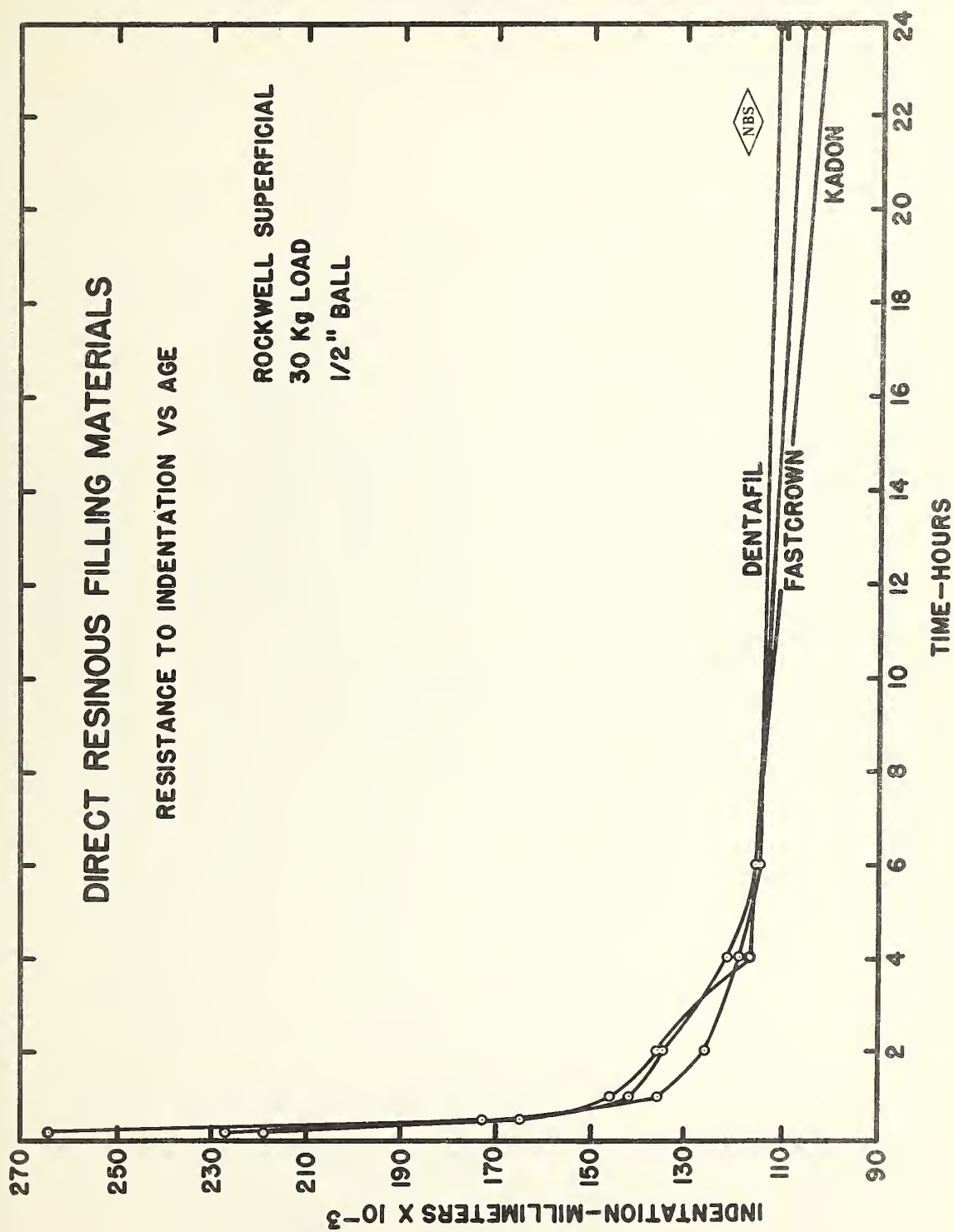


Fig. 9. Hardness increases with age as shown by plotting indentation against the age of three different specimens.

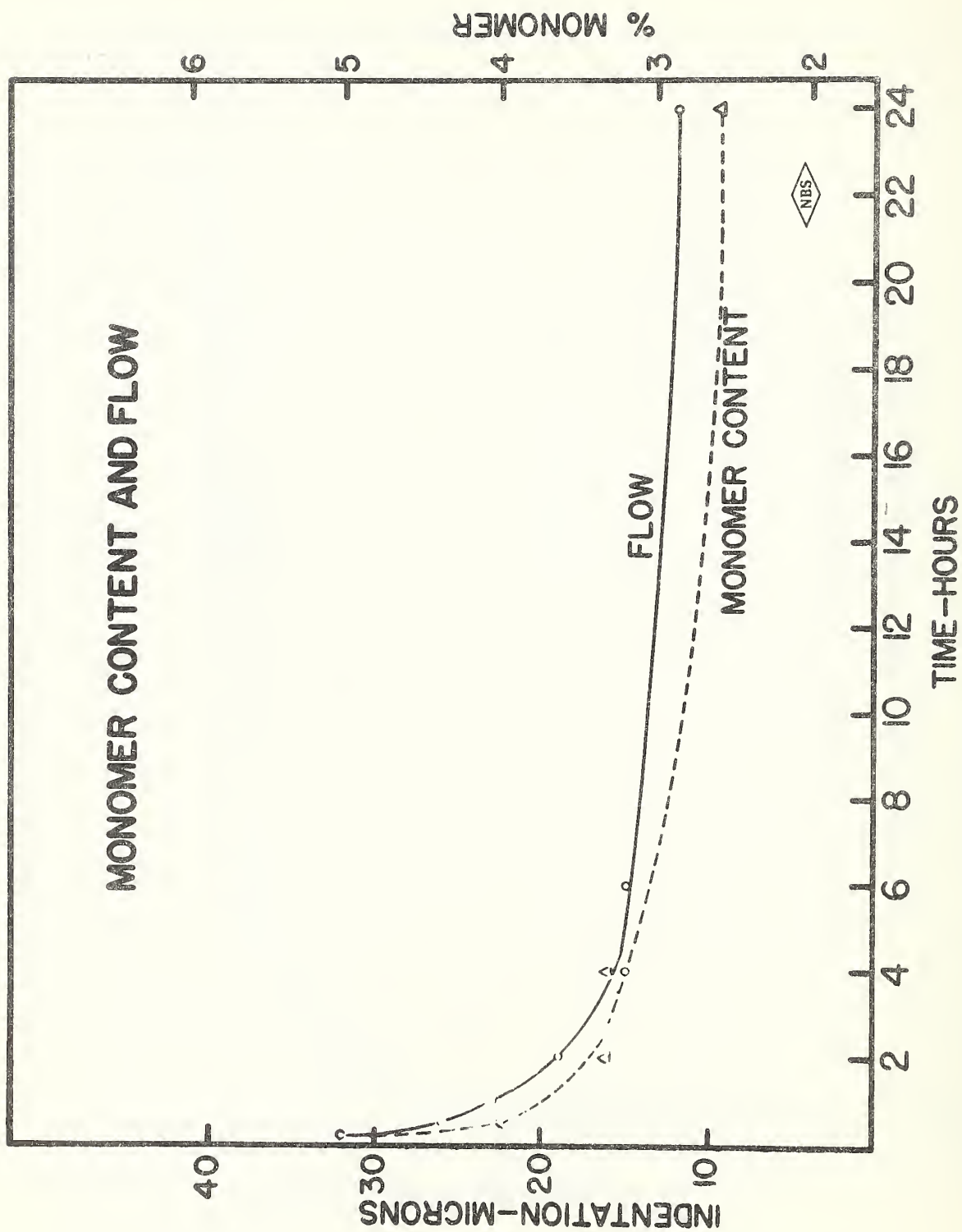


Fig. 10. Relationship between monomer content and flow.

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