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NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1954

Dental Research Laboratory

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

U. S. DEPARTMENT OF COMMERCE
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NATIONAL BUREAU OF STANDARDS
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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. Resistance and Reactance Measurements. Electrical Instruments. Magnetic Measurements. 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. 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-Ray. Betatron. Nucleonic Instrumentation. Radiological Equipment. Atomic Energy Commission Radiation Instruments Branch.

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 Control.

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.

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

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

●Office of Basic Instrumentation

●Office of Weights and Measures.

NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1954

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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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

The work of the Dental Research Laboratory of the National Bureau of Standards has been concerned with several materials used in dentistry, with tooth structures and with the development of equipment. These researches have covered a rather wide range of tasks. Summaries of results obtained on work now in progress as well as copies of reports issued on completed tasks during the half year ending June 30, 1954, are given below:

2. REPORTS ISSUED

NBS Report 3350	Effect of Temperature and Molecular Weight on the Water Sorption of Polymethyl Methacrylate.
NBS Report 3375	Self-Curing Resins for Repairing Dentures: Some Physical Properties and A Specification.
NBS Report 3379	Physical Properties of Plastic Teeth and A Proposed Specification.
NBS Report 3380	Measurement of Strain in POLY Methyl Methacrylate Caused by Water Sorption.

3. WORK IN PROGRESS

3.1 Structure of Human Tooth Enamel and Dentin

Investigation of tooth structures by means of their fluorescence ~~characteristics~~ was continued. An electronic depolarization fluorometer For ~~to be used in~~ obtaining data on the molecular weight of fluorescing materials was designed and calibrated. A special photomultiplier tube selected from a group of approximately 300 was found necessary for satisfactory operation at degrees of polarization below one percent because of the excessive dark current in standard tubes. An ammonium dihydrogen phosphate crystal was obtained for use as the electro-optic shutter of the decay fluorometer. A 10,000 volt power source and hydrogen thyratron tube will be used to actuate the shutter at speeds of the order of a billionth of a second. Work on assembling and perfecting the technique for applying these improvements to fluorescence of tooth and other substances is in progress.

3.2 Method for Measuring Contours of Dental Impressions, Models and Dentures

Work has been started on the development of a quick and accurate method of measuring and defining the irregular contours of a model or impression of the oral cavity. The need for such a system is very apparent as it can be used for quantitatively evaluating different technics and materials used to obtain accurate reproductions of the surfaces of the mouth.

The instrument is in the preliminary stage of development. Surfaces of laboratory dentures can be measured to a relative accuracy of the order of 0.001 inch in three dimensions using manual recording and sensitive dial indicators.

3.3 Low Temperature Alloys

The fundamental investigations of alloys containing gallium which may have properties comparable or superior to dental amalgams have been continued.

Determinations of the compressive strengths of various alloys of gallium-nickel, gallium-indium-nickel and gallium-copper-tin showed one of the latter to be the strongest (53,000 lb/in^2). There are indications that the strength of the Ga-Cu-Sn alloys increases with an increasing tin content up to 38% tin with the gallium content constant. Work is in progress on heat treatments to stabilize the structure of these alloys as indicated by the microstructure. A setting expansion of approximately 30 microns per centimeter was observed on a Ga-Cu-Sn alloy with 35% gallium content. An alloy containing 41% copper and 59% tin was found to have a much lower melting range than do the higher copper content alloys.

3.4 Resins

(a) Polymerization of Resins: Work has been continued on the effect of amine accelerators on the polymerization of methyl methacrylate. Effects of variations in catalyst concentration on polymerization kinetics were also investigated. Setting times of monomer-polymer mixtures were measured with a penetrometer. The relative efficiency of amine accelerators varies somewhat when monomer-polymer mixtures are employed as compared to the polymerization of monomer only.

A preliminary study was made of sulfinic acid derivatives as accelerators in methyl methacrylate polymerizations. A series of amine salts of p-toluene sulfinic acid, some of which have not been reported in the literature, have been synthesized. Most salts of primary and secondary amines gave colorless solids whereas the salts of tertiary amines are oily liquids. All amine salts of p-toluene sulfinic acids investigated so far were polymerization accelerators. Colorless polymers were obtained on using sulfinic acid or the sulfinic acid salts of aliphatic amines. Sulfinic acid salts of aromatic amines are more efficient accelerators but form colored polymers.

(b) Water Sorption of Acrylic Resins. Sorption rate at 37°C of methyl methacrylate polymer ~~specimens~~ was investigated. The rate was slow with the exception of specimens used previously in water sorption-desorption studies at 100°C. It is likely that swelling of the material in boiling water may not be completely reversible. On desorption, holes or discontinuities remain at the original water sites. On placing such a sample in water at 37°C sorption becomes abnormally large since water can fill these voids readily.

The glass temperature of specimens of purified methyl methacrylate polymers of varying molecular weight was determined. Above a molecular weight of around 500,000 the increase in glass temperature with molecular weight is insignificant. The maximum value of the glass temperature was 103°C.

The effect on molecular weight of extended exposure of polymer samples to boiling water was investigated. The intrinsic viscosity of specimens

stored at room temperature and in boiling water has been measured.

(c) Dental Resins: A survey of the physical and chemical properties of dental resin cements and resin filling materials was made. Using, to a large extent, test methods based on Federal and American Dental Association specificationsfor silicate and zinc phosphate cements and for denture base resin, data were obtained on consistency, opacity, color stability, setting time, compressive strength, film thickness, sorption, solubility, temperature rise on polymerization, refractive index of monomer, composition of inorganic filler, abrasiveness of filler, and arsenic content. Although the survey is not yet completed, it appears that some of the ten brands of resins tested will comply with most of the applicable requirements of the specifications referred to. In general, color stability was not satisfactory, however.

The method of determining monomer content of dental resins by infra-red absorption examination of the sublimate from frozen polymer-benzene solutions was further refined. It is believed that the method can be made accurate to ±0.1% monomer in polymer specimens.

Investigation of self-curing denture repair resins has been continued and a specification has been prepared.

3.5 Zinc Oxide-Eugenol Material

The research on the zinc oxide-eugenol reaction has been very productive of new information on this material widely used in dental treatment and restorative processes. The work accomplished during the period covered by this report supports the previous idea that the reaction produces a chelate structure. A better understanding of this will assist the producers to supply more uniform products for the dental applications. Molecular weight determinations of the reaction products are now being attempted.

Due to the solubility characteristics of zinc eugenolate, attempts to determine its molecular weight by boiling point elevation have thus far been unsuccessful. The solubility of zinc eugenolate in twenty-eight solvents has been determined. Zinc eugenolate was found to be soluble in, and to complex with, ammonium hydroxide and pyridine and to be very slightly soluble in hot chloroform. It is soluble in hot gamma butyro lactone and acetamide. Cryoscopic molecular weight determinations may be possible with these solvents.

Zinc guaiacolate was prepared and its infra-red spectrum compared with the spectra of guaiacol, 8-quinolinate, eugenol, zinc quinolinolate, and zinc eugenolate. This study gave further confirmation to previous suggestions of a chelate structure for the zinc oxide-eugenol reaction product.

Several known chelating agents, previously untried, were substituted for eugenol under conditions of clinical use. Salicylaldehyde was found to set in a hard mass when mixed with Hyperfine zinc oxide under these conditions. A quantitative analysis of the reaction mixture is being made.

3.6 Chrome-Cobalt Alloys

The mechanical properties of specimens of chromium-cobalt alloys cast by various Federal dental laboratories and by manufacturers were determined. Results obtained for the five different brands of alloys tested varied as follows: modulus of elasticity, 25.7-30.8x10^6psi; yield strength, 49,000-65,700 psi; ultimate tensile strength, 84,700-117,300 psi; elongation, 1.2-6.0%; Rockwell 30N hardness, 38.1-60.4.

While there was a large variation from alloy to alloy in the values determined, there was also a considerable difference in the measured properties of a single alloy as cast by various sources.

A study of the grain number and structure was also made. Some of the alloys proved difficult to etch and revealed only the characteristic dentritic structure. The data obtained are being used in the preparation of a specification.

3.7 Rotating Dental Cutting Instruments

The study of methods for determining the cutting efficiency of dental burs and diamond instruments has been active.

High-speed motion picture studies of steel and carbide burs and diamond cutting instruments have been continued. The information gained from this method of study has been further substantiated by standard laboratory procedures based on weight loss of human enamel and dentin and other test materials. The data obtained indicate that none of the materials such as bakelite cast resin, glass filled phenolic resin and various types of glass used as substitutes for dentin and enamel in cutting tests give results comparable to those obtained when actual teeth are cut. There is some indication that the harder test materials used give an indication of the wear resistance of the cutting instruments while the softer materials give an indication of the effectiveness of the design of the instruments. Results obtained on burs are complicated by the very great variations in the performance of individual burs of the same manufacturer.

It appears that arbitrary test materials will have to be used for evaluating and specifying test methods in this field. The accumulation of data under controlled conditions will be necessary before definite standards can be recommended.

3.8 Panographic X-ray Investigation

Excellent progress has been made on this project specifically supported by the U. S. Air Force for the development of methods and equipment for making satisfactory x-rays of the entire dental arch on a single film.

An experimental device was constructed and used to produce x-ray exposures of human skulls and their dental structures. An x-ray source and appropriate mechanical apparatus and controls were used to determine proper relationships of subject and film and to accomplish the various motions required to project a satisfactory image of the dental structures onto a strip of x-ray film. Radiographs of the

entire dental arch were produced in approximately 30 seconds of exposure.

Conferences were held with Electronics Instrumentation Section, regarding progress on the project. A survey of dentists in the various Federal Services was conducted to obtain opinions as to the practical usefulness of radiographs obtained and general enthusiasm was expressed with reference to the quality and scope of these radiographs.

Working drawings are being made and preliminary machine work is being accomplished for construction of a pilot model panoramic x-ray machine.

Upon completion of the pilot model x-ray machine, exposures on human subjects will be made. Details of design on film carrying mechanism, screening of secondary radiation by the use of appropriate grids, etc. will be studies. Pilot models will be modified as necessary to improve the quality of the radiographs and improve the efficiency of operation. Technics for the employment of the device in mass dental surveys will be worked out. Plans for production and use of the machine by the Armed Services will be made.

3.9 Periapical X-ray Film Survey

Exposed X-ray films and questionnaires have been returned by the 70 dentists cooperating in the X-ray film survey. Data obtained from the questionnaires and from densitometer measurements on the films are being used by the X-ray Section of the Bureau in revising Handbook 41- X-ray Protection. This data will also be available for the preparation of a specification for dental X-ray film for purchase by government agencies who are at present experiencing considerable trouble with the X-ray film purchased for dental use.

3.10 Motion Pictures

The motion picture, "Hazards of Dental Radiography," which was given a premier showing at the I.A.D.R. meeting in March was awarded second place in the medical category at the International Exhibition of Cinematographic Art in Venice, Italy. Duplicates are ready for distribution. A script on the 1954 picture, The Specification and Certification Program on Dental Materials," has been prepared. The five pictures that have been produced have had a wide acceptance, as shown by the following table. This data is as of February 23, 1954.

Date Produced	Title	No. Loans	No. Copies Sold
1948	Silicate Cement	486	102
1949	Dental Amalgam: Failure Caused by Moisture Contamination	474	92
1950	Denture Resin	219	27
1951	The Casting of Dental Gold Alloys: Thermal Expansion Technic	168	22
1952	A Method of Mixing Silicate Cement	35	4
	Total	1362	247

These data apply only to loans made by the National Bureau of Standards. Loans made by the A.D.A. film library and by purchasers of the films provide additional audiences.

3.11 Evaluation of Material

Materials evaluated for the cooperating Federal Agencies and the American Dental Association included many items for which specifications are available and some items which required the development of special test methods. Included were alginate impression materials, amalgam alloys, amalgamators, abrasive points, denture base resins, denture base repair materials, hydrocolloidal impression materials, investments, mercury and silicate cement.

For the Director
by
W. T. Sweeney
W. T. Sweeney, Chief
Dental Research Section

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report
on
EFFECT OF TEMPERATURE AND MOLECULAR WEIGHT ON THE WATER SORPTION OF POLYMETHYL METHACRYLATE

by

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

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EFFECT OF TEMPERATURE AND MOLECULAR WEIGHT ON THE WATER SORPTION OF POLYMETHYL METHACRYLATE

Abstract

The effect of temperature and molecular weight on the water sorption of methyl methacrylate polymers has been investigated. Water sorption is independent of temperature from 0° to 60°C. Above the glass temperature, sorption increases markedly and the polymer tends to sorb water for an indefinite period. Molecular weight affects greatly the water sorption at elevated temperatures. It is believed that the increase in water sorption above the glass temperature is caused by the less rigid linkage in the polymer chains and an expansion of the structure which allows water to permeate more readily into the material.

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1. INTRODUCTION

Polymers in contact with water or water vapor will sorb greater or smaller amounts of water depending on the number of polar groups in the molecule [1, 2,] [3]and others . The time necessary to reach sorption equilibrium depends on the thickness, water permeability and diffusion rate of the material. For many polymeric materials, sorption equilibrium is reached only after prolonged exposure. At the surface, however, equilibrium conditions are reached within a relatively short time.

Recently, a number of investigators have dealt with the kinetics of vapor sorption by polymer films. Kokes, Long and Hoard [4] and Long, Bagley and Wilkins [5] reported a pronounced change in the character of the diffusion which takes place in the region of the glass temperature of the polymer-penetrant mixture. With both the polar acetone-polyvinyl acetate and the non-polar benzene-polystyrene system, diffusion was found to obey Ficks law only when the system was above the glass temperature. A similar behavior was observed for the diffusion of gases through polyvinyl acetate [6] .

Richards [7] showed that high molecular weight polythenes are less soluble and absorb less organic liquid than low molecular weight polythenes. Samples of the same molecular weight which contain a higher portion of short chain material are more soluble and swell more in organic liquids.

The effect of temperature and molecular weight on the water sorption of polymethyl methacrylate was studied in the present investigation.

2. EXPERIMENTAL PROCEDURE

(a) Water Sorption of Molded Specimens.

To make water sorption specimens, polymethyl methacrylate powder was placed in a mold cavity 5 cm in diameter and 0.05 cm in thickness. The material was molded into discs in a Carver laboratory press at 10,000 lb/in^2 and 150 ± 5°C for 1 hour. The specimens were dried at 70°C to constant weight, placed in holders and kept in water at the indicated temperature. At various time intervals the discs were transferred to another water bath kept at room temperature. After 10 minutes, the specimens were dried with a clean towel for 20 seconds, dried in air by waving for 20 seconds and weighed within 20 seconds. The discs were then placed back in the original water bath until constant weight was obtained. After the discs had reached sorption equilibrium, they were dried to constant weight at 70°C or over sulfuric acid at room temperature. Duplicate measurements were made for all determinations.

(b) Water Sorption of Polymethyl Methacrylate Plates.

Specimens of purified polymethyl methacrylate of approximately 0.63 cm thickness were obtained from the Rohm and Haas Co.* Table 1 shows the values for the viscosity molecular weight as reported by the manufacturer, approximate number average molecular weight determined by the method of Caul and Schoonover [8], Knoop Hardness and glass temperature.

The samples were dried to constant weight and placed in boiling water. After various time intervals, samples were dried and weighed by the procedure described above. Desorption measurements were made by placing the specimens over anhydrous calcium sulfate (Drierite) in a desiccator first at 21 °C and finally at 70°C. All measurements were made in duplicate. Another series of sorption measurements of specimens of the same thickness was made at 37°C.

(c) Effect of Molding on Water Sorption.

Specimens of heat-cured polymethyl methacrylate, 6.0 x 6.0 x 0.7 cm in dimension, were prepared. To avoid any temperature rise, several of these samples were cut under water into strips 0.05 cm thick, 6.0 cm long and 0.7 cm wide. Another series of specimens was molded to the same thickness in a Carver laboratory press at 150°C. Water sorption in boiling water was determined as previously described.

(d) Water Vapor Sorption Measurements.

Attempts to measure water vapor sorption with the McBain balance did not prove satisfactory. Since the water sorption of polymethyl methacrylate at 30°C is comparatively small (maximum water sorption less than 2%), a large sample was required which greatly reduced the sensitivity of this procedure. The weighing bottle and salt solution method reported in detail by Mellon, Korn and Hoover [9] was finally adopted. Approximately 4 g samples were placed in weighing bottles (diameter, 7 cm; height, 3 cm) and dried to constant weight at 70°C and a pressure of less than 5 mm Hg. Weighing bottles and samples were kept over various saturated salt solutions in evacuated dessiccators at 30.0 ± 0.3°C in an air bath. Weighing bottles were weighed after a few days using the precau-

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* The authors wish to thank W. F. Bartoe of the Rohm and Haas Co. for supplying the samples.

tions given by Mellon et al [9] . Weighings at each humidity were repeated until the change in weight was less than ± 2 mg. The samples were kept a minimum of 10 days at each humidity. Samples were started at the lowest and highest humidities and on reaching equilibrium were moved to the next higher or lower humidity respectively. This was continued until the maximum (or minimum) humidity had been reached. After completion of the last sorption measurement, the samples were dried again by the procedure described above to check the original weight. An empty weighing bottle was used as tare for all weighings. This bottle accompanied the bottles containing the samples through all manipulations. Water vapor sorption measurements by this procedure are considered precise within 0.05%.

(e) Hydrolysis of Polymethyl Methacrylate.

A 100 g sample of polymethyl methacrylate (duPont HG1 powder) and 300 ml water were placed into a 500 ml round bottom flask. The flask was connected through a ground glass joint to a 35 cm drip tip Friedrichs condenser. To avoid loss of volatile constituents, the condenser was connected to a mercury seal. The water was heated to boiling. Continuous agitation was accomplished by means of a magnetic stirrer. At various time intervals, 1 ml portions of the supernatant liquid were removed for analysis. Methanol content was determined by mass spectrometry. The minimum concentration which can be detected by this procedure is less than 0.02 mole percent. The pH of the solution was determined with a Beckman pH meter.

(f) Determination of the Glass Temperatures (T_g).

Glass temperatures (T_g) were determined refractometrically [10,11] using a Zeiss-Abbe refractometer. Specimens of the molded material were placed directly between the prisms. Strips were cut from the polymethyl methacrylate plates under water and then placed in the refractometer. Films from the polymer powders were cast from acetone solutions on the lower prism of the refractometer. The films were carefully dried at room temperature for at least 24 hours, and at 110°C for 1/2 hour.

Refractive index measurements were made by slowly heating the refractometer to 110°C, a temperature well above T_g, and lowering the temperature to obtain subsequent readings. Emphasis was placed on relative and not absolute accuracy of the n_D readings. T_g values were determined with an accuracy of better than ± 2°C by locating the intersection of the linear portions of the temperature versus n_D plot.

(g) Molecular Weight Determinations.

Viscosity average molecular weights were determined by measuring the intrinsic viscosity $[\eta]$ of chloroform solutions of the polymers at 25°C in a calibrated Ostwald-Fenske viscometer. Molecular weight was calculated using the relationship

$$[\eta] = 2.52 \times 10^{-3} \; M_V^{0.80} \quad [12].$$

Viscosity average molecular weights reported for the polymer plates are those given by the manufacturer.

Approximate number average molecular weights were determined by the method of Caul and Schoonover [8]. All determinations were made in duplicate.

on specimens .5 mm plates

3. RESULTS AND DISCUSSION

Effect of temperature on the water sorption of molded polymethyl methacrylate discs (duPont HG 4 fine) is shown in Figure 1. In the 2° to 50°C range, sorption is constant and independent of the temperature. The samples reached constant weight within 30 days. It has been reported [13] that no further change in weight takes place even after storage for an additional 5 years. At 70°C, in the neighborhood of T_g, water sorption starts to increase. Two samples stored at 100°C (Table 2) continued to gain weight after immersion in water for about 200 days. During this time period, the increase in weight amounted to approximately 10% (Figure 1). This is nearly 7 times as large as the equilibrium water sorption value at 37°C (1.48%). The difference in water sorbed by the two specimens stored at 100°C may be caused by variations in molding conditions.

Polymer discs kept in the boiling water became cloudy. This indicates that a marked internal inhomogeneity is present giving rise to refractive index gradients, and that presumably water is localized as submicroscopic droplets in the neighborhood of polar groups [14-15].

On redrying to constant weight, samples immersed at 2° and 37°C showed an insignificant weight loss (less than 0.1% of the original weight); those stored at 50° and 70°C decreased in weight by less than 0.25%. Samples stored at 100°C gave a 2.5% loss in weight. This is probably caused by the increased solubility of low molecular weight products and plasticizer at elevated temperatures. As can be seen from Figure 2, molded samples have a much increased water sorption compared to the unmolded specimens. Apparently degradation takes place during the molding process. The larger concentration of monomer and low molecular weight material in the molded specimen will result in an increased sorption. Further evidence of the formation of water soluble compounds during molding was the increased weight loss on drying.

also affected by strain on solubility.

The formation of polar hydrolysis products such as methacrylic acid, even in small concentrations, will greatly increase sorption. Hydrolysis of polymer in boiling water was therefore investigated. Mass spectrometer analysis showed the absence of methanol in samples removed from water-polymer powder mixtures after stirring for 3 days at room temperature. When the polymer was kept for 4 days at 100°C, 0.4% yield of methanol (based on the theoretical yield of methanol formed from polymer) was obtained. The water solution was acidic (pH=3) and gave a positive Bayer test for unsaturation. Prolonged (30 days) exposure to boiling water did not give an appreciable increase in the concentration of the hydrolysis products formed. This concentration of low molecular weight polar compounds formed is not sufficient to be considered the primary cause for the increased water sorption. Mass spectrometer analysis of the final fraction obtained on distillation of the aqueous solution of the hydrolysis products indicated the presence of methacrylic and possibly pyruvic acid. The presence of the latter compound would suggest the formation of an unstable hydroperoxide as an intermediate in the degradation mechanism.

[illegible]

Sorption at 100°C of varying molecular weight samples 0.63 cm in thickness is shown in Figure 3 and Table 3. The properties of these samples are shown in Table 1. Lowering of the molecular weight resulted in increased water sorption. The sorption curves are made up of two distinct parts. After a rapid rise, the curves become nearly linear. Sorption values are most sensitive to variations in molecular weight in the lowest molecular weight range. Differences in weight gain of specimens of molecular weight 393,000 and 1,615,000 are small. Sorption is not significantly altered by changes in molecular weight above a limiting value of about 500,000. The logarithmic plot of both water sorption and time gives a nearly linear curve for the sample of molecular weight 1,615,000 only (Figure 4).

Placed over anhydrous calcium sulfate, the specimens (thickness 0.63 cm) lose the sorbed water (Figure 3). Loss in weight after complete desorption is caused by soluble constituents. It is small and, after drying for 206 days, amounts to a minimum of 0.02% and a maximum of 0.21%, respectively, for the 1,615,000 and 45,000 molecular weight materials. [illegible] shown in FIG 3.

Thin samples (thickness 0.1 cm) of the same materials, when placed in water at 37°C, reached constant weight in less than 2 months. The sorption amounted to approximately 2.5%. The water sorption rate of samples of 0.63 cm thickness was slow. However, samples (thickness 0.63 cm) used previously in the water-sorption-desorption studies at 100°C, when stored at 37°C, had an increased sorption rate. After 520 days' exposure, the lowest molecular weight sample showed a gain in weight of 12.4% as compared to 4.6% for material of the highest degree of polymerization (Figure 5). Plotting the logarithms of time and water sorption gives a straight line only for the sample of lowest molecular weight. Failure to reach equilibrium conditions, dependence on molecular weight, and the increased water sorption rate of these thick specimens may be caused by voids. Swelling of the sample in boiling water may not be completely reversible. On desorption, the water diffuses to the surface and evaporates. Holes or discontinuities remain at the original water sites. On placing such a sample in water at 37°C, sorption becomes abnormally large since water can fill these voids readily. Larger sorption for the lowest molecular weight materials can be expected since more voids remained after desorption.

Water sorption measurements, in the 4° to 70°C range, of discs (thickness 0.05 cm) molded from fractionated polymer are reported in Table 4. The substantial lowering of the viscosity molecular weight indicates that degradation takes place during molding. Constant weight or water sorption equilibrium was obtained in all determinations. Sorption is independent of molecular weight in the 4° to 37°C range. Between 60° and 70°C, in the vicinity of the glass temperature, sorption values rise with a smaller increase at higher molecular weights. The small difference between the water sorption values of the specimens of approximately 180,000 molecular weight and those of approximately 390,000 molecular weight is not consistant with the previous results. The lowest molecular weight specimens had an abnormally high glass temperature. In the absence of detailed data on polymerization methods and history of these samples, it is difficult to clarify this discrepancy.

On raising the water temperature above 70°C, the high molecular weight specimens decomposed into granules similar to those from which they were molded (Figure 6). The fractionated high molecular weight polymer does not contain enough low molecular weight constituents which can act as plasticizers during the molding process. Although the discs appear homogeneous on visual inspection, the granules are imperfectly cemented together. On heating the discs in water above the glass temperature, the adhesive forces at the grain boundaries weaken to such an extent that the discs fall apart. This phenomenon may also be explained by means of viscoelastic behavior.

Results of the studies of the sorption of water vapor by methyl methacrylate polymer at various relative humidities at 30°C are given in Table 5. For most samples, water uptake is nearly linear from 10 to 50% relative humidity. In this range, water probably dissolves in the resin; the quantity dissolved is proportional to the relative humidity in accordance with Henry's law. Above 80% relative humidity, there is generally a more rapid increase in the amount of water sorbed. This upswing may reflect condensation of water on active sites. Within experimental error, vapor sorption appears to be independent of molecular weight.

The equilibrium desorption values are slightly higher than the corresponding sorption values in the 10 to 50% relative humidity range. These variations are not considered significant. From the limited data available, it is not possible to state if vapor exposure at 100% relative humidity and liquid immersion sorption procedures give identical results. Investigations by Kovacs [16] show that the water immersion procedure gives about 3% higher weight increase values.

The rapid rise of the water sorption in the neighborhood of T_g of the samples immersed in water may be explained by an increase in the mobility of the polymer segments. Above T_g, the chains have a greater degree of freedom. The chain network is expanded as compared to its normal arrangement below the glass temperature. This allows the water molecules to permeate more easily between the polymer chains. A larger quantity of water is sorbed. Swelling accompanying the sorption will result in an increase in the number of sorptive sites for the attachment of water molecules. Equilibrium saturation is not fixed but increases due to the continuous swelling process. Water sorption equilibrium above T_g, if at all obtainable, will be reached only after many years exposure.

The larger water sorption and diffusion rate of low molecular weight specimens, especially above T_g, may be caused by increased solubility of water in the polymer. The larger internal surface of the low molecular weight polymer will result in an increase in the number of sorptive points exposed within the structure. The probability of attachment of water molecules between ends of polymer chains is increased. Some form of structural discontinuity is also more likely to be encountered. Thus, if capillary condensation is involved in the sorption process, a higher water sorption value will be obtained. The amount of liquid sorbed is also affected by molecular weight distribution. The presence of monomer or very short chain polymer is likely to affect greatly the sorption behavior.

4. SUMMARY

The weight of water sorbed by a series of methyl methacrylate polymers has been studied as a function of temperature and molecular weight. Below the glass temperature T_g, sorption is nearly independent of temperature. Thin specimens reach an equilibrium value within a short time. In the vicinity of T_g, the water sorption value increases rapidly. The polymers show large weight increases on exposure to water above the glass temperature. The polymer tends to sorb water for an indefinite period. Sorption equilibrium above T_g was not obtained in this study. Such values, if experimentally obtainable, will only be reached after extraordinarily long periods if at all.

Sorption is markedly affected by molecular weight. Samples of larger molecular weight show smaller weight increases. Sorption of the polymers is reversible. Degradation takes place during molding at 150°C. Slight hydrolysis occurs on exposure to boiling water.

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Table 1

Properties of Polymethyl Methacrylate ~~Samples~~

Sample No.	Average Viscosity Molecular Weight	No. Avg. Molecular Weight	Knoop Hardness	Glass Temp. T_g, °C
1	45,000	2000	17.7	79
2	64,000	2900	18.6	86
3	123,000	3500	20.4	91
4A	393,000	4500	21.3	100
5A	1,615,000	5500	21.8	103

Table 2

Water Sorption of Polymethyl Methacrylate

Material : HG4 Fine = Sample
Temperature : 100°C
Thickness of discs: 0.04 cm

Specimen ~~Sample~~ 1		Specimen ~~Sample~~ 2	
Days in H_2O	Wt. Increase %	Days in H_2O	Wt. Increase %
3	3.0	4	3.0
27	5.6	32	6.9
73	6.4	61	8.5
102	7.2	99	9.2
213	9.0	172	11.7

Table 3

Effect of Molecular Weight on the Water Sorption of Polymethyl Methacrylate

Thickness of samples = 0.63 cm
Temperature = 100°C

	Weight Increase[1]				
Time Days	M.W.[2] 45,000 %	M.W. 64,000 %	M.W. 123,000 %	M.W. 393,000 %	M.W. 1,615,000 %
1	2.25	2.17	2.16	2.11	2.00
2	2.73	2.65	2.61	2.55	2.48
4	3.34	3.10	2.99	2.88	2.81
10	4.56	3.92	3.55	3.25	3.10
15	5.48	4.48	3.94	3.43	3.27
25	6.86	5.43	4.53	3.68	3.47
63	11.90	8.85	6.38	4.61	4.17
108	17.69	12.42	8.48	5.40	4.56

[1] Average values for 2 specimens. Variations from average were less than 4%.

[2] M.W. = Molecular weight.

Table 4

Effect of Molecular Weight and Temperature on the Water Sorption of Polymethyl Methacrylate[a]

Thickness of molded discs = 0.05 cm.

Molecular Weight		Glass Temperature, °C		Water Sorption in Percent at Temperature, °C				
Original Samples	Molded Samples	Original Sample	Molded Sample	4	30	37	60	70
195,000	180,000	77	93	2.07	1.94	2.00	2.18	2.80
195,000	187,000	77	75	2.05	1.98	2.01	2.22	2.61
600,000	380,000	62	55	2.04	1.94	1.99	2.12	2.77
600,000	398,000	62	59	2.07	1.94	2.00	2.18	2.80
1,560,000	824,000	68	68	2.05	1.97	1.97	2.11	2.35
1,560,000	---	—	—	2.06	1.95	1.92	2.05	2.26

[a] Specimens were obtained from H. D. Justi and Son, Inc.

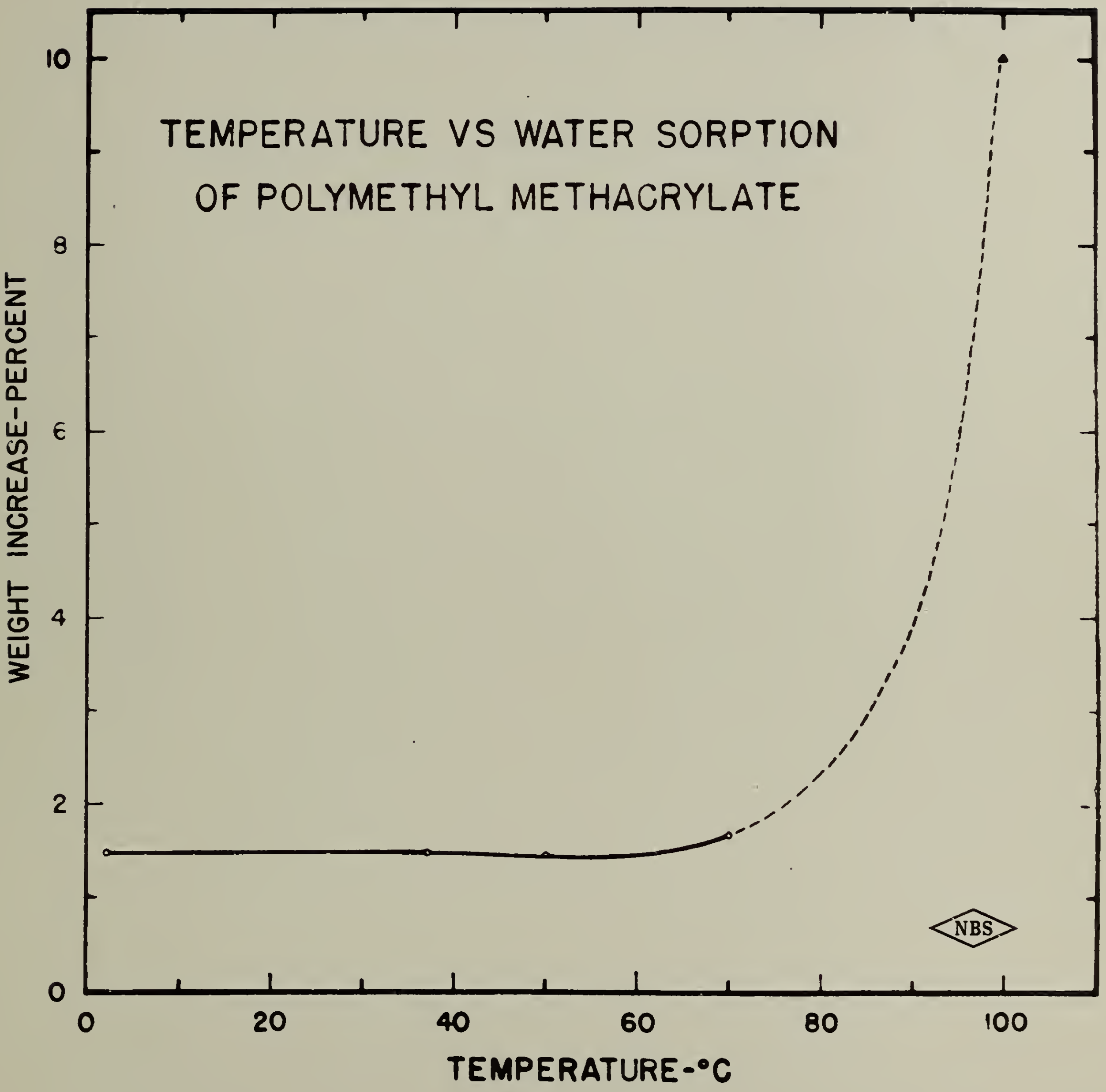
Table 5

Sorption of Water Vapor by Polymethyl Methacrylate

Temperature = 30.0 ± 0.3°C

Saturated Salt Solution	Relative Humidity %	Weight Increase, %					
		HG4 Fine		Fractionated Polymer			
				M.W. = 195,000		M.W. = 1,560,000	
		Sorption	Desorption	Sorption	Desorption	Sorption	Desorption
LiCl	11.8	0.04	0.11	0.09	0.12	0.06	0.12
$MgCl_2$	31.4	0.27	0.35	0.35	0.42	0.32	0.44
$Mg(NO_3)_2$	50.9	0.57	0.64	0.53	0.74	0.54	0.70
NaCl	75.1	1.04	0.97	1.13	1.04	1.16	1.04
KCl	83.6	1.18	1.13	1.32	1.31	1.35	1.29
KNO_3	93.3	1.33	1.49	1.83	1.56	1.67	1.62

Figure 1. Temperature versus water sorption of polymethyl methacrylate.



TEMPERATURE VS WATER SORPTION OF POLYMETHYL METHACRYLATE

Figure 2. Effect of molding on water sorption of polymethyl methacrylate.

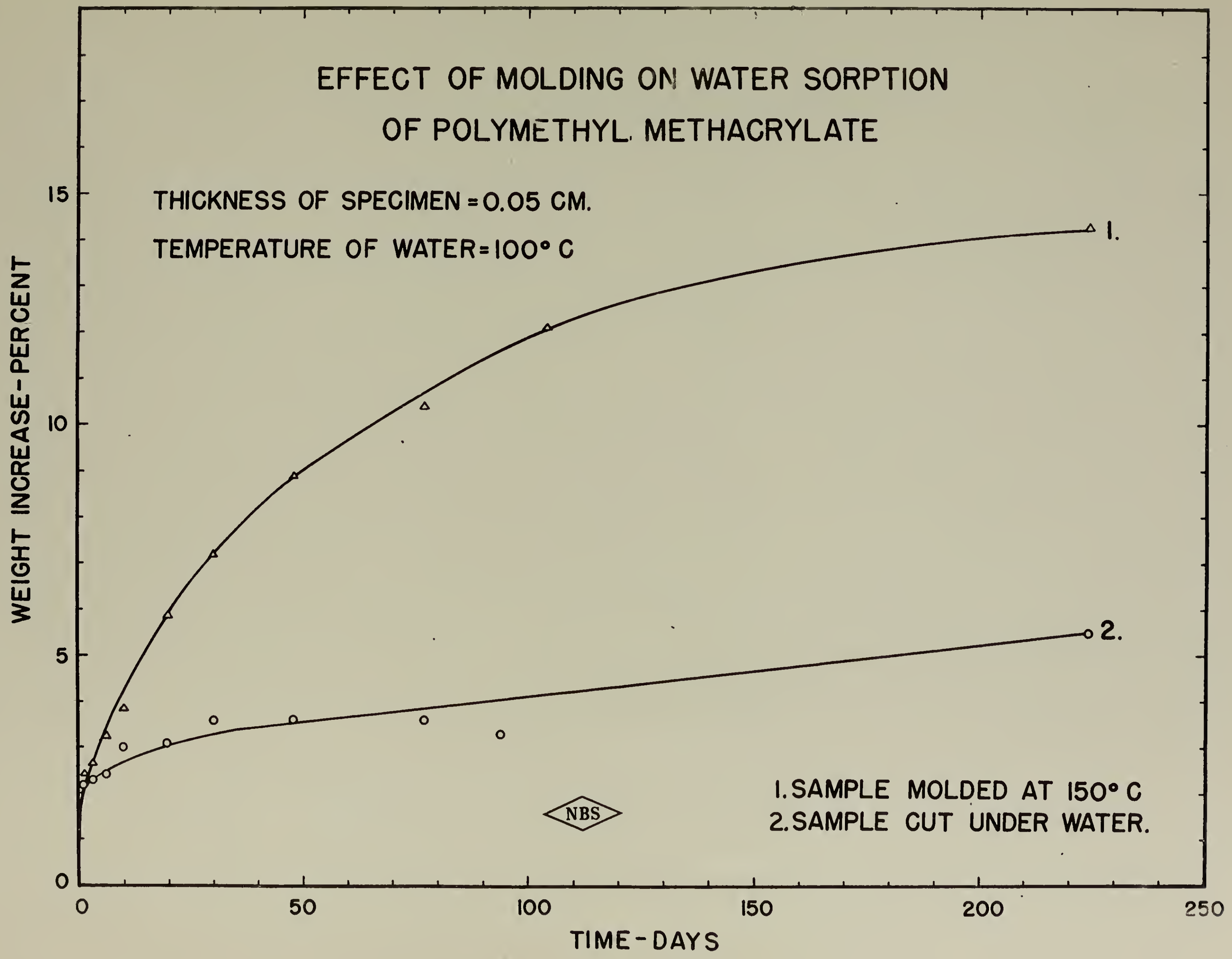
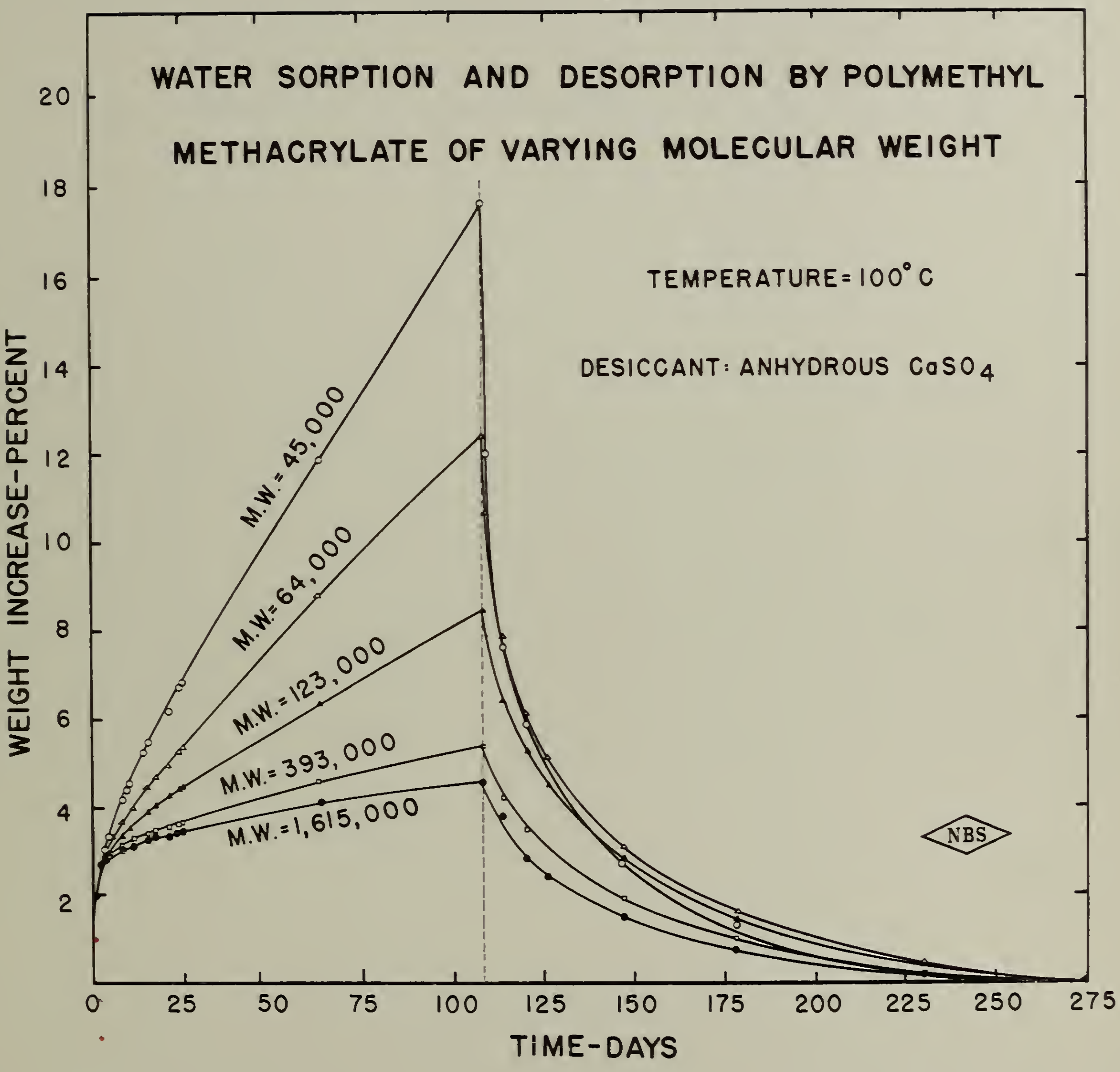

EFFECT OF MOLDING ON WATER SORPTION
OF POLYMETHYL METHACRYLATE
THICKNESS OF SPECIMEN = 0.05 CM.
TEMPERATURE OF WATER = 100° C
1.
2.
1. SAMPLE MOLDED AT 150° C
2. SAMPLE CUT UNDER WATER.
NBS
WEIGHT INCREASE - PERCENT
0
5
10
15
TIME - DAYS
0
50
100
150
200
250

Figure 3. Water sorption and desorption by polymethyl methacrylate of varying molecular weight at 100°C.



WATER SORPTION AND DESORPTION BY POLYMETHYL METHACRYLATE OF VARYING MOLECULAR WEIGHT

Figure 4. Water sorption of polymethyl methacrylate of varying molecular weight at 100°C.

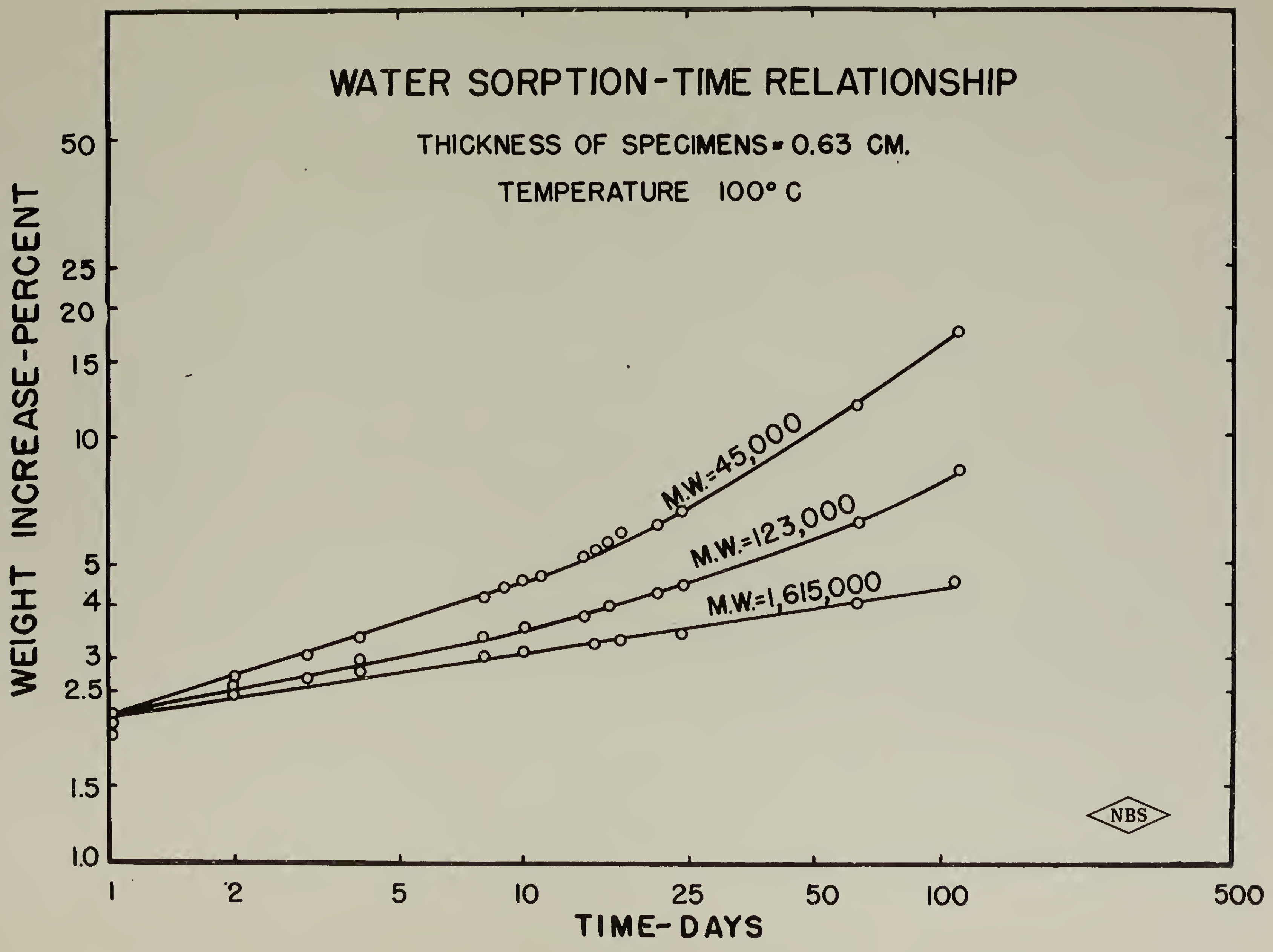

WATER SORPTION-TIME RELATIONSHIP
THICKNESS OF SPECIMENS = 0.63 CM.
TEMPERATURE 100° C
WEIGHT INCREASE-PERCENT
50
25
20
15
10
5
4
3
2.5
1.5
1.0
TIME-DAYS
1
2
5
10
25
50
100
500
M.W.=45,000
M.W.=123,000
M.W.=1,615,000
NBS

Figure 5. Water sorption of polymethyl methacrylate of varying molecular weight at 37°C.

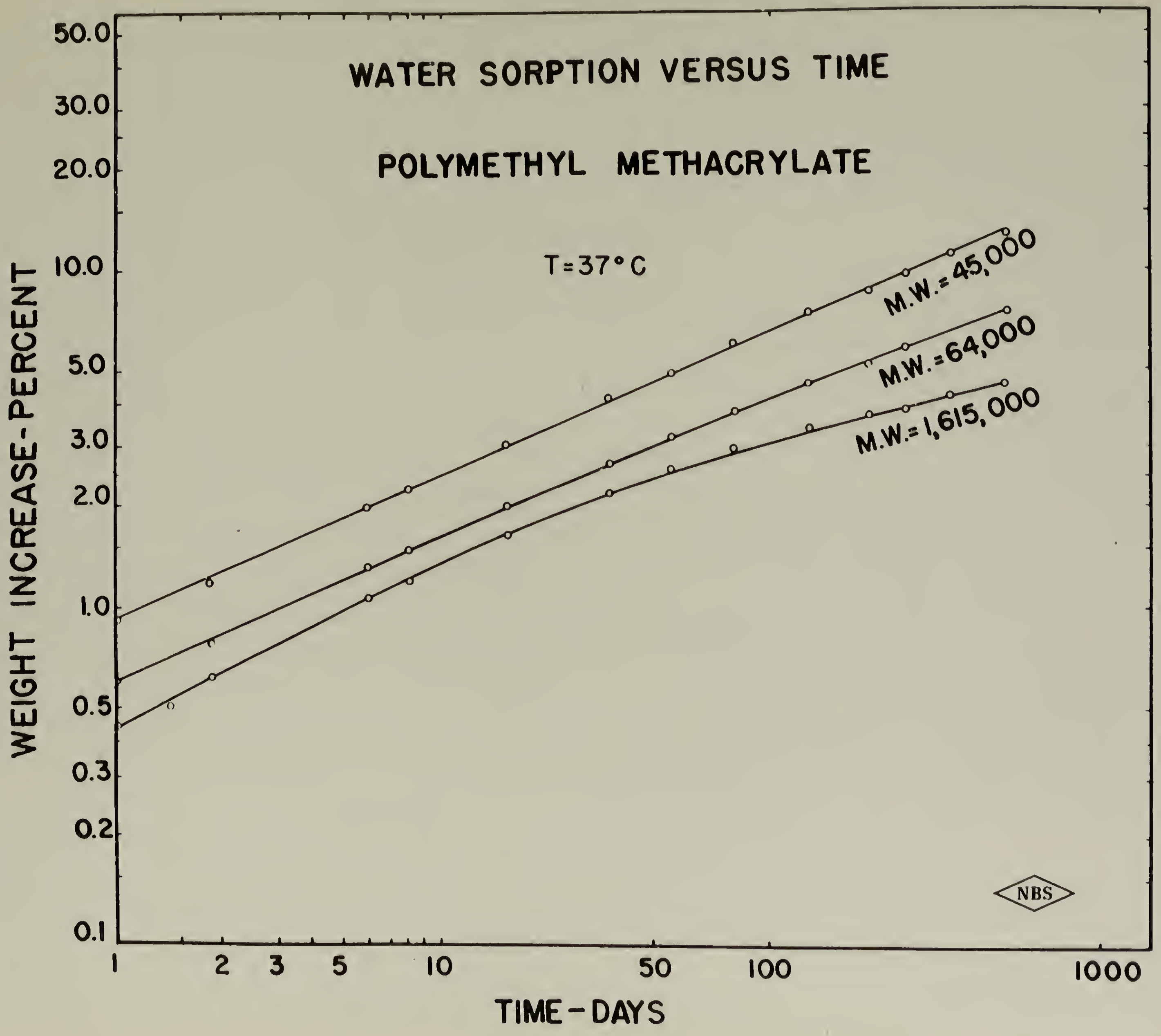
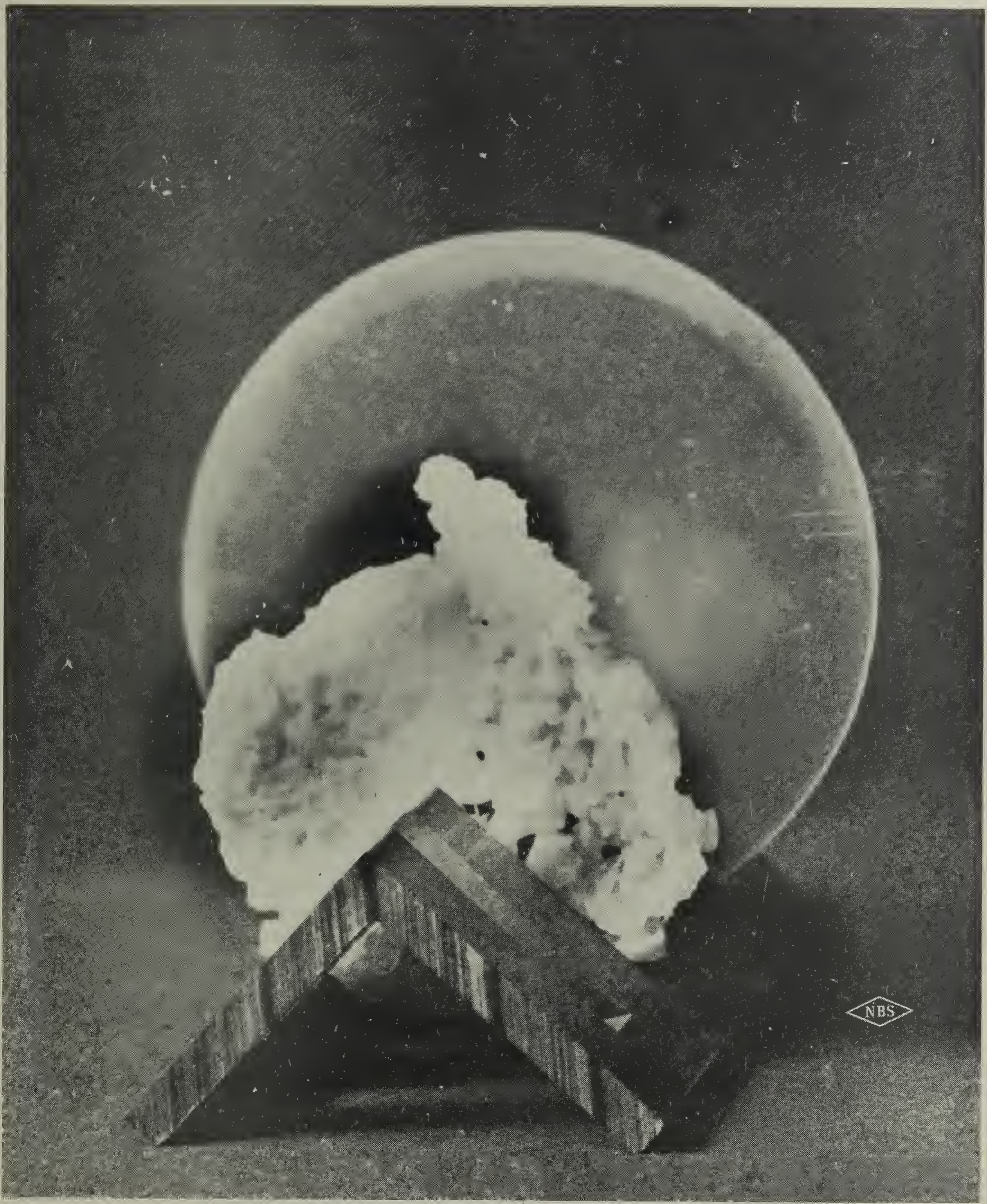

WATER SORPTION VERSUS TIME
POLYMETHYL METHACRYLATE
T=37° C
M.W.=45,000
M.W.=64,000
M.W.=1,615,000
WEIGHT INCREASE-PERCENT
50.0
30.0
20.0
10.0
5.0
3.0
2.0
1.0
0.5
0.3
0.2
0.1
1
2
3
5
10
50
100
1000
TIME-DAYS
NBS

Figure 6. Effect of immersion in hot water on molded discs.

Front: Disc after storage in water above 70°C.

Rear : Freshly molded disc.


NBS

NATIONAL BUREAU OF STANDARDS REPORT

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SELF-CURING RESINS FOR REPAIRING DENTURES: SOME PHYSICAL PROPERTIES AND A SPECIFICATION

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

SELF-CURING RESINS FOR REPAIRING DENTURES: SOME PHYSICAL PROPERTIES AND A SPECIFICATION

ABSTRACT

A comparison of some physical properties of self-curing resins and heat-curing resins, used in repairing artificial dentures, when tested as outlined in American Dental Association Specification No. 12, for Denture Base Resins, shows: (1) the self-curing resins attain a working plasticity in from 1/4 to 1/5 the time of the heat-curing type; (2) there is no important difference in water sorption and solubility; (3) the self-curing resins are less color stable, have less strength, and are less stiff; (4) repairs effected with the self-curing resins had approximately 59 percent of the original strength of the resin, similar repairs with the heat-curing resins had 82 percent; (5) dentures repaired by the self-curing resins warped the least. The greater dimensional accuracy of the self-curing resins is believed to be preferable to the higher strength of the heat-curing materials for repairing dentures.

SELF-CURING RESINS FOR REPAIRING DENTURES: SOME PHYSICAL PROPERTIES AND A SPECIFICATION

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1. INTRODUCTION

One of the first dental uses of the new self-curing resins, based on methyl methacrylate, was as a repair material for artificial dentures. However, little data on their physical properties have been published. This paper not only presents data on some physical properties of the self-curing repair resins but also compares the strength of repairs effected and the dimensional change during repair of artificial dentures when the self-curing repair resins are used with the strength and dimensional changes of repairs accomplished with the heat-curing resins. Because self-curing repair resins are being used, a tentative specification is also offered.

The self-curing resins appear to offer the following advantages over the heat-curing type for use in repairing dentures: (1) the repair can be made quickly with the self-curing resins, while the patient waits. In the conventional methods of repairing a denture with the heat-curing resins, the patient may be without the denture for many hours; (2) no heating equipment is needed to process the self-curing resins. On the other hand, controlled heaters are necessary to maintain the temperature and time of processing properly the conventional repair; (3) since no external heat need be applied to polymerize the self-curing resins, the denture is not warped. When heat-curing resins are used in the customary repair process, and if the repair is made in boiling water, warpage invariably results as the high expanding resin

is confined in the low expanding plaster of Paris mold. The resin is thereby strained. The strain is partially released when the repaired denture is removed from the gypsum model. This is evidenced by a change in dimension as the denture will not reseat properly on the model. Data and observations are presented concerning this point in a later portion of this paper.

2. PHYSICAL PROPERTIES

Materials investigated. For the purpose of determining some of the physical properties of the self-curing resins, the data presented were obtained by the tests described for Type II (self-curing) resins in American Dental Association Specification No. 12 for Denture Base Resin.[1] Five brands of self-curing resins and three brands of certified heat-curing resins (Table 1) were investigated. Other brands are available, but these were felt to be representative of each type.

Mixing and processing technics. The directions of the respective manufacturers of the brands used had recommended a variety of processing technics. All specimens made for determining values for the physical properties of the resins were prepared by compression molding as described by the manufacturer. The heating schedule was 1½ hours at 73°C (163.4°F) followed by ½ hour at 100°C (212°F) for the heat-curing resins. The flasks were then cooled in air for 30 minutes, followed by immersion in water at 23 ± 10°C (73 ± 18°F) for 15 minutes.

Plasticity. The rate of polymerization of the self-curing resins governs the available time for trial packing at room temperature. The working time is controlled by the changes in the plasticity of the resin. The proper plasticity for starting the packing was arbitarily taken as the time when the doughy material separated cleanly from the sides of the mixing jar. The packing test employed was that described in Specification No. 12[1]. The time elapsed between start of mix until it would separate cleanly from the jar varied from 3.5 to 4.5 minutes for the five brands of self-curing resins investigated. The three certified heat-curing resins reached this plasticity in 18 minutes on the average. In accordance with the specification, the packing test was not started until 5 minutes after this proper plasticity was reached. All brands investigated were satisfactory.

Porosity. The porosity test as outlined in the specification consists of a visual inspection of the cured resin. Examination of the repair resins showed that Biofast, Duz-All, Fastcure, and Nuweld were not porous. Nu-Densoform had small bubbles or voids. None of the heat-curing resins were porous.

Water sorption and solubility. All of the resins tested met the requirements of the specification for water sorption and solubility (Table 2). There was no important difference in solubility or water sorption among the brands of each type.

Color stability. On the basis of the existing specification requirement for color stability, three of the five brands of self-curing resin (Biofast, Nu-Densoform, Duz-All) failed definitely, assuming a brownish or yellowish tinge; one (Fastcure) discolored so very slightly that the change in color was barely perceptible; the remaining one (Nuweld) complied easily with the requirement, that is, no change in color was perceptible. Figure 1 shows the specimens two months after exposure. The heat-curing resins were color stable. This test is qualitative and relies on a visual inspection of exposed and unexposed portions of the specimens.

Transverse tests. Data on the strength and stiffness of resins in transverse bending are given in Table 3. The specification values for deflection at loads of 3,500 g (7.7 lb) and 5,000 g (11.0 lb) for denture base resins of both self-curing and heat-curing types are given in the table also. In addition, graphs showing the deflection of the resins with respect to load applied are shown in Figure 2. The data (Table 3 and Fig. 2) show that none of the brands of self-curing repair resins complied with the requirements of the specification for a Type II self-curing denture base resin. Failure of all self-curing repair resins occurred at or before the 5,000 g (11.0 lb) load; therefore, no deflection readings could be obtained for this load (Table 3).

3. STRENGTH AND STIFFNESS OF REPAIRS MADE WITH SELF-CURING AND HEAT-CURING RESINS

After comparing the strength and stiffness (in transverse bending) of the self-curing repair resins with heat-curing resins, it was decided to investigate the strength of the bond made to the denture base resin by the two types. The method chosen was based on the transverse test in the specification. Plates of each of the clear resins of the three heat-curing brands (Table 1) were made in a gypsum mold as shown in Figure 3. A $\frac{1}{4}$-inch section was cut from the center of these plates. The two pieces were replaced in the mold and the cut-out section was filled with pink repair resin (Fig. 4). This process resulted in a butt joint which is not generally used in repairing dentures; however, it gave the most consistent results among the various types of joints tested.

To determine the effect of the time of packing on the strength of the repair, the self-curing repair resins were packed at three different stages of plasticity. These stages were dependent upon the elapsed time from the beginning of the mix to completion of the packing of the repair. The heat-curing resins were packed when they pulled free from the sides of the mixing jar. Five specimens were machined from each repaired plate. A typical specimen is shown at the bottom of Figure 4. After the specimens were tested they were examined to determine the type or condition of break. The two typical breaks obtained are shown in Figure 5. The specimen at the top was repaired with

heat-cured resin. The fracture in this case, as in the case of all the heat-cured repairs, was through the center of the repaired area where the stress was applied. However, the specimens repaired with the self-curing resin shown at the bottom of Figure 5 broke at the bond without exception. There was a definite bonding between the repaired area and the original block in the case of the heat-cured repair, whereas an inferior bond occurred with the self-cured repair. These results are summarized in Table 4. Table 5 presents sufficient data on the self-curing repair resins to permit a statistical analysis. In these two tables data are given on the self-curing repair resins packed at three different plasticities depending upon the amount of time elapsed from the beginning of the mix to completion of the packing. These times are designated as stages 1, 2 and 3.

The average strength of specimens repaired with the heat-curing resins was approximately 5,400 g (Table 4) . This was approximately 82 percent of the original strength of the clear heat-cured resins (6,600 g). There was no significant difference in strength of the repaired specimens among the brands of heat-curing resin used in repairing the blocks. The best average strength of the self-curing repairs was 59 percent of the original strength as shown by stage 1 in Table 4. For a statistical analysis of the three stages, Table 5 presents the average load at failure for each of the 45 plates constituting this part of the investigation. From each block five specimens were

prepared so 225 specimens were tested. The variability among the observed loads for five specimens prepared from any plate is characterized by a standard deviation of about 200 g.

There appears to be a significant decrease in strength, approximately 400 g, when the self-curing resin is packed at stage 2, rather than stage 1 (Table 5). However, the evidence is not conclusive that the further decrease between stages 2 and 3 is significant. The specimens repaired with the self-curing resins in this experiment appear to fall into two groups based upon the strength in transverse bending. Specimens repaired with Biofast and Duz-All represent the group of lower strength, while Fastcure, Nu-Densoform and Nuweld form the group of slightly higher strength. This follows in order the strength in transverse bending of the foregoing resins (Table 3). The three heat-curing resins may not be equally susceptible to repair. The strength of the repair made on these resins appears to fall into two groups based upon strength in transverse bending. However, the evidence is not conclusive except, possibly, in stage 3 (Table 5).

In reaching these conclusions an analysis of variance was made to evaluate the differences due to the nature of the heat-curing resin, of the self-curing resin, and of the stage of packing. It was found that, while these conclusions could be made, within the limits of precision of the experiment, the effects of these three factors were independent of each other.

In addition to these tables of results two graphs are presented (Figs. 6 and 7) to show the stiffness of these repairs by plotting the deflections in millimeters versus the loads applied in kilograms. The curves in Figure 6 show that the original resins were stiffer than the heat-cured repairs which were in turn stiffer than the self-cured repairs. The end point of the curves is the average load of failure.

The three curves in Figure 7 depict the average deflections obtained on specimens repaired with the self-curing resins at three different stages of plasticity. The differences in loads required for failure can be seen in this graph. There was not any significant difference in the stiffness of the repairs made by the three stages of packing.

4. CHANGE IN DIMENSION ON REPAIR

The changes in dimension of eleven upper dentures repaired by different materials and technics were determined by the following procedure. Stainless steel pins, having cross marks upon them, were inserted into the second molars. A gypsum model was made of the tissue-bearing surface of each denture and the molar-to-molar dimensions were determined with a toolmaker's microscope. Each denture was cut through the center from the central incisors to the posterior margin by a band saw. Approximately 1/8 inch was removed from each half. The sections were then seated on the tinfoiled model and the molar-to-molar distance was again measured.

In the case of the heat-cured repairs, the process was carried out in the conventional dental manner of investing and packing. Three of the dentures were repaired by heating for 1½ hours at 73 ± 1°C (163.4 ± 1.8°F) followed by ½ hour in boiling water. Three additional dentures were repaired by heating at 73 ± 1°C (163.4 ± 1.8°F) for 8 hours. At the completion of the curing cycles the flasks were bench cooled for 30 minutes in air and then immersed in water/[23 ± 10°C (73 ± 18°F)]/ for 15 minutes. The flasks were opened and the molar-to-molar dimensions were measured before and after removing the repaired denture from the model.

Five dentures which had been cut in two and replaced on their respective models were repaired using the five self-curing resins. These repairs were effected by using a gypsum matrix of the lingual side of the unbroken denture. The matrix was held in place by a C-clamp during the curing process. The self-curing resins were all packed at the optimum time from beginning of mix so that they would have their greatest possible strength (stage 1 in Table 4). After the repairs had been completed, the dentures were again measured. The dimensional changes in dentures repaired by the foregoing procedures are shown in Table 6. The values are the differences between measurements of the unbroken and the repaired dentures. The average change for the dentures repaired with the heat-curing resins, which were boiled during the curing cycle, was approximately 2½ times the change taking place in the dentures repaired with the heat-curing resins which were heated for 8 hours at 73 ± 1°C (163.4 ± 1.8°F).

This tends to support the general observation made at the beginning of this paper that the heating of the flask causes a definite strain in the high-expanding resin during confinement in the low-expanding plaster of Paris mold. This strain was possibly released in the form of dimensional change as shown by the data in Table 6. The changes in the artificial dentures repaired with the heat-curing resins were in the minus direction, that is, the molar-to-molar dimensions were smaller than originally. However, the changes taking place in dimension in dentures repaired with the self-curing resins were in the plus direction. Here the final measurement was greater than the original. If the minus changes in the dentures repaired with the heat-curing resins held at 73°C (163.4°F) for 8 hours are compared with the plus changes in the dentures repaired with the self-curing resins, it will be noted that they appear to be of the same order of magnitude. However, there is considerable difference in the fit of the repaired dentures when they are reseated upon the gypsum models (Fig. 8. Invariably the dentures repaired by the self-curing resins fit the model much better than any dentures repaired with heat-curing technics and resins. It would appear that the distortion of the denture's shape is not necessarily reflected in the molar-to-molar measurements. When the eleven dentures which were repaired were handed to an observer as unknowns he was able to sort them correctly in the categories A, B and C (Figs.8 and 9. The repaired dentures shown in Figures 8 and 9 are typical.

5. SPECIFICATIONS

The specification for Type II self-curing denture base resin, as given in the American Dental Association Specification No. 12 for Denture Base Resin[1], is a suitable specification with certain exceptions for these self-curing repair resins. So the following specification is suggested.

AMERICAN DENTAL ASSOCIATION
SPECIFICATION NO. 13 FOR SELF-CURING REPAIR RESIN

1. Scope and Classification.

1.1 Scope. This specification is for self-curing resins used primarily for repairing denture base resins.

1.2 Types and Classes. Repair resins covered by this specification shall be of the self-curing type, powder and liquid class, and of two colors, pink and clear.

2. Applicable Specifications

2.1 Specification. American Dental Association Specification No. 12 for Denture Base Resin (Acrylic Resins or Mixtures of Acrylic and Other Resins) Second Revision[1] shall be applicable, as it applies to Type II self-curing resins with the following exceptions:

Paragraph 3.4.1, Working Qualities, American Dental Association Specification No. 12, shall be changed to read:

3.4.1 Working Qualities. The self-curing repair resin when processed according to instructions furnished by the manufacturer shall yield a satisfactory repair.

Paragraph 3.4.7 , Transverse Deflection, of American Dental Association Specification No. 12 shall be changed to read:

3.4.7 Transverse Deflection. The deflection of at least three of the five specimens prepared as outlined in 4.3.5 shall meet the following requirements when tested in water at 37 ± 1°C (98.6 ± 1.8°F):

Class	DEFLECTION for loads* 1,500 g (3.30 lb) to	
	2500 g (5.50 lb)	4000 g (8.80 lb)
	Max.	Max.
	mm	mm
Self-Curing Repair Resins	1.5 (0.058 in)	4.5 (0.177 in)

* Deflections shall be measured from an initial load of 1500 g (3.30 lb) to the load indicated.

There may be some questions raised as to why the stiffness and strength of the repair resins in transverse bending was used in the foregoing specification instead of the same properties on repaired specimens. There were two main reasons: 1) a comparison of the data in Tables 3 and 5 shows that generally the strength of the repaired specimens followed the strength of the self-curing resins used in the repair; 2) the data in Table 5 indicate that all denture base resins do not repair equally well and it would be very awkward and extemely difficult to specify a resin which was to be repaired and which would serve as an unchanging standard.

6. SUMMARY AND CONCLUSIONS

Some physical properties of five self-curing resins advocated for repair of artificial dentures were measured using the test methods of American Dental Association Specification No. 12 for Denture Base Resins[1] (Type II, Self-curing Resins). These properties were compared with those of three heat-curing denture base resins.

The working plasticity of the self-curing resins was attained in from 3½ to 4½ minutes after beginning the mix, while 18 minutes were required on the average for the three heat-curing resins. The self-curing resins maintained a suitable working plasticity for at least 5 minutes. This is sufficient time to trial pack properly.

One of the self-curing resins had small bubbles or voids. None of the heat-curing resins were porous.

There was no important difference in water sorption and solubility between the self-curing and heat-curing types.

Three out of five of the self-curing resins failed to pass the color stability test of American Dental Association Specification No. 12[1]. One discolored so very slightly that the change in color was barely perceptible. The remaining resin easily complied with the specification.

All of the self-curing resins were weaker and less stiff than the heat-curing resins in transverse bending.

The average strength in transverse bending of specimens repaired by heat-curing resin was approximately 82 percent of the average of the original strength of the denture base resins. If the repair was made with the self-curing resins, the average strength was approximately 59 percent when the optimum technic was used. In general it appeared that the optimum technic was to pack the self-curing repair resin so that the elapsed time from the beginning of the mix to the completion of the packing would be from 2 to 3 minutes.

There was a change of -0.8 percent in the molar-to-molar dimension of full upper dentures repaired by heat-curing resins which were heated to boiling during processing. If instead of boiling the repairs were heated at 73°C (163.4°F) for 8 hours, the shrinkage was reduced to 0.3 percent. There was an increase of 0.2 percent in the molar-to-molar distance when the repairs were made with self-curing resins. While there may appear to be only an academic difference between a -0.3 and a +0.2 percent change in the molar-to-molar distance, the fit of the dentures repaired by the self-curing resins when reseated on the original gypsum models was invariably much better than the fit of the dentures repaired with the heat-curing resins. It is, therefore, suggested that the self-curing resins be used even though they are weaker than the heat-curing resins.

It is recommended that the American Dental Association Specification No. 12 for Denture Base Resin (Second Revision)[1] as it applies to Type II, Self-curing denture base resins be made applicable to the self-curing repair resins with the exceptions noted.

REFERENCE

1. Swaney, Aubrey C., Paffenbarger, George 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 Jan. 1953.

Figure 1

Appearance of resin disks after right side has been subjected to color stability test in A.D.A. Specification No. 12[1].

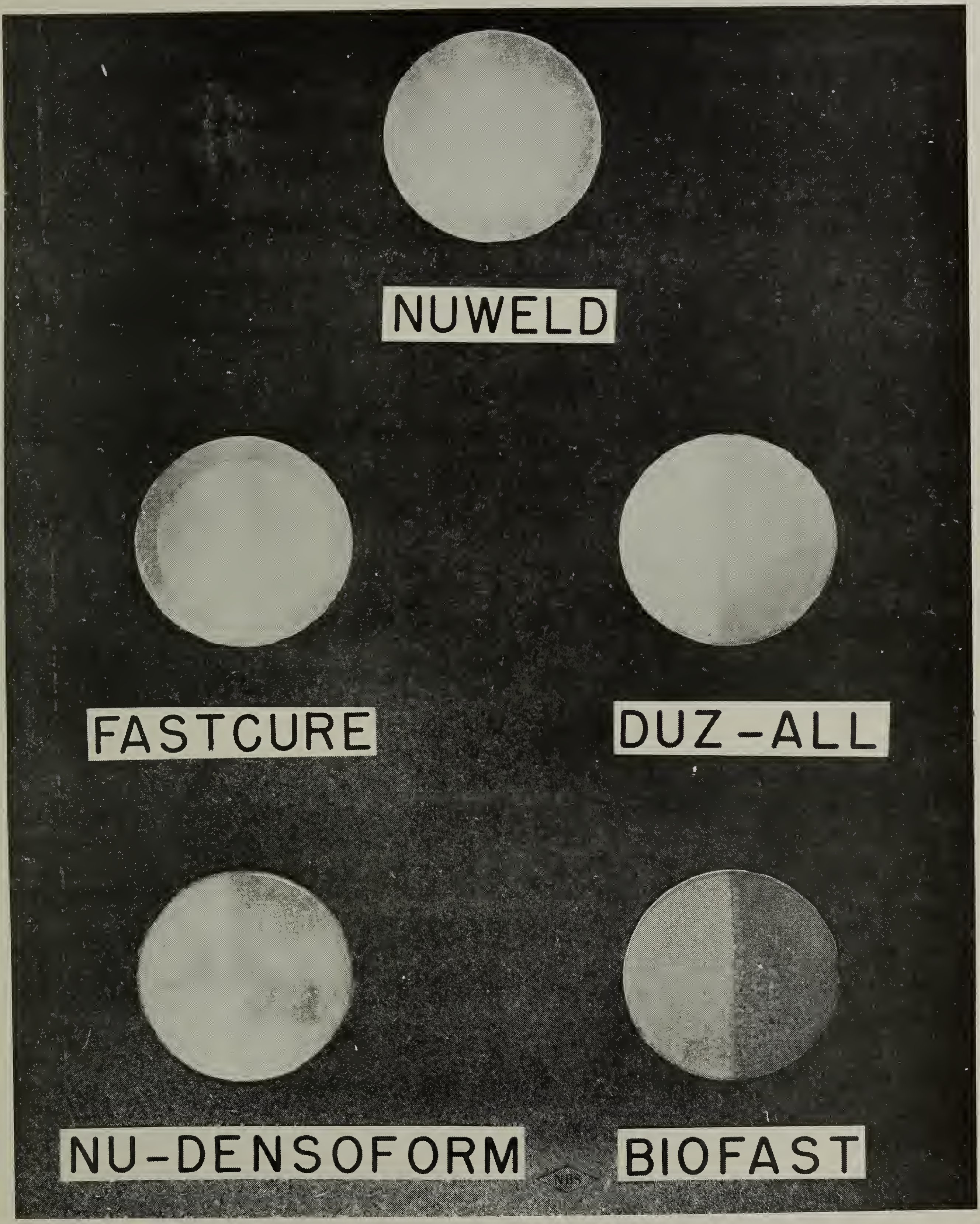

NUWELD
FASTCURE
DUZ-ALL
NU-DENSOFORM
BIOFAST
NBS

Figure 2

Deflection and strength in transverse bending of self-curing repair resins and heat-curing resins.

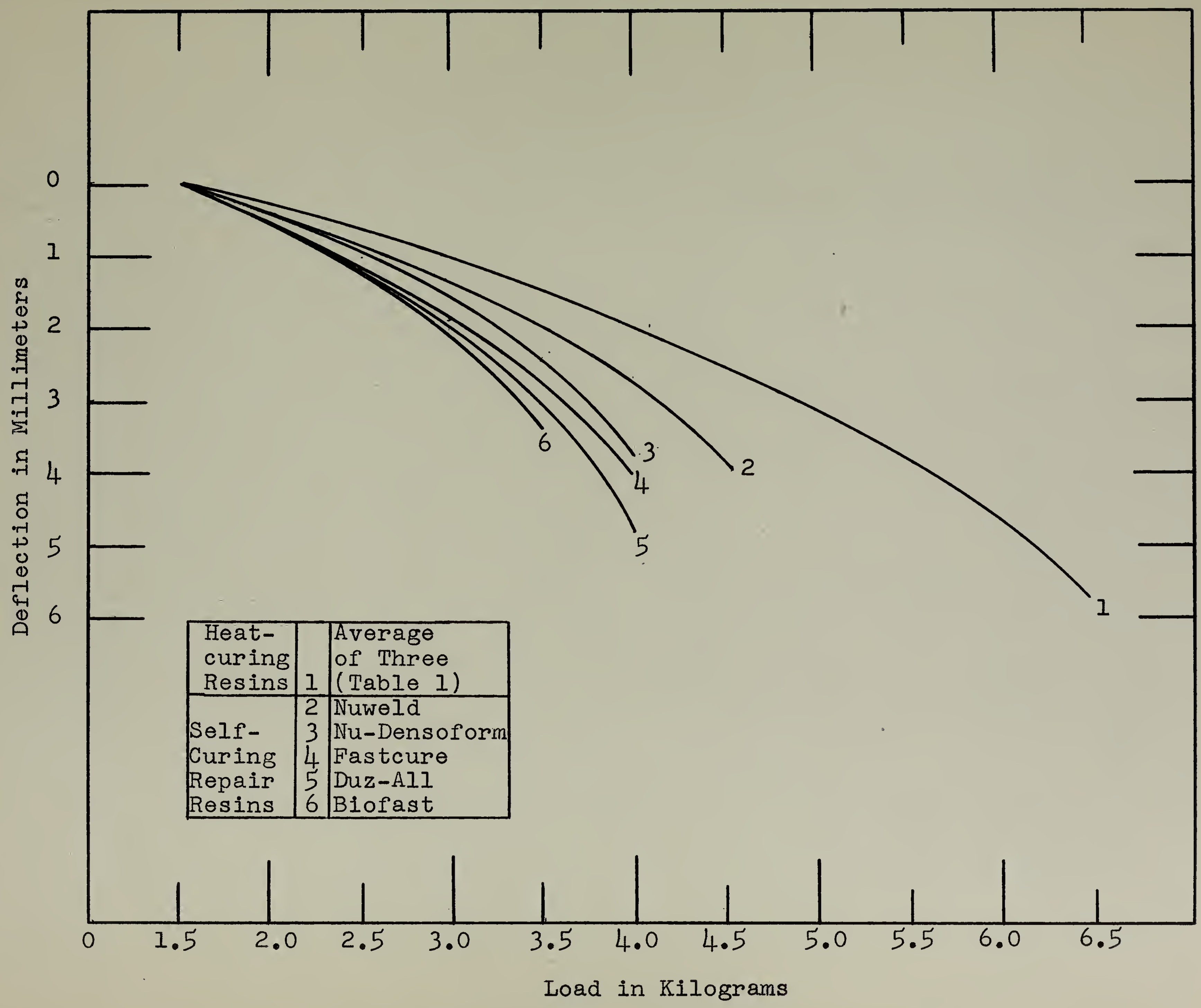
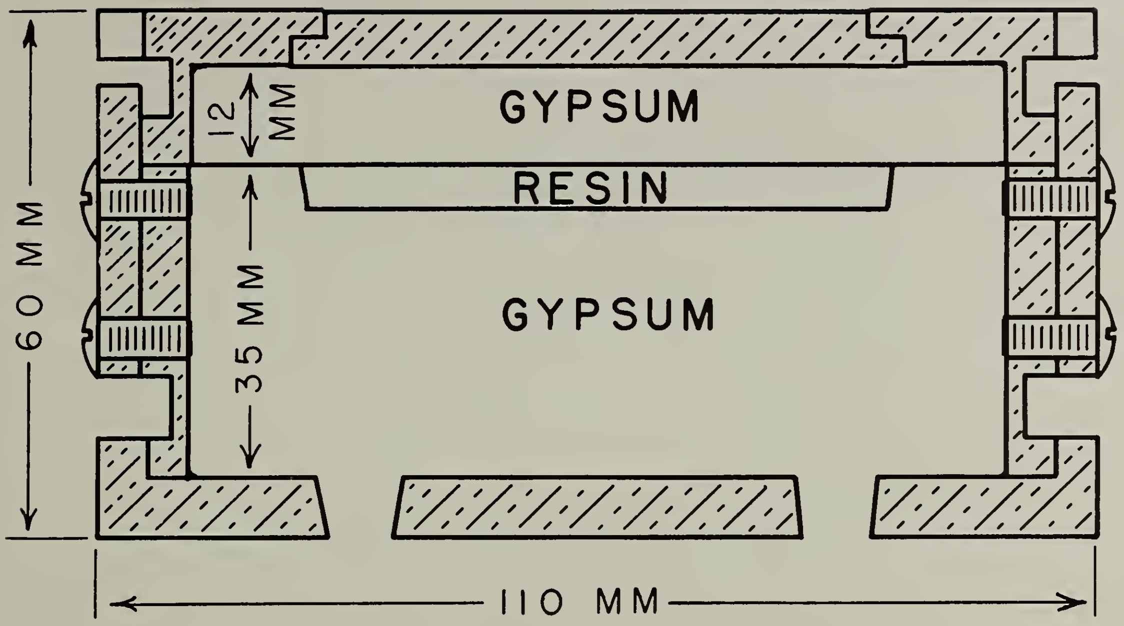
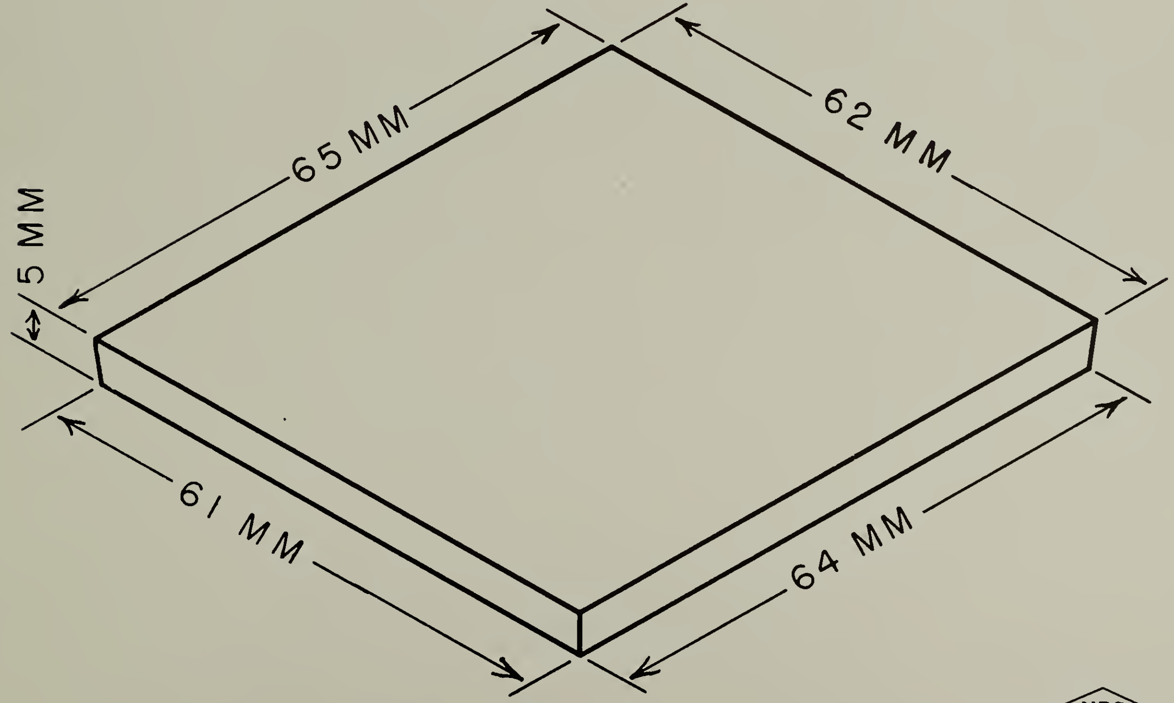

Deflection in Millimeters
0
1
2
3
4
5
6
Load in Kilograms
0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
1
2
3
4
5
6
Heat-curing Resins 1 Average of Three (Table 1)
Self-Curing Repair Resins
2 Nuweld
3 Nu-Densoform
4 Fastcure
5 Duz-All
6 Biofast

Figure 3

Resin plate and its position in the flask during processing.



DENTURE FLASK



SPECIMEN PLATE

Figure 4

Repaired resin plate and example of specimen machined from it.

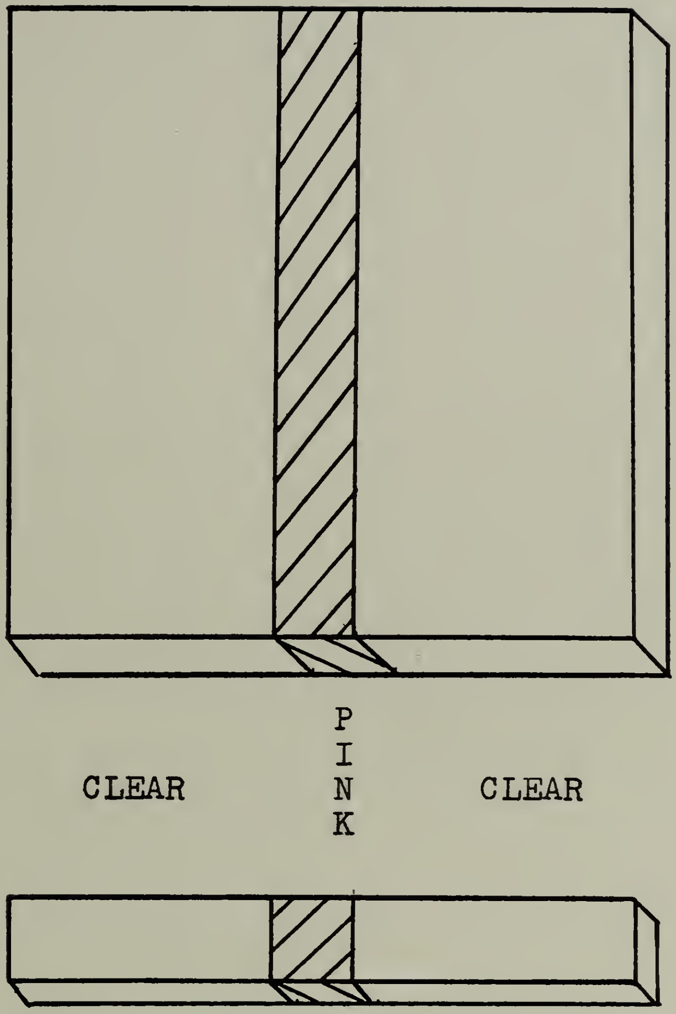

CLEAR
PINK
CLEAR

Figure 5

Typical breaks of repaired resin specimens. The specimen at the top was repaired with heat-curing resin. The specimen at the bottom with self-curing resin.

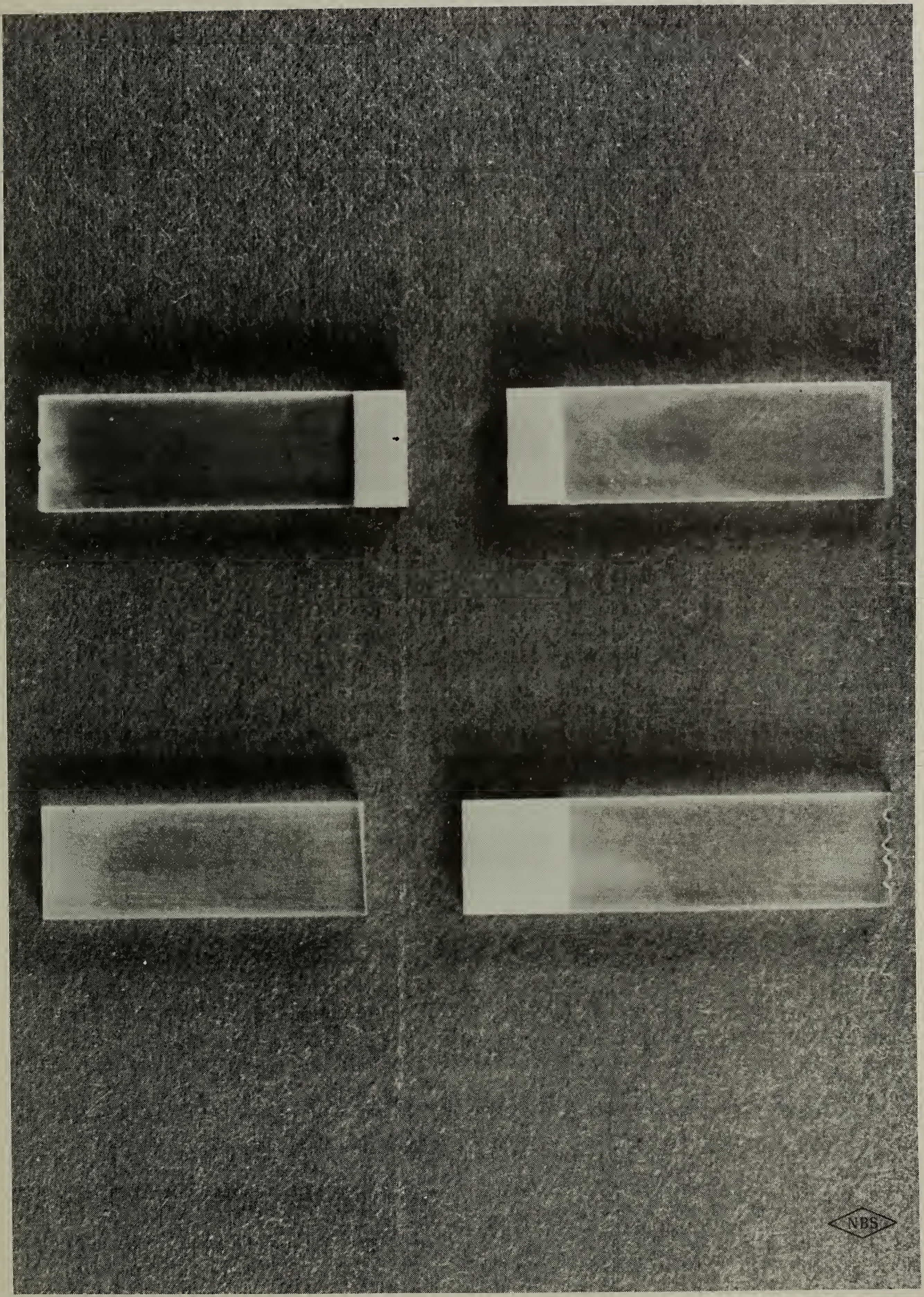

NBS

Figure 6

Transverse test on original and repaired specimens.

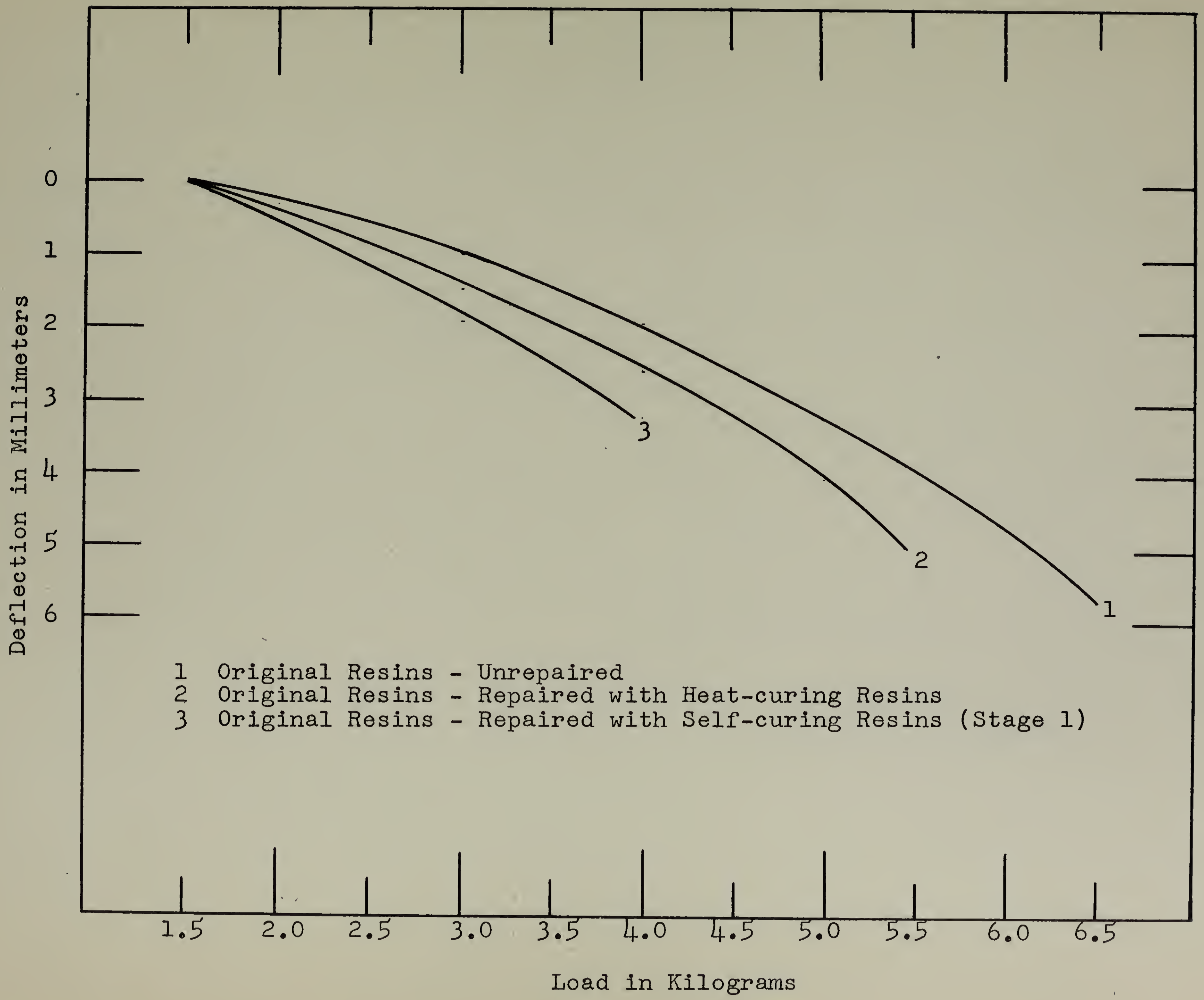

Deflection in Millimeters
0
1
2
3
4
5
6
Load in Kilograms
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
1
2
3
1 Original Resins - Unrepaired
2 Original Resins - Repaired with Heat-curing Resins
3 Original Resins - Repaired with Self-curing Resins (Stage 1)

Figure 7

Transverse test on specimens repaired with self-curing resins.

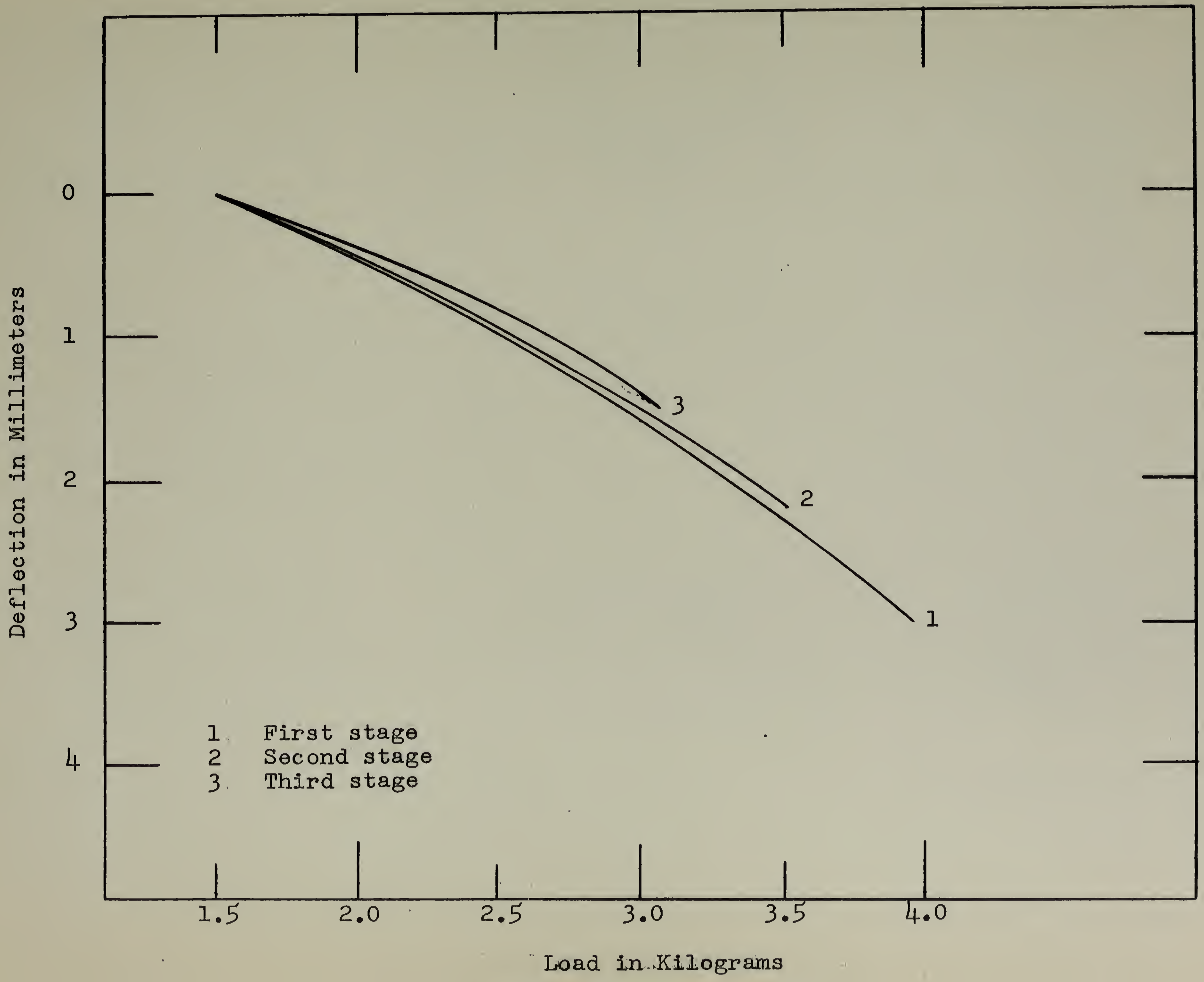

0
1
2
3
4
Deflection in Millimeters
1.5
2.0
2.5
3.0
3.5
4.0
Load in Kilograms
1
2
3
1 First stage
2 Second stage
3 Third stage

Figure 8

Change in molar-to-molar dimension during heating. Posterior view. A. Heat-curing repair for 1½ hrs at 73°C (163.4°F) plus ½ hr boiling. B. Heat-curing repair for 8 hrs at 73°C (163.4°F).

C. Self-curing repair for ¼ hr at room temperature, 20-25°C (68-77°F).

Areas shown in lower half of figure are magnifications on the order of 8X.

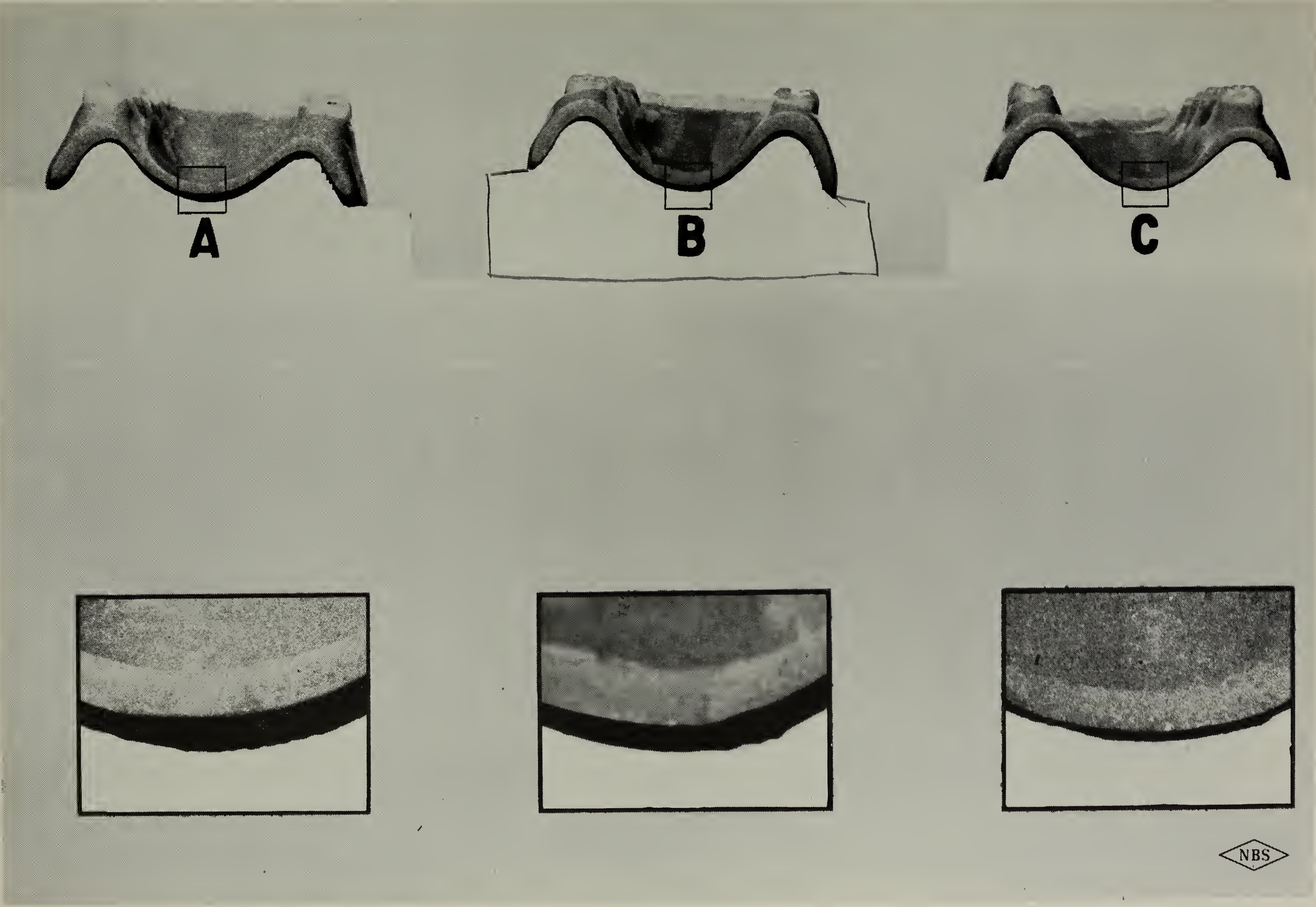

A
B
C
NBS

Figure 9

Change in molar-to-molar dimension during heating. Left buccal view. A. Heat-curing repair for 1½ hrs at 73°C (163.4°F) plus ½ hr boiling. B. Heat-curing repair for 8 hrs at 73°C (163.4°F). C. Self-curing repair for ¼ hr at room temperature, 20-25°C (68-77°F).

Areas shown in lower half of figure are magnifications on the order of 8X.

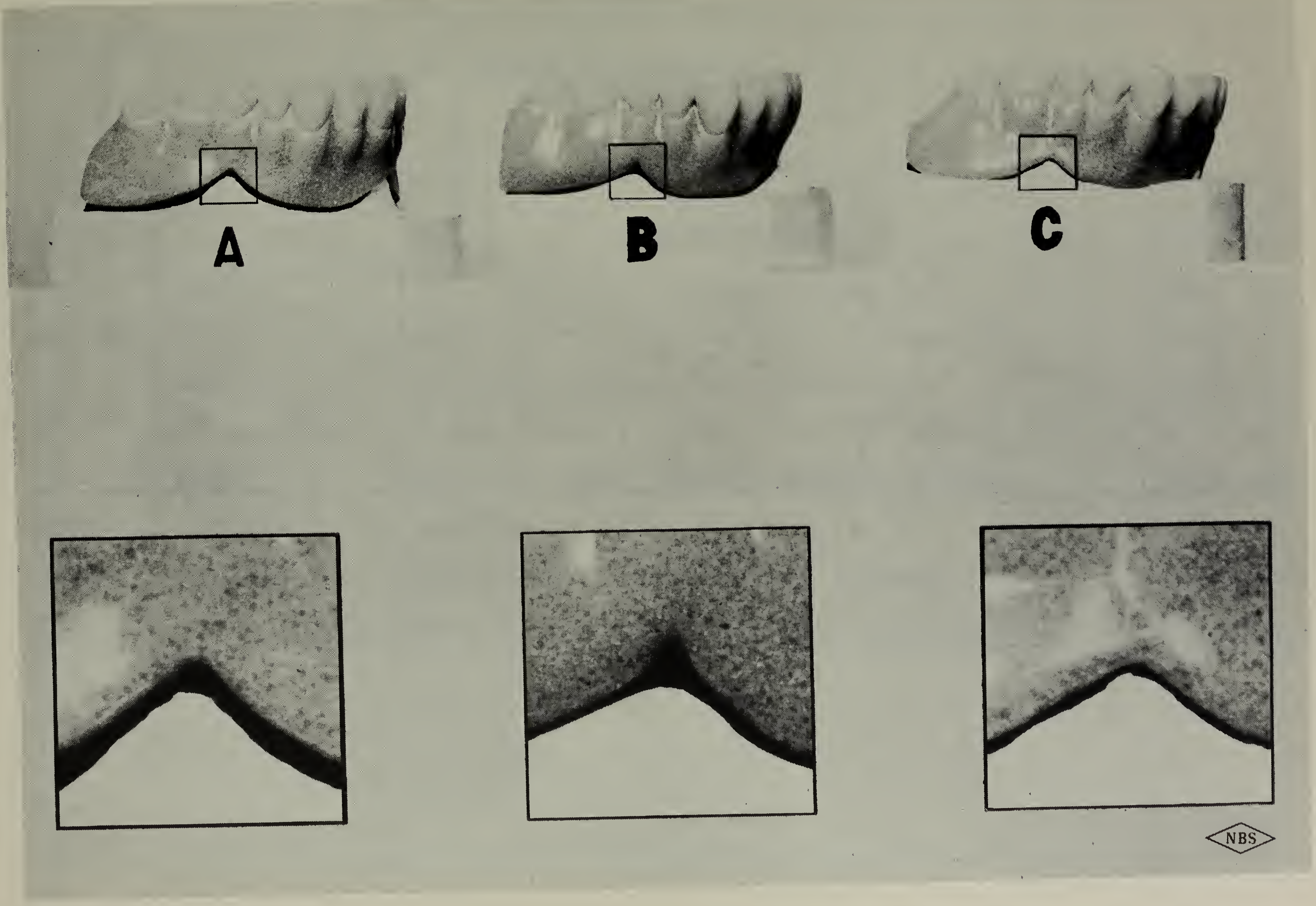

A
B
C
NBS

Table 1

Resins Investigated

TYPE	BRAND	MANUFACTURER	DATE MATERIAL RECEIVED
Self-curing	Biofast	B. L. Dental Co., Richmond Hill, N. Y.	Nov. 1952
	Duz-All	Coralite Dental Products Co., Chicago, Ill.	July 1953
	Fastcure	Acralite Co., Inc., New York, N. Y.	Oct. 1953
	Nu-Densoform	Cosmos Dental Products, Inc., New York, N. Y.	Nov. 1952
	Nuweld	The L. D. Caulk Company, Milford, Delaware	July 1953
Heat-curing	Acralite	Acralite Co., Inc., New York, N. Y	June 1953
	Certified	Lee S. Smith & Son Mfg. Co., Chicago, Ill.	June 1953
	Denture Acrylic	The S.S.White Dental Mfg. Co., Philadelphia, Pa.	June 1953

(A31-A62)

Table 2

Water Sorption and Solubility of Self-Curing Repair Resins and Heat-Curing Resins

TYPE OF RESIN	WATER SORPTION	WATER SOLUBILITY
	mg/cm^2	mg/cm^2
Self-curing	0.4	0.03
Heat-curing	0.6	0.01
A.D.A. Spec. No. 12 for Denture Base Resin	max. 0.7	max. 0.04

Table 3

Transverse Tests of Self-curing Repair and Heat-curing Resins

BRAND	NUMBER SPECIMENS TESTED	DEFLECTION FOR LOADS 1500 g TO					LOAD OF FAILURE
		2500 g	3500 g	4000 g	4500 g	5000 g	
		mm	mm	mm	mm	mm	g
Biofast	5	1.3	3.4	(1)	-	-	4,000
Duz-All	5	1.3	3.1	4.8	-	-	4,100
Fastcure	5	1.2	2.7	4.0	(1)	-	4,500
Nu-Densoform	5	1.1	2.5	3.8	-	-	4,300
Nuweld	5	1.0	2.2	2.9	4.0	(1)	5,000
A.D.A. Spec.#12 Self-curing Resins	-	-	2.5 max.	-	-	3.5 min. 6.5 max.	-
Acralite	5	-	1.6	-	-	3.0	6,500
Certified	5	-	1.6	-	-	3.4	6,700
Denture Acrylic	5	-	1.4	-	-	3.0	6,600
A.D.A. Spec.#12 Heat-curing Resins	-	-	1.8 max.	-	-	2.0 min. 5.0 max.	-

(A31-A62)

(1) Specimens broke before reading could be taken.

Table 4

Strength in Transverse Bending of Repaired Resin Specimens

MATERIAL	Stage	Average Time(1)	NUMBER SPECI- MENS	AVERAGE LOAD REQUIRED FOR FAILURE(2)
		min.		g
Original resins unrepaired			15	6600
Original resins repaired by heat-curing resins.			45	5400
Original resins repaired by self-curing resins.	1	$2\frac{1}{2}$	75	3900
	2	$4\frac{1}{2}$	75	3500
	3	$7\frac{1}{2}$	75	3200

(A31-A62)

(1) Elapsed time from the beginning of the mix to completion of the packing of the repair.

(2) Average deviation plus or minus 200 g.

Table 5

Strength in Transverse Bending of Specimens Repaired with Self-curing Resins

Plasticity Stages (See Table 4)	Clear Heat-curing Resins Used for Specimen Plates	PINK SELF-CURING RESINS USED IN REPAIRING SPECIMEN PLATES					
		Biofast	Duz-All	Fastcure	Nu-Densoform	Nuweld	Average
		g	g	g	g	g	g
1	Acralite	3,000	4,100	4,200	4,000	4,500	4,000
	Certified	3,700	3,900	3,800	4,100	4,100	3,900
	Denture Acrylic	3,800	3,100	4,400	4,200	4,000	3,900
	Average	3,500	3,700	4,100	4,100	4,200	3,900
2	Acralite	3,700	3,400	3,400	3,300	4,400	3,600
	Certified	3,500	3,000	3,600	3,800	3,700	3,500
	Denture Acrylic	2,500	2,900	3,800	3,400	3,800	3,300
	Average	3,200	3,100	3,600	3,500	4,000	3,500
3	Acralite	3,500	3,800	3,500	4,100	3,600	3,700
	Certified	3,400	2,900	3,500	3,500	3,300	3,300
	Denture Acrylic	3,100	2,300	2,700	2,800	2,800	2,700
	Average	3,300	3,000	3,200	3,500	3,200	3,200
	Average of Stages	3,300	3,300	3,600	3,700	3,800	

Table 6

Dimensional Changes Occurring in Artificial Dentures During Repair.
(Degree of variation is expressed as average deviation.)

TYPE OF REPAIR RESIN	NUMBER OF DENTURES	HEATING SCHEDULE	AVERAGE DIMENSIONAL CHANGE in.	AVERAGE CHANGE %
Heat-curing	3	$1\frac{1}{2}$ hr. at 73°C $\frac{1}{2}$ hr. at 100°C	-0.013 ±0.002	-0.8 ± 0.1
	3	8 hr. at 73°C	-0.005 ±0.000	-0.3 ±0.0
Self-curing	5	15 min. at room temp. 20-25°C	+0.003 ±0.002	+0.2 ± 0.1

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PHYSICAL PROPERTIES OF PLASTIC TEETH AND A PROPOSED SPECIFICATION

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

PHYSICAL PROPERTIES OF PLASTIC TEETH AND A PROPOSED SPECIFICATION

Abstract

The development and extensive use of plastic teeth in recent years has caused the dental profession to desire technical information on their physical properties. The results on eleven brands of teeth are reported. Modulus of elasticity, hardness, stress-strain relationship, crazing, abrasion and recovery data are included. New methods of tests were developed and procedures used to evaluate these properties are given. A specification for plastic teeth is proposed.

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1. INTRODUCTION

Plastic teeth have been used by the dental profession for approximately ten years. During this period, considerable clinical evaluation has occurred. Although dentists are not in total agreement as to the relative value of plastic as compared to porcelain teeth, the continued widespread sale of plastic teeth indicates that the dental profession has found them useful in restorative dentistry.

A recent survey of prosthestic specialists indicates that over 90% of them have used or are using plastic teeth. One-tenth of these men use plastic teeth exclusively whereas others use them in varying degrees. The majority of the dentists answering this questionnaire are users of plastic teeth in particular situations where very short teeth are required.

The replies of this group indicate that plastic teeth are deficient in some physical properties and that other physical properties are satisfactory and desirable for dental use. It is also evident that different commercial brands of plastic teeth vary widely in some properties. Since differences have been noted, it is necessary to establish laboratory tests and data for the evaluation of plastic teeth. This report includes data obtained on several brands of plastic teeth.

2. PROPERTIES OF DENTAL SIGNIFICANCE

Plastics have many properties which make them attractive materials for making teeth. The resins which have been most used are methyl methacrylate and copolymers in which it is a major constituent. The chemical properties are very satisfactory. Methyl methacrylate polymers are non-poisonous, are insoluble in the fluids found in the oral cavity and the monomer is sufficiently chemically reactive to other methacrylates under heat and pressure to form a chemical bond. When mixtures of methacrylate polymer and monomer are subjected to heat and pressure in processing dentures a chemical union results. The reaction of the monomer in the uncured denture base with the plastic teeth also forms a chemical bond between the denture base and the tooth. Methyl methacrylate is soluble

more or less in most organic solvents such as ketones, aromatic hydrocarbons, etc. and it is, therefore, important that the denture not be cleansed in an organic solvent.

In general, mechanical properties of these resins are low in comparison with other dental restorative materials such as amalgam, gold alloy, etc. The low mechanical properties, strength, abrasion resistance, modulus of elasticity and hardness, however, have some advantages. The modulus of elasticity being lower than that of porcelain contributes to the elimination of the "clicking" sound when teeth come in contact with each other. The low hardness and abrasion resistance facilitate the adjustment of the occlusion. Also plastic teeth have a high degree of toughness, therefore, less shattering or breaking occurs with plastic teeth. Plastic teeth have a very desirable esthetic appearance. The optical properties of these teeth make it possible to match shades and colors with those of natural teeth.

A serious drawback of some plastic teeth is crazing. The mechanism of crazing is not completely understood. It is thought to be caused by the relieving of localized strain. Crazing is commonly noticed after repair or rebasing of a denture. Many of the currently manufactured teeth are so formulated that they do not exhibit crazing.

3. MATERIALS INVESTIGATED

The trade names and manufacturers of teeth included in this investigation are as follows:

Trade Name	Manufacturer
Micromold	Austenal Laboratories, Inc.
Vitalon	Austenal Laboratories, Inc.
Trubyte Acrylic	The Dentists' Supply Co. of New York
Trubyte Dentron	The Dentists' Supply Co. of New York
Denta-Pearl	H. D. Justi and Son, Inc.
Denta-Pearl S-R	H. D. Justi and Son, Inc.
Luxene	Luxene, Inc.
Dura-Blend	Myerson Tooth Corporation
Plastic-Five-Phase	Universal Dental Co.
Verident	Universal Dental Co.
Biocryl	Biodent Mfg. Co., Heidelberg, Germany

4. EXPERIMENTAL PROCEDURE AND RESULTS

4.1. CRAZING

A study of the crazing of plastic teeth was made on all brands listed above. This consisted of observing the effect of a solvent on the teeth after giving them definite treatment. Craze tests were made on plastic teeth in three conditions; (a) as received from the manufacturer, (b) after a curing cycle such as dentures normally receive in dental laboratories and (c) after a curing

---

* All teeth procured and tested 1950-52.

cycle in which special precautions were taken to prevent water from coming into contact with the tooth.

It was found that it was unnecessary to process the teeth in denture base material for the curing cycle. The technique used was as follows:

(a) The teeth were invested in gypsum.

(b) The invested teeth were heated in a temperature-controlled water bath.

(c) The flask was bench cooled to room temperature.

(d) The case was deflasked and the teeth were allowed to dry to room temperature for several hours or longer.

The craze test consisted of immersing the teeth three times for short intervals (5 sec.) in a solvent (methyl methacrylate monomer or ethyl alcohol). At first several solvents were used. Methyl methacrylate monomer and alcohol were finally chosen for test solvents as they would more likely be encountered in practical use: the monomer, when a denture is repaired or rebased, and the alcohol when beverages are taken orally.

The crazing was observed by visual inspection and also by the use of a binocular microscope. The specimens were given a second treatment after a day of storage if they did not show crazing immediately.

Table 1 shows 5 brands that did not craze, one brand that exhibited crazing on some specimens and no crazing on other specimens and 5 brands that showed very definite crazing by the solvent test.

The types of crazing observed were quite varied as shown by examples in Figures 1, 2 and 3. It was not possible to judge accurately the degree of crazing because some specimens contained many fine cracks while others contained fewer but larger cracks.

Examination of sections of crazed teeth, under a microscope, indicated that the depths of the cracks were quite varied ranging from 0.2 to 1 mm. Teeth heated to 212°F in water after investing showed more crazing than those heated to 160°F.

Experiments were conducted to determine if craze-susceptible teeth would craze when heated under conditions such that no water came in contact with them during heating. Several procedures were used for this, such as (a) drying out free water from the gypsum by heating or reduced pressure, (b) surrounding the teeth with tin foil, and (c) coating the teeth with a thick layer of wax before investing.

In all cases where water, either in liquid or vapor phase, was prevented from coming in contact with the teeth, no crazing was produced by the solvent tests. This leads to the conclusion that water plays an important roll in the crazing phenomena.

Practical cases of dentures worn by patients exhibit this same crazing but usually to a much less degree. Figure 4 shows a practical immediate denture which was rebased after eight months. The crazing appeared in the plastic teeth after rebasing, all six of the anterior teeth showed severe crazing and had to be replaced.

4.2 MECHANICAL PROPERTIES

Data were obtained on the hardness (Knoop), indentation resistance, strength, modulus of elasticity and elastic recovery of the plastic teeth investigated.

(a) Hardness.

The hardness was observed with the Knoop indentation method at a temperature of 70° ± 2°F, using a 100 gram load with a 10 second descent, and 20 second contact. The teeth were cut and polished to a smooth flat surface about 2 mm from the tip of the cusps. The final polish was made with fine polishing paper (3/0) followed by fine whiting. The teeth were measured in the "as received" condition, that is, not dried or stored in water before testing. The Knoop numbers are given in Table 1.

(b) Indentation Resistance and Recovery.

Flat specimens 2 to 3 mm thick were cut from plastic teeth. The surfaces were finished with 1 G sand paper. The specimen was placed in a Rockwell Superficial Hardness Tester and subjected to a 30 KG major load with a 1/2 inch ball for ten minutes. At the end of this period the depth of indentation was observed, the major load was removed and the minor load of 3 KG was applied for 10 additional minutes. At this time the depth of indentation was again observed. The recovery value is expressed in per cent of the depth of indentation. The results are shown in Table 1 for the various brands of teeth.

(c) "Indentation Strength"

Since in the procedure described above the indentor sphere will continue to penetrate the resin until the area of contact is sufficient to resist the force exerted on the specimen, it is possible to calculate the strength of the resin from the data obtained. The projected area of the indentation can be calculated from the depth reading on the Rockwell Superficial Hardness Tester with a correction for the slight indentation of the minor load. The load divided by this area gives a measure of the strength in simple terms such as pounds per square inch [1]. The data obtained for indentation strength specimens cut from plastic teeth are shown in Table 1.

(d) Stress-strain Relationship.

Cylindrical specimens 3 mm in diameter by 6 mm long were machined from the plastic teeth. The specimens were placed in a Tinius Olsen Testing Machine and loaded in compression with a head speed of 0.20 inches per minute. The specimens were so mounted that steel pins 1/2 inch in diameter contacted the specimen in such a way that two Tuckerman strain gages could be straddled over the specimens, Figure 5. The strain was recorded at 2 1/2 pound load increments.

The modulus of elasticity was calculated from the straight portion of the stress-strain curve below 7000 psi (Figures 6, 7 and 8). The yield strength was arbitrarily taken as the stress at which the deformation produced by a unit stress equals or exceeds 1.25 times that observed in the first few increments of stress. The values for the modulus of elasticity and yield point are shown in Table 1.

4.3 ABRASION OR WEAR RESISTANCE

The data obtained on abrasion of teeth is of a very preliminary nature and is reported at the present time for evaluation of the test method. The method used involves abrading the teeth in a ball mill and observing the loss of weight. The mill used was a one-quart Abbe porcelain jar mill rotating at 69 revolutions per minute. To compare the wear of different brands of teeth the mill was charged with the abrasive material and a total of 40 to 50 teeth of various brands and was run for periods of time ranging from 2 hours to several hundred hours. The relative effect of several different abrasive materials and of different tooth shapes is shown in Tables 2 and 3. Relative wear of eight brands of teeth when placed in the mill with steel balls with and without additional abrasives is given in Table 4. Most consistent results were obtained when 1/4 inch steel balls with #200 aloxite powder in water was used as the abrasive materials according to the following technic:

1. Wash 1350 grams of 1/4-inch carbon steel balls with distilled water and drain off as well as possible.

2. Place the balls, 20 grams of #200 aloxite powder, and 100 grams of water in the one-quart jar; center it on the mill and run it for 2 hours to clean and condition the jar and balls.

3. Immediately after the above step, clean out the used aloxite powder, rinse the jar and balls with distilled water, and add 20 grams of fresh #200 aloxite, 100 grams distilled water, and from 40 to 50 weighed teeth. The actual test should be run immediately after the cleaning charge.

4. The teeth used should be fairly large---from 0.3 to 0.5 grams except in the case of teeth with mechanical retention holes. For these a range of 0.25 to 0.45 grams will give about the same size teeth as the others. These teeth should be marked clearly. The method used was to bore shallow holes in recessed parts of the teeth and then fill these holes with drawing inks of various colors.

5. Each tooth should be weighed separately before and after treatment in the mill, and the percentage loss of weight calculated.

6. For comparison of brands the average loss for a given brand can be divided by the loss for some brand selected as a standard. This gives a number that seems to be relatively constant for any run made with the same abrasive and conditions.

While the data obtained from the ball mill tests do show differences between the various brands of teeth, no data have yet been obtained indicating whether or not the test results approximate wear which occurs in service. Much more research will be needed before any statement can be made on the relative clinical wear resistance of the various brands of teeth.

5. DISCUSSION OF RESULTS

The data obtained indicate that crazing is affected by the amount of internal strain present in the teeth. Thus, the craze resistance is a function of the processing conditions. It is evident that the water absorbed by plastic teeth which are susceptible to crazing plays an important role, since it was shown that when water is prevented from contacting the tooth all the teeth so treated were craze resistant. Also teeth invested in dental stone and heated in boiling water exhibit more crazing by the solvent test than do those heated to 160°F in water. This may be caused by the greater mutual solubility of resin and water at the higher temperature. Although the mechanism of crazing is not established, studies are being made on the theory that the relative solubility of water and resin changes with temperature and that the dimensional change caused by curing and cooling is the basic cause of the residual strain in the resin [2]. So far as the present experimental data are concerned the facts correlate satisfactorily, but more observations of a precise nature are necessary to prove the validity of this concept. No correlation between complete craze resistance and the amount of water sorption was found in this investigation. In general, crazing was less for brands of teeth which showed good mechanical properties as evaluated by the methods used in this investigation.

Unfortunately there is no practical method for fabricating dentures under water-free conditions, as an excess of free water is present in the set dental stone or plaster used to invest cases for processing. It is considered best, therefore, to use teeth that do not exhibit crazing if this difficulty is to be overcome.

The indentation hardness values determined by the Knoop Method show that the range in hardness is small, only about 4 Knoop numbers. This is to be expected because the teeth are essentially methyl methacrylate polymers with the exception of Luxene which contains considerable vinyl polymer.

The ability of the tooth to resist deformation from pressure applied to a local area such as biting on a hard particle of food, bone, etc. is important. To evaluate this property the rate of indentation of a sphere under constant load was used. The rate of indentation is dependent upon the elastic and plastic properties. The ball penetrates rapidly for the first few seconds and then gradually decreases until it comes to rest. For practical procedures a 10-minute load application was found to approach very closely a static condition. This provided a simple method for observing the flow properties and resistance to indentation. The probable error of the depth of indentation under the best condition is of the order of 2 per cent. The depth of indentation for the different brands of teeth studied varied from 0.090 mm to 0.148 mm with the values for most of the brands between 0.095 and 0.105 mm. This average value 0.103 mm, is between those of denture base resin 0.096 mm and average acrylic filling resins (0.108 mm) and is much greater than that of dental amalgam (0.043), Figure 9 .

One of the fundamental properties of resins is the property of absorbing energy by deformation and returning closely to its original position. This is a factor in denture prosthesis as the energy absorbed by oral structures probably plays an important role in resorption of tissue. The recovery of the plastic teeth as measured by the decrease in depth of the indentation of a spherical ball when the load is removed or reduced, was used to obtain numerical values for the different teeth. The values are expressed in per cent of the original depth of the indentation.

The strength of plastic teeth is low. The yield point as calculated from the stress-strain curves ranges from 6,400 to 8,600 psi. These values are considerably lower than the maximum calculated stress of 17,000 psi on cuspids as reported by Skinner [3] . The fact that clinical cases do not exhibit such deformation is partially explained by the high recovery value. The best mechanical test developed as indicated by precision and repeatability is the application of the Tuckerman strain gage to small specimens. The data so obtained with constant rate of loading were plotted to show the stress-strain relation. The modulus of elasticity computed over stress ranges of 1,000 to 7,000 psi is shown in Table 1. The variation of different brands was from 280,000 to 420,000 psi. This property is very significant as it indicates the stiffness of these materials. The teeth having a low modulus exhibit extreme crazing.

Abrasion or wear resistance of plastic teeth is one of their weakest properties. At present the work on abrasion measurement is only in the developmental stage. It is considered essential that new and more practical test methods must be developed to evaluate this factor.

The data reported in this paper in combination with previous data and clinical experience have been utilized for the preparation of a proposed specification (see below) for plastic teeth. No abrasion test is included in this specification since none of the tests so far devised have yet been correlated with clinical wear.

6. SUMMARY

1. Data is presented on mechanical properties of eleven brands of plastic teeth.

2. The mechanical properties are quite low in comparison with other materials used for restorative purposes in the oral cavity.

3. Some brands of teeth were found to be susceptible to crazing after processing as would be done in curing a denture. Five brands crazed consistently, five brands did not craze and one brand crazed in some instances. Crazing was not observed on any teeth if water was prevented from contacting them during heating.

4. Crazing is caused by relief of internal strain and water is an important

factor in this mechanism.

5. The resistance to crazing was found to be the most outstanding difference between the commercial brands studied.

6. No definite correlation was found between the physical properties studied and crazing although, in general, the high physical properties were exhibited by materials not susceptible to crazing.

8. PROPOSED SPECIFICATION FOR PLASTIC TEETH

1. SCOPE AND CLASSIFICATION:

1.1 The teeth described under this specification shall be plastic. Teeth shall be life-like and so molded and colored that they shall closely approximate natural teeth in overall appearance. The teeth shall be suitable for the construction of complete and partial dentures by techniques in general use at the present time by the dental profession.

1.2 Types - This specification covers three types of teeth and one grade:

Type I - Anterior Teeth: Shall consist of molds of teeth approximating the various forms of human anterior teeth, labially and lingually.

Type II - Anatomic Posterior Teeth: Shall consist of molds of teeth approximating the forms of human posterior teeth.

Type III - Non-Anatomic Posterior Teeth: Shall consist of molds of teeth approximating the forms of human posterior teeth in respect to lateral surfaces but having modified occlusal surfaces.

1.2.1 Grade - All types shall be of the highest grade.

2. APPLICABLE SPECIFICATIONS:

2.1 The following Federal Specification, of the issue in effect on date of invitation for bids, form a part of this specification:

U-D-226 - Denture-Base-Material (Acrylic resin or mixtures of acrylic and other resins)

2.2 Other Publications: American Dental Association Specification No. 12. Journal American Dental Association, Vol. 44, 285 March 1952.

3. REQUIREMENTS:

3.1 Material - Shall be a plastic capable of attaining and maintaining a high polish under conditions found in the oral cavity. The material shall not be adversely affected by processing and reprocessing against Plaster of Paris or artificial stone (hydrocal) using normal techniques employed in the repair and rebasing of dentures made from resins which meet American Dental Association Specification No. 12 or Federal Specification U-D-226. The material shall be methyl methacrylate polymer, copolymer of methacrylates, or combinations of other resins having suitable properties for the use intended.

3.2 Workmanship - The workmanship shall be free of all defects and shall be first-class in every respect.

3.3 General Requirements:

3.3.1 The plastic teeth shall be life-like in appearance.

3.3.2 The teeth shall contain no ingredients which shall be toxic or irritating to the oral tissues.

3.3.3 The teeth shall have a smooth glossy surface and shall be capable of being cut and repolished to a glossy surface.

3.3.4 The teeth shall be free of any porosity, either on the surface or when sectioned and observed by low magnification (10X).

3.3.5 Translucence: All teeth, anterior and posterior, shall consist of a gingival, or body, color and a translucent incisal or occlusal, the two to be blended together in such a manner as to simulate the color blend of natural teeth, with no line of demarcation between incisal (occlusal) and gingival on the labial (buccal) aspects of the teeth.

3.3.6 Color: The shades of teeth shall be reproductions of those found in the human mouth, ranging from the light shades of young persons to the dark shades of the elderly, including both translucent and semi-translucent incisal tips, as found in natural teeth. The shades of the teeth shall so color-match the corresponding tooth on the shade guide that no perceptible difference can be noted by visual observation in daylight.

3.4 Detail Requirements:

3.4.1 Bonding: The teeth shall form a chemical bond with acrylic denture base resin when cured by the heat processing technique. Strength of the bond shall be not less than 4,500 lbs per sq in.

3.4.2 Hardness: The teeth shall have a Knoop Indentation Hardness of 17.0 kg/mm^2 or more.

3.4.3 Indentation Resistance: The teeth shall not be penetrated more than 0.11 mm by a 1/2" steel ball loaded at 30 kg for 10 minutes. The recovery of the depth of the indentation shall be at least 80% in 10 minutes after the 30 kg load is released.

3.4.4 Blushing: The teeth shall not blush, blanch, or change color when processed in boiling water.

3.4.5 Distortion: The teeth shall not distort or change in shape when heated in water at 100°C for one hour.

3.4.6 Craze Resistance: The teeth shall be craze resistant to solvents both before and after being subjected to the curing heating cycle in a water bath.

4. INSPECTION AND TEST:

Methods of Inspection and Test - Compliance with all detail requirements of this specification shall be determined by the following methods and procedures. The tests shall be conducted at room temperature (20 to 25°C.) unless otherwise stated.

4.4.1 Bonding: Prepare cylindrical molds, approximately 3 inches long and 0.3 inch in diameter, in a denture flask using dental stone (hydrocal) as the mold material. Place a posterior tooth in the center with the occlusal and ridge lap surface normal to the long axis of the mold. Flush the mold with three applications of hot modern synthetic household detergent solution (one teaspoon to one pint of water) and rinse with clean boiling water. Pack the mold, with the tooth in the center, by the normal denture packing technique using clear denture base resin which complys with American Dental Association Specification No. 12 or Federal Specification U-D-226. Close the flask, process for one hour at 74 ±1°C, and then place the flask in boiling water for 30 minutes, remove it and allow it to cool to room temperature in air. Open the flask, remove the specimen of resin and machine it to 0.25 inch diameter so that none of the base resin remains on the sides of the tooth and that only the occlusal and ridge lap surfaces contact the base resin. Place the resin in a suitable tension machine and pull apart at approximately 0.2 inch per minute head speed. The average of three specimens shall be used to determine the bonding strength. (Ref. J. Am. Dental Assoc., Vol. 44; 285, March 1952).

4.1.2 Hardness: The hardness shall be determined by the Knoop Indentation Method, using 10 seconds descent and 20 seconds contact with 100 gram load. The specimens used shall be prepared from sections of the teeth polished flat and parallel using progressively finer polishing paper. The final finish shall be produced with No. 3/0 emery paper followed by magnesium oxide powder on a wet polishing wheel. The test specimens shall be between 2 and 3 mm in thickness and have a smooth glossy surface. The hardness shall be determined on two anterior and two posterior teeth, with 10 indentations on each, and the average of all 40 of the indentations shall be recorded to the nearest 0.1 kg per sq. mm.

4.1.3 Indentation Resistance: Indentation resistance shall be determined on a Rockwell Superficial Hardness Tester. Specimens of teeth shall be prepared as described under the section on Hardness, or the same specimens shall be used. The specimen shall be subjected to a load of 3 Kg on a 1/2 inch diameter steel ball, designated as the minor load, then a load of 30 kg shall be applied, designated as the major load. The major load shall be allowed to contact the specimen for 10 minutes and the depth of indentation of the ball due to the major load shall be measured on the dial gage of the instrument. The major load shall be released, leaving the minor load on the steel ball. After 10 minutes from the release, the depth of indentation shall be recorded again. The pene-

tration shall be the amount of indentation of the ball at the end of 10 minutes of major load application. The recovery shall be the percent of return of the ball in 10 minutes from the release of the major load with only the minor load on the ball. The depth of the indenataion shall be recorded to 0.001 mm for individual determinations and the average of at least three values to the nearest 0.01 mm for the final result. The recovery shall be the average indentation at 10 minutes major load application divided into the average difference between the major load indentation and indentation after the major load has been released (minor load in contact) for 10 minutes expressed in percent. The same indentations shall be averaged for the penetration and the recovery.

4.1.4 Blushing Distortion, Craze Resistence: One or more anterior and posterior teeth of each shade purchased shall be used for this test. The test specimens shall be submerged in test tubes of water. The tubes shall be placed in a water bath so that they do not contact the vessel. The water bath shall be heated from room temperature to 100°C in from 5 to 20 minutes and held at boiling temperature (100°C) for one hour. The teeth shall be removed and cooled to room temperature in air. Then the teeth shall be immersed in methyl methacrylate monomer for 5 seconds and removed. This immersion is repeated after one minute and the teeth allowed to dry on a towel for two hours at room temperature. If any blushing, blanching, or change in color, any distortion or any cracks can be seen, by visual examination or low power magnification, the teeth fail to meet these requirements.

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3. Skinner, E. W., The Science of Dental Materials, Third Ed., p. 17 (W. B. Saunders Co., 1946).

Table 1. Physical Properties of Plastic Teeth

Trade Name	Craze*	Knoop Number		Indentation at 10 min. 1/2"ball, load-30 Kg. Recovery after 10 min. under 3 Kg load.		Indentation Strength	Modulus of Elasticity	Yield Point
		Range	Average	Indentation	Recovery			
		Kg/mm^2	Kg/mm^2	mm	%	psi	x10^5, psi	psi
Micromold	#	17.8-18.2	18.2±0.4	0.098	91	9,900	3.8±0.3	8,600
Vitalon	Yes	17.2-19.7	18.2±0.5	0.148	70	6,400	2.8±0.5	6,400
Trubyte Acrylic	Yes	18.2-19.2	18.6±0.2	0.106	82	9,200	3.6±0.1	7,100
Trubyte Dentron	No	18.2-26.0	21.0±1.6	0.090	91	10,800	3.8±0.1	8,600
Dental Pearl	Yes	19.6-19.8	19.6±0.3	0.099	87	9,800	3.9±0.2	8,600
Dental Pearl "SR"	No	19.4-21.2	20.0±0.4	0.090	88	10,800	3.8±0.3	8,100
Luxene	No	14.5-14.6	14.5±0.4	0.099	82	9,800	4.1±0.1	8,400
Dura-Blend	No	18.2-19.4	18.9±0.4	0.103	88	9,400	4.2±0.4	8,400
Plastic Five-Phase	Yes	17.9-18.9	18.2±0.3	0.104	87	9,300	3.6±0.2	7,600
Verident	No	19.0-20.9	19.7±0.4	0.098	89	9,900	3.4±0.3	6,700
Biocryl	Yes	17.9-20.8	19.4±0.4	0.098	88	9,900	3.1±0.3	8,100

* Solvents used: methyl methacrylate monomer and ethyl alcohol.

\# Some specimens crazed, others did not.

Table 2

Effect of Various Abrasives on Weight Loss of Teeth in Ball Mill Test

Abrasive	Weight loss per hour,%	
	dry	wet
Oxford crystal feldspar	0.002	----
No. 18 glass beads	0.002	----
Flint pebbles	0.01	0.04
Steel balls 1/4 inch	----	0.02
Steel balls 1/2 inch	----	0.1
Flint pebbles roughened with carborundum	----	0.2
No. 200 aloxite, 1/4 inch steel balls	0.2	0.7
Fine carborundum, 1/4 inch steel balls	0.3	----

Table 3

Effect of Tooth Shape on Weight Loss of Teeth in Ball Mill Test

Brand	Abrasive	Time	Cuspid		Lat. Incisor		Cen. Incisor	
		hr.	Wt.g	Loss,%	Wt.g	Loss,%	Wt.g	Loss,%
G	Wet 1/2" balls	25	.35	2.34	.23	3.60	.37	2.36
E	"	25	.39	1.65	.28	2.29	.43	1.67
B	"	25	.33	2.24	.21	2.72	.33	2.55
G	Wet 1/4" balls	20	.38	.37	.28	.50	.27	.48
E	"	20	.40	.18	---	----	.48	.17
B	"	20	.35	.37	.23	.75	.37	.44

Table 2

Effect of Various Abrasives on Weight Loss of Teeth in Ball Mill Test

Abrasive	Weight loss per hour,%	
	dry	wet
Oxford crystal feldspar	0.002	----
No. 18 glass beads	0.002	----
Flint pebbles	0.01	0.04
Steel balls 1/4 inch	----	0.02
Steel balls 1/2 inch	----	0.1
Flint pebbles roughened with carborundum	----	0.2
No. 200 aloxite, 1/4 inch steel balls	0.2	0.7
Fine carborundum, 1/4 inch steel balls	0.3	----

Table 3

Effect of Tooth Shape on Weight Loss of Teeth in Ball Mill Test

Brand	Abrasive	Time	Cuspid		Lat. Incisor		Cen. Incisor	
		hr.	Wt.g	Loss,%	Wt.g	Loss,%	Wt.g	Loss,%
G	Wet 1/2" balls	25	.35	2.34	.23	3.60	.37	2.36
E	"	25	.39	1.65	.28	2.29	.43	1.67
B	"	25	.33	2.24	.21	2.72	.33	2.55
G	Wet 1/4" balls	20	.38	.37	.28	.50	.27	.48
E	"	20	.40	.18	---	----	.48	.17
B	"	20	.35	.37	.23	.75	.37	.44

Table 4

Relative Wear of Various Brands of Teeth in Ball Mill test

Brand	Wet aloxite powder and 1/4" steel balls*			Dry Aloxite 1/4" steel balls	Dry fine carborundum 1/4" steel balls	Wet 1/2" steel balls	Wet 1/4" steel balls
I	1.92	2.12	1.96	1.95	1.93	----	.98
C	----	1.21	1.17	1.28	1.17	----	----
H	1.16	1.09	1.04	1.49	1.08	----	----
D	1.09	1.12	1.13	1.28	1.13	----	.95
G	1.03	1.04	1.07	1.15	1.04	1.09	.89
B	1.00	1.00	1.00	1.00	1.00	1.00	1.00
F	.99	.96	.99	1.16	.99	----	----
E	.52	.46	.54	.36	.53	.75	----
K	----	----	----	----	----	.86	.75

* Values for three runs are given to show repeatability of results.

Figure 1. Example of crazing produced by immersion of plastic tooth in solvent.

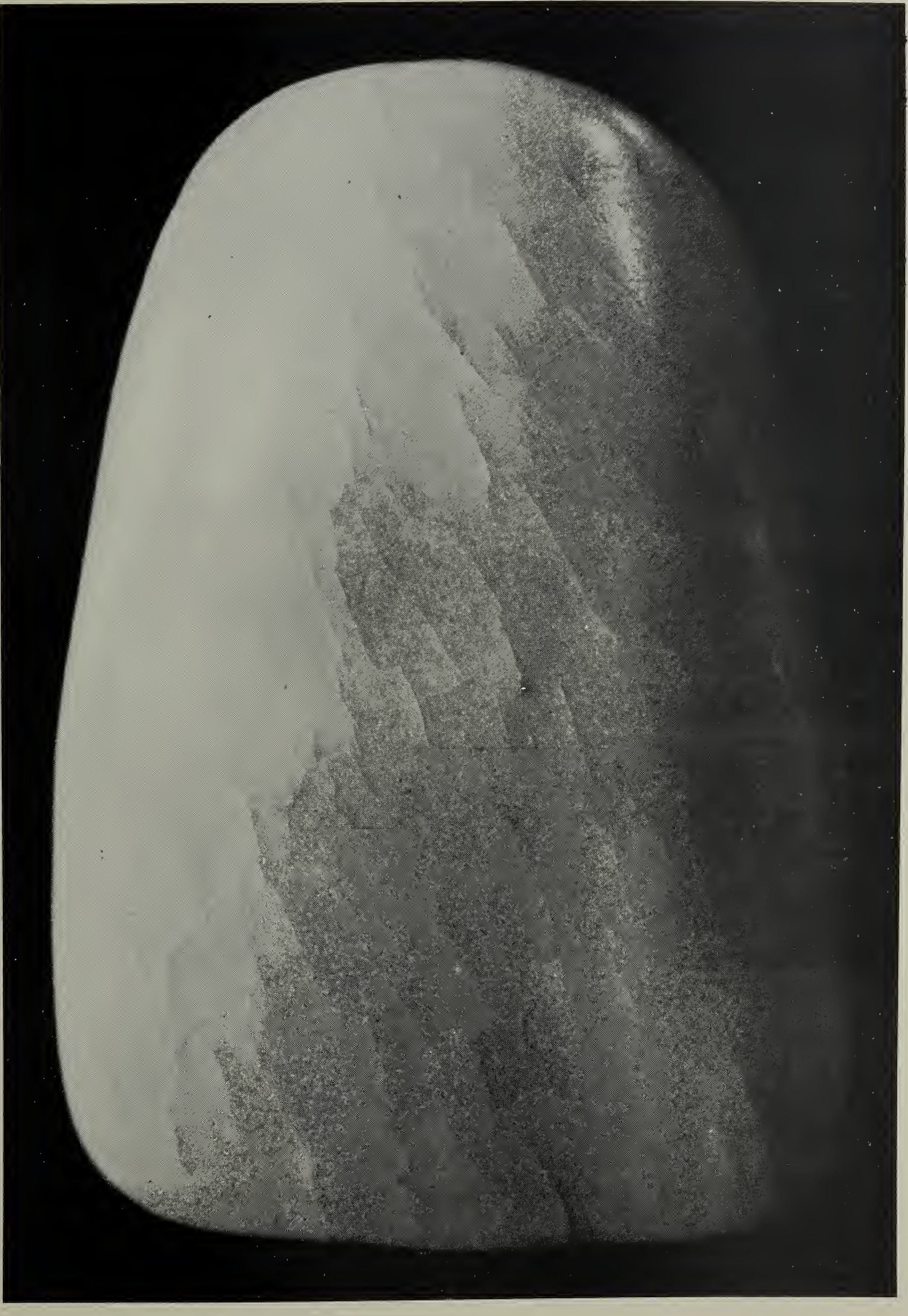


Figure 2. Example of crazing produced by immersion of plastic tooth in solvent.

Figure 3. Example of crazing produced by immersion of plastic tooth in solvent.

Figure 4. Crazing of teeth on immediate denture after rebasing.

Figure 5. Specimen and gages in position between the platens of the testing machine used to record stress-strain relationships.

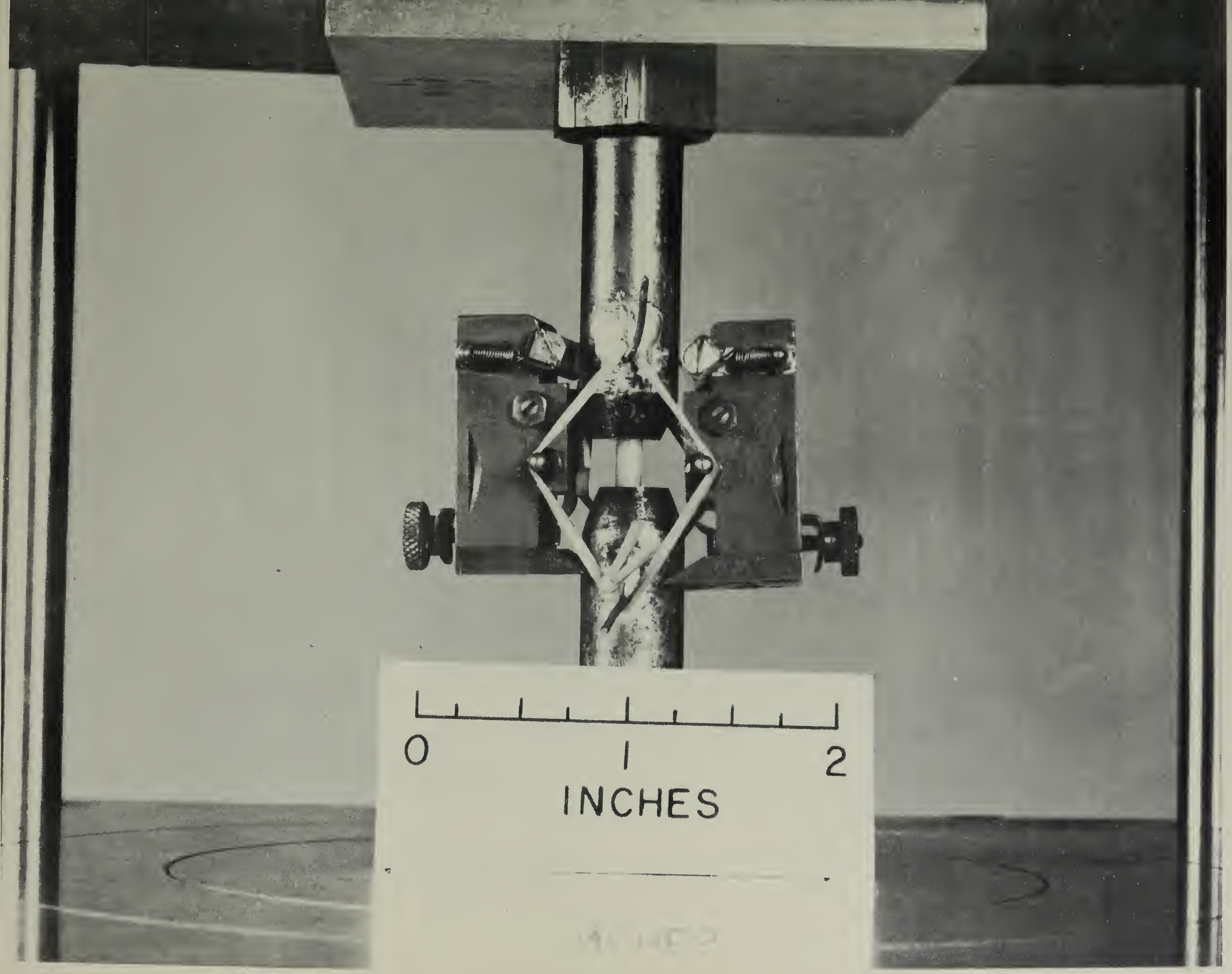

0
1
2
INCHES

Figure 6. Stress-strain curves for five brands of plastic teeth.

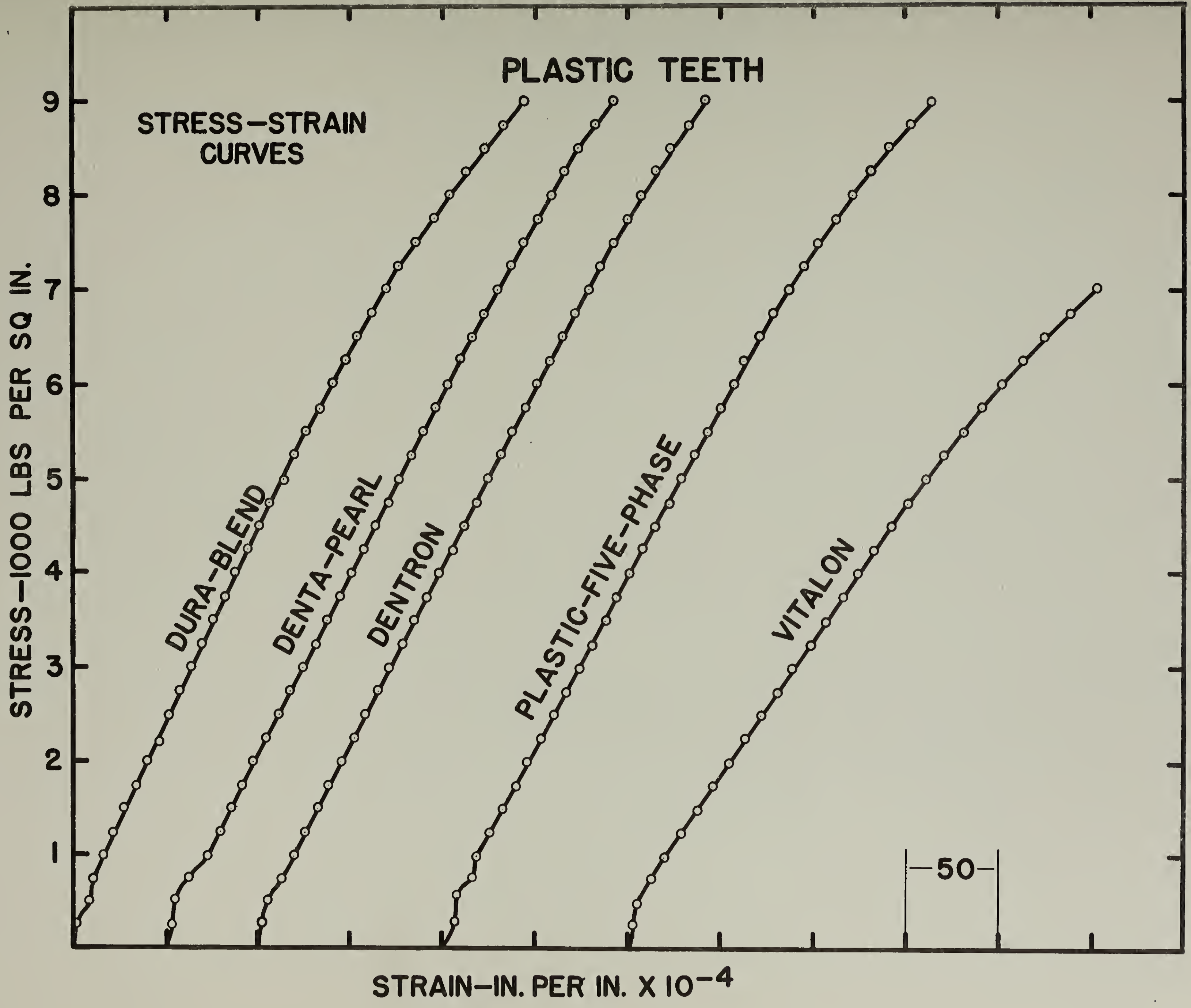

PLASTIC TEETH
STRESS—STRAIN CURVES
DURA-BLEND
DENTA-PEARL
DENTRON
PLASTIC-FIVE-PHASE
VITALON
—50—
STRESS—1000 LBS PER SQ IN.
9
8
7
6
5
4
3
2
1
STRAIN—IN. PER IN. X 10^{-4}

Figure 7. Stress-strain curves for four brands of plastic teeth.

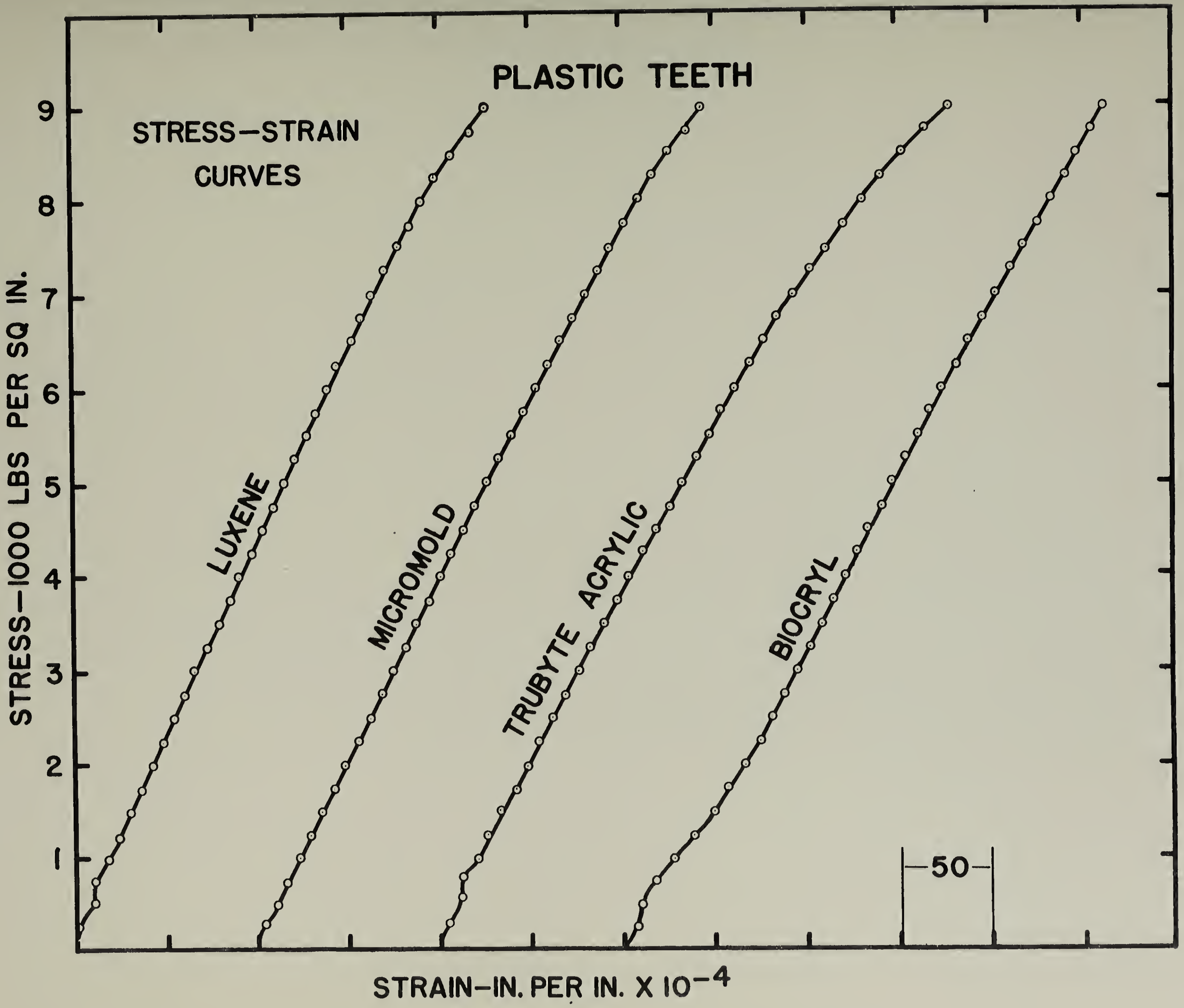

PLASTIC TEETH
STRESS—STRAIN
CURVES
LUXENE
MICROMOLD
TRUBYTE ACRYLIC
BIOCRYL
—50—
STRESS—1000 LBS PER SQ IN.
9
8
7
6
5
4
3
2
1
STRAIN—IN. PER IN. X 10−4

Figure 8. Stress-strain curves for two brands of plastic teeth.

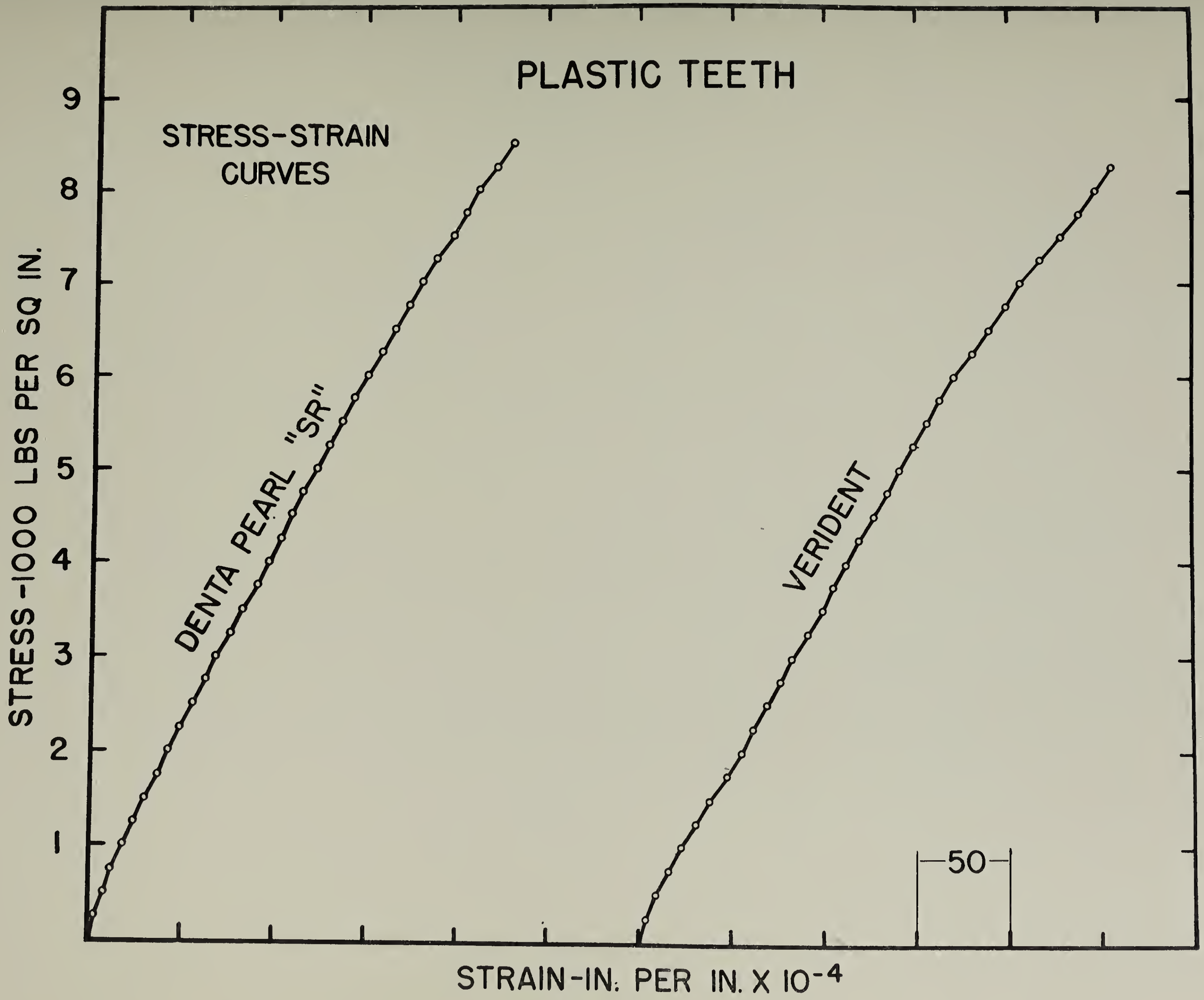
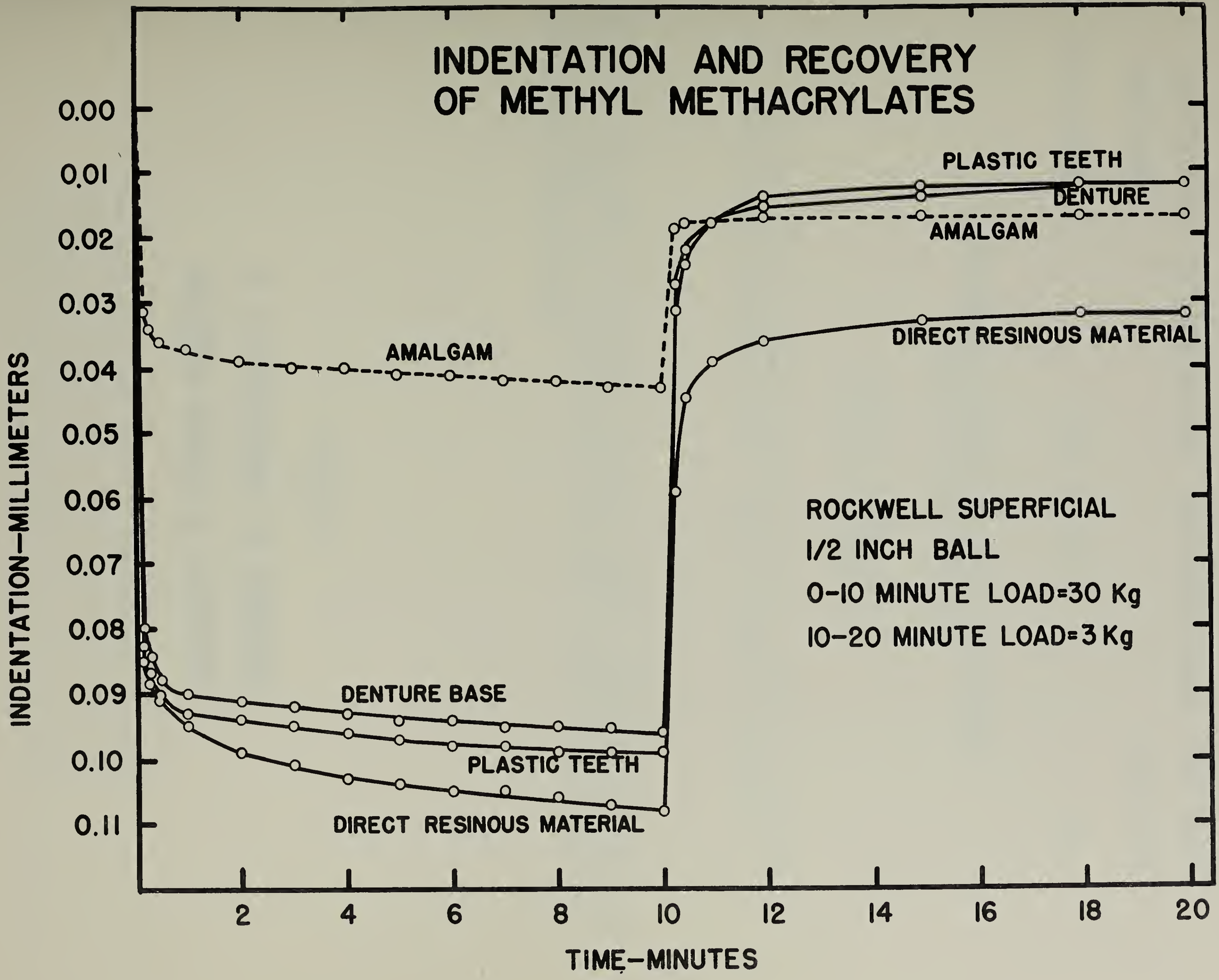

PLASTIC TEETH
STRESS-STRAIN CURVES
DENTA PEARL "SR"
VERIDENT
STRESS-1000 LBS PER SQ IN.
9
8
7
6
5
4
3
2
1
—50—
STRAIN-IN. PER IN. X 10^{-4}

Figure 9. Comparison of indentation and recovery of plastic teeth (average of ten brands), denture base resin, direct filling resins, and amalgam.


INDENTATION AND RECOVERY
OF METHYL METHACRYLATES
PLASTIC TEETH
DENTURE
AMALGAM
DIRECT RESINOUS MATERIAL
AMALGAM
DENTURE BASE
PLASTIC TEETH
DIRECT RESINOUS MATERIAL
ROCKWELL SUPERFICIAL
1/2 INCH BALL
0-10 MINUTE LOAD=30 Kg
10-20 MINUTE LOAD=3 Kg
INDENTATION-MILLIMETERS
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
0.11
TIME-MINUTES
2
4
6
8
10
12
14
16
18
20

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
0708-20-3824	June 30, 1954	3380

MEASUREMENT OF STRAIN IN METHYL METHACRYLATE CAUSED BY WATER SORPTION

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

MEASUREMENT OF STRAIN IN METHYL METHACRYLATE CAUSED BY WATER SORPTION

Abstract

A method of determining the change in the internal residual strain in polymerized methyl methacrylate during its sorption of water has been developed. A bonded, wire strain gage embedded within the polymer is employed to determine the strain increments. Henry's and Fick's laws appear to be inapplicable for large specimens totally immersed in water. An assumption is made to the effect that the change in the strain is in a direct linear relationship to the amount of water sorbed. It is not believed that this assumption causes so great an error as to result in the contradiction of Henry's and Fick's laws.

1. INTRODUCTION

The crazing of resins has been attributed mainly to the change in the characteristics of the internal residual strain in the resin during its action as an absorbent of water. For this reason the development of a method of determining the change in the internal residual strain in polymerized methyl methacrylate was desirable. Since the primary concern was with the internal effects, such strain gages as the Tuckerman, acoustical, etc., could not be used. The technique of photoelasticity was thought to be of practical use, but, since the specimens were to be placed in a water bath thereby making the determination of the change in the strain extremely difficult and since each specimen would have to be calibrated for the effective use of this technique, this method was discarded in favor of using bonded wire strain gages. The advantages of this type of gage lie in the remote measurement of the change in the strain and in the manufac-

urers calibration of the gages. There are, however, three major disadvantages in the use of these gages.

Since the change in the strain is determined by resistance measurements, any water sorption by the gage causing electrical leakage is detrimental to the results. Also excessive strains and temperatures will destroy their effectiveness, although the standard gages will withstand strains as high as 1% and temperatures up to 80°C for paper gages and 150°C for phenolic impregnated paper gages.(1) Finally, the effective modulus of elasticity of the gages must be lower than that of the material in which they are to be used. The gage's modulus of elasticity may be lowered by the addition of lamina of paper and cement to the surface of the gage.

The theory of the gage is based upon the phenomenon that a wire's resistance, to a first approximation, is directly proportional to a distortion along its longitudinal axis. Hence, any change in strain will result in a corresponding change in the resistance of the gage, both in sign and relative magnitude. The strain is determined from the gage factor which is determined by the manufacturer. The gage factor is defined by $K = \frac{dR/R}{dS}$, where K is the gage factor, R is the resistance of the gage and S is the strain.

METHOD

The gages used were the type designated by the manufacturer, Baldwin-Lima-Hamilton Corporation, as type A-5 with a gage factor of 1.99±1% and a resistance of 120±0.5% ohms. A photograph of the type of strain gage used is shown in Figure 1. The wheatstone bridge employed was the Baldwin-Lima-Hamilton Corporation's type L strain indicator which gives the readings directly in u in/in. This was complimented with their six channel switching and balancing unit

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(1) Domestic price list, p. 4, July 15, 1953. Balwin-Lima-Hamilton Corp. Philadelphia 42, Pennsylvania.

which permits the use of six gages simultaneously and places the strain readings at the same fiducial point if desired. The arrangement of the apparatus is shown in Figure 2.

The mold used was formed by casting artificial stone around a brass master form, the gage leads being sealed in one wall. The mold was then linedwith 0.003" foil of pure tin as shown in Figure 3. A mix of methyl methacrylate polymer(1) and methyl methacrylate monomer(2) was then placed around the gage, pressure and heat were then applied to further polymerize the mixture. The specimens were cured for a period of twenty hours in an air bath at a temperature of 55°C. Since air has a low specific heat, the heat of polymerization of the resin cannot be removed rapidly enough to maintain a constant temperature within the specimen. To prevent any damage to the gage, the temperature must be kept below 80°C. Hence, it was necessary to use a low initiating temperature in order to keep the temperature within the specimen below the desired limit and eliminate any thermal damage to the gage. Since a flash type mold was used, the true pressure is not known, although it is estimated to be of the order of 2000 psi.

The positioning of the gage within the resin is shown in Figure 4.

The specimens having been cured and allowed to cool to room temperature, were removed from the mold and placed in a water bath at a temperature of 37°C ±0.1°. The specimens were then allowed 45 minutes to attain thermal equilibrium and the bridge balanced so that it registered a strain of 1000 u in/in. The changes in the strain were determined in the following manner: the first gage was placed in the bridge circuit by closing the corresponding switch in the switching and balancing unit and then given a thirty-second stabilizing period before the strain change was read from the strain indicator. Having determined

(1) Manufactured by E. I. duPont de Nemours and Co., Polychemicals Department, Washington, West Virginia. Color: H 7500 Composition HG41

(2) Manufactured by the Rohm and Haas Co., Philadelphia, Pa., with 0.006% Hydroquinone added as an inhibitor.

The contradiction of Fick's and Henry's laws is probably due to one, or both, of the following two reasons:

(1) Fick's and Henry's laws are not applicable to the type of specimens studied under the conditions of the experiment.

(2) The assumption that the strain change is in a linear relationship to the amount of water sorbed is false.

Although it is not likely that the change in strain is in a direct linear relationship to the water sorbed, it is not believed that the error caused by this assumption is so great as to cause a contradiction of the predictions of the general sorption laws. It therefore appears to be far more reasonable that the predictions of Fick and Henry are inapplicable to the type of specimens studied.

SUMMARY

The change in the internal residual strain of polymerized methyl methacrylate during water absorption was determined by embedding a bonded wire strain gage in the polymer. Henry's and Fick's laws were found to be inapplicable for the type of specimen under investigation.

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6. Testing Topics, issued quarterly by Baldwin-Lima-Hamilton Corp., Philadelphia 42, Pennsylvania.

Figure 1. An enlargement of the type A-5 strain gage.

The length of the measuring portion of the gage is 1/2 inch, its width 15/64 inch. The overall dimensions of the gage body are 3/8 inch by 13/16 inch.

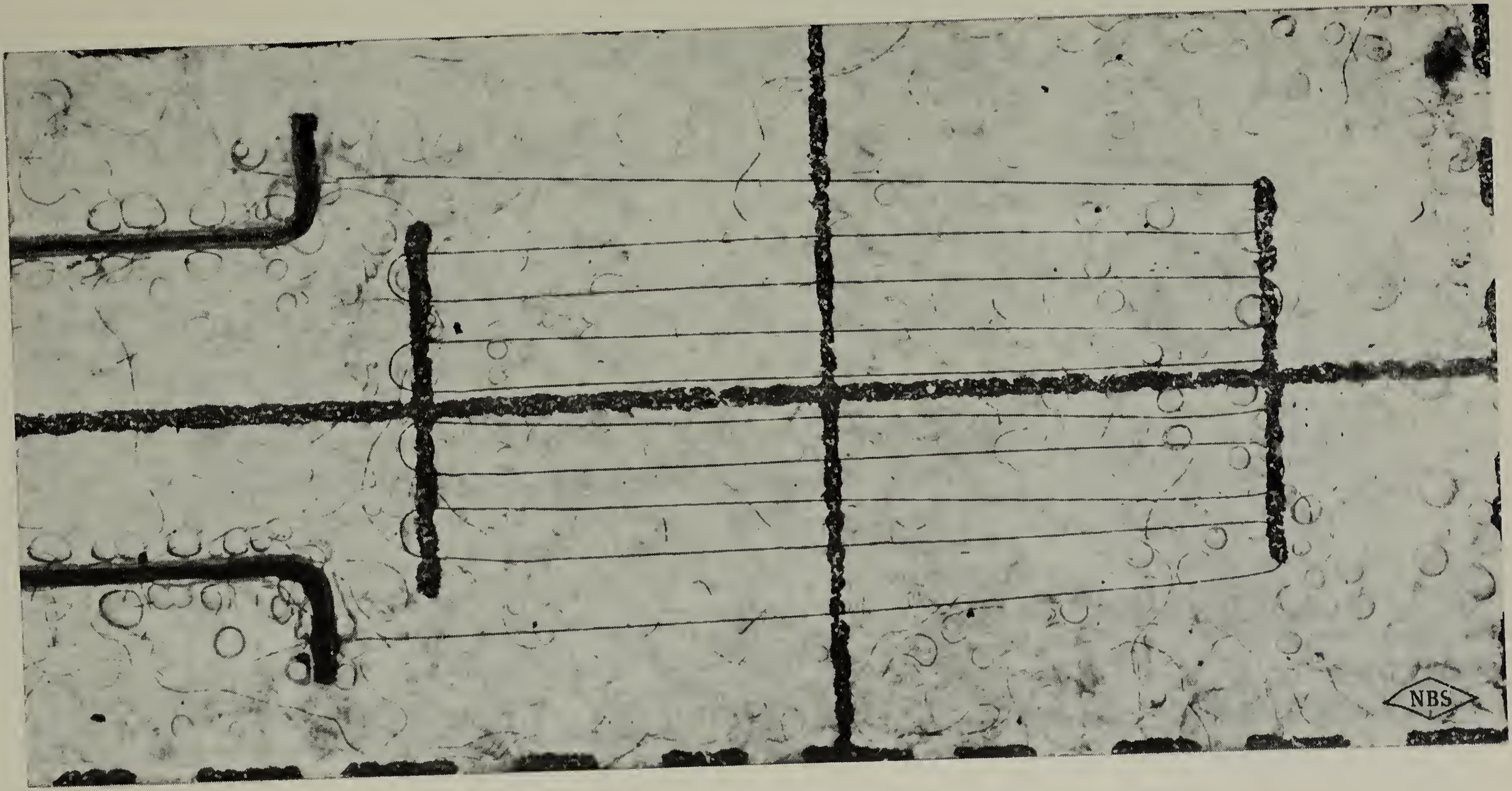
NBS

Figure 2.
- A. Water bath with its thermoregulator, stirrer, heater and immersed gages.
- B. Mercury relay switch, 12 volt relay transformer and the gage balancing and switching unit.
- C. Strain indicator.
- D. The power supply for the indicator.
- E. The constant voltage transformer for the power supply.

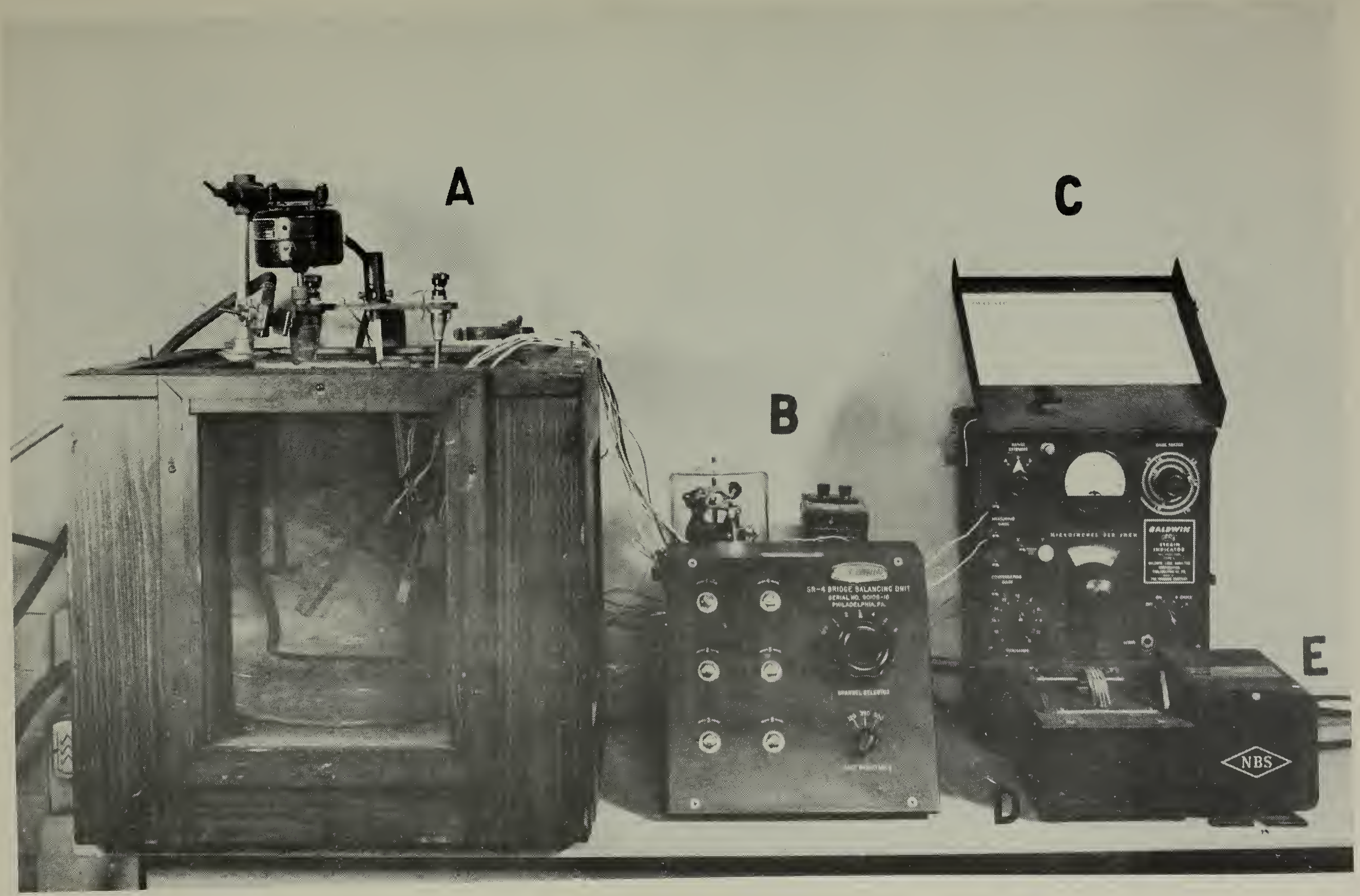
A
C
B
SR-4 BRIDGE BALANCING UNIT
PHILADELPHIA, PA.
BALDWIN
STRAIN INDICATOR
MICROINCHES PER INCH
E
D
NBS

Figure 3. Flash mold used in preparing the specimen for investigation.


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Figure 4. This figure displays the general position of the gages in the specimens.

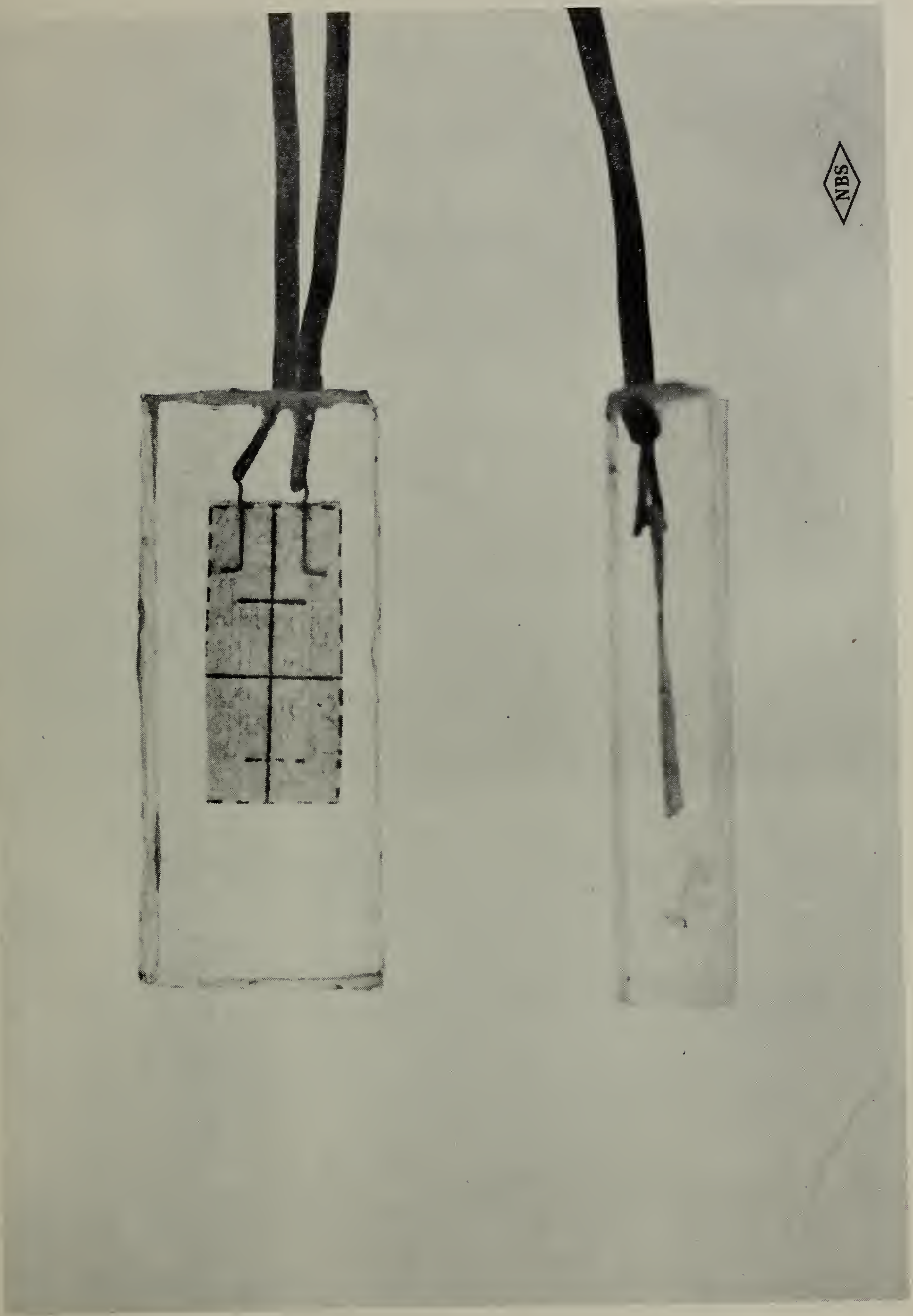
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Figure 5. A linear plot of the change in strain vs the time of immersion.

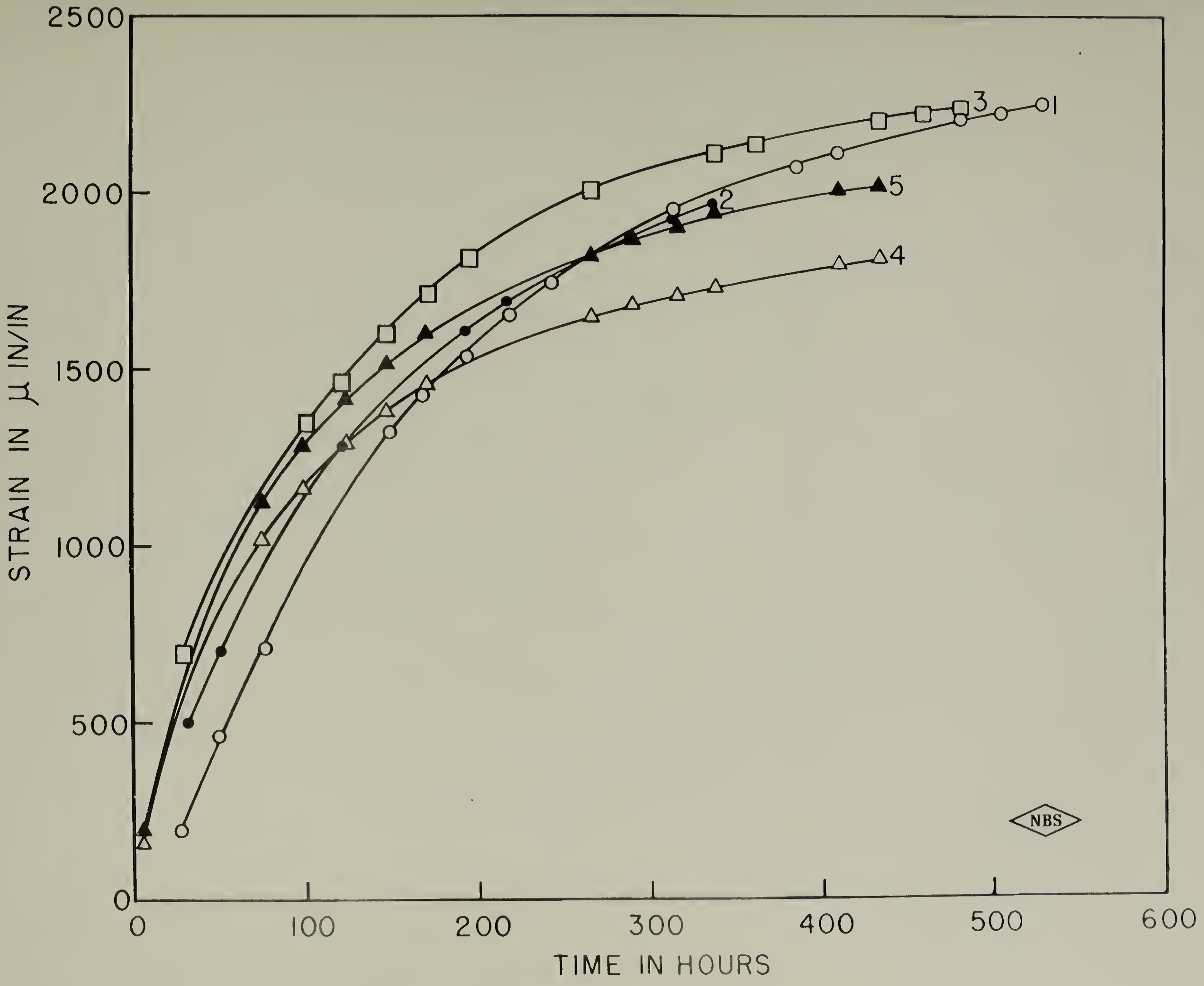

2500
2000
1500
1000
500
0
STRAIN IN µ IN/IN
0
100
200
300
400
500
600
TIME IN HOURS
1
2
3
4
5
NBS

Figure 6. A semi-logarithmic plot of the logarithm of the change in strain vs the time.

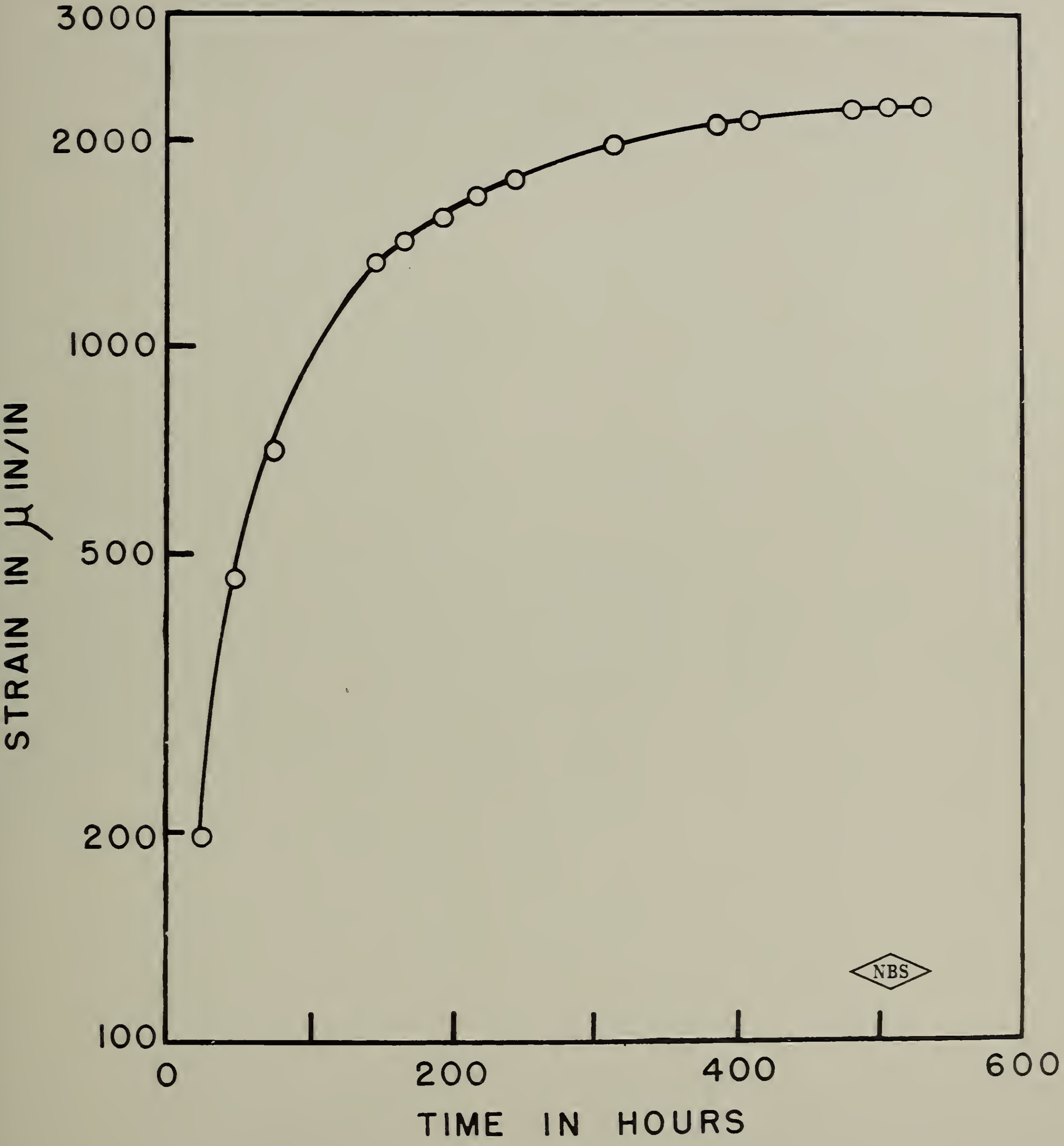

3000
2000
1000
500
200
100
STRAIN IN μ IN/IN
0
200
400
600
TIME IN HOURS
NBS

Figure 7. A semi-logarithmic plot of the change in strain vs the logarithm of the time.

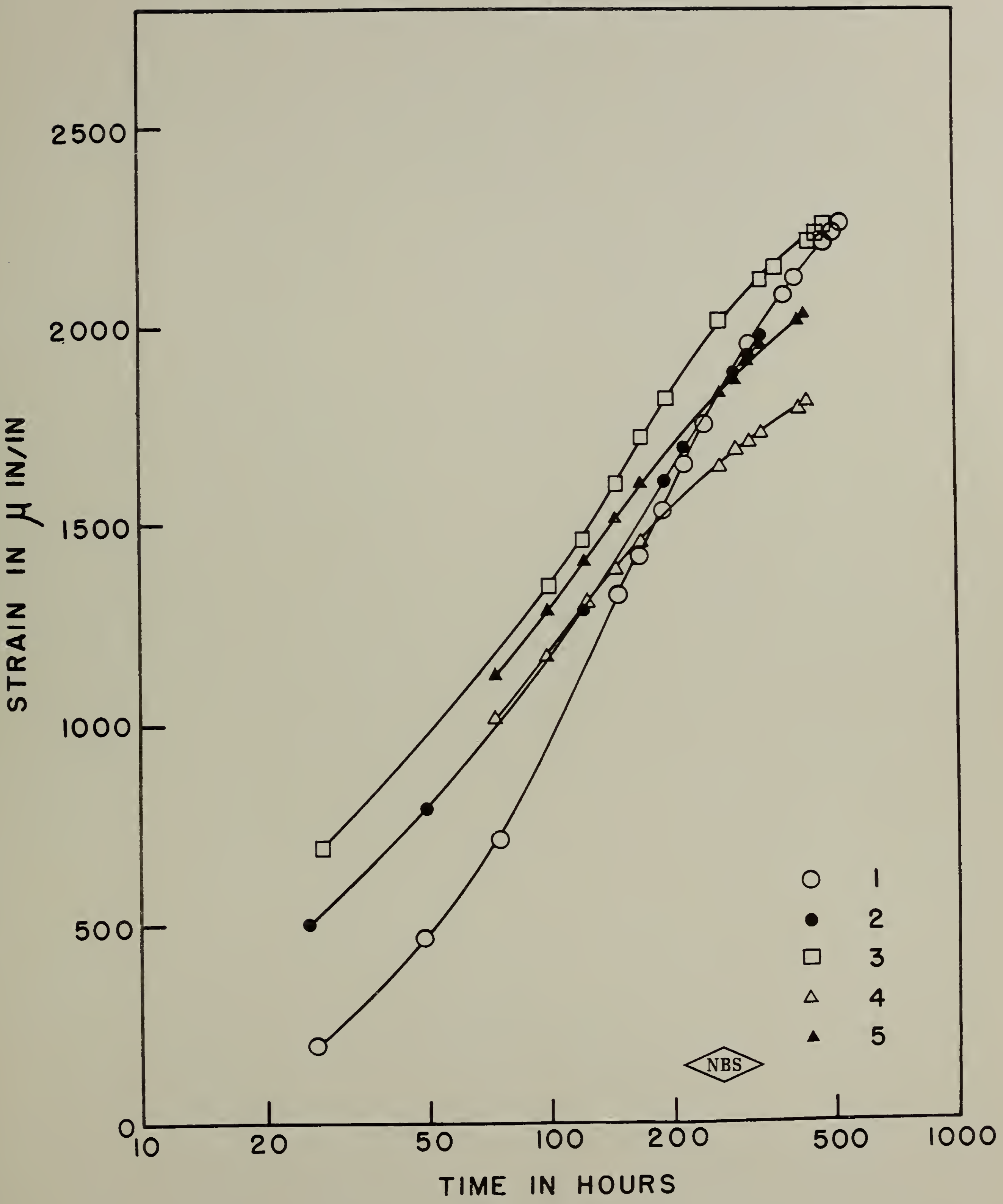
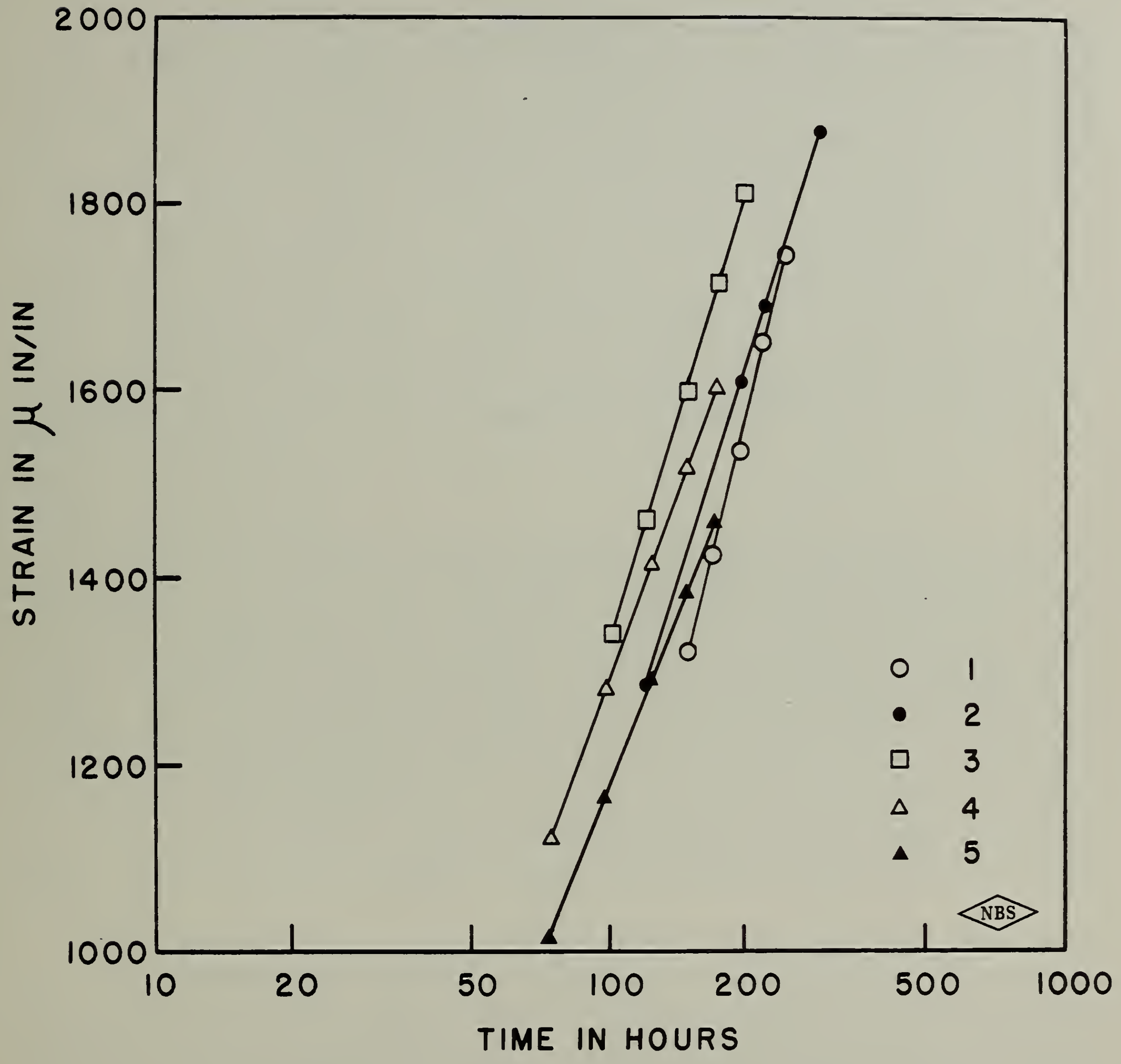

STRAIN IN μ IN/IN
2500
2000
1500
1000
500
0
10
20
50
100
200
500
1000
TIME IN HOURS
○ 1
● 2
□ 3
△ 4
▲ 5
NBS

Figure 8. A semi-logarithmic plot of the change in strain vs the logarithm of the time.


2000
1800
1600
1400
1200
1000
STRAIN IN μ IN/IN
10
20
50
100
200
500
1000
TIME IN HOURS
○ 1
● 2
□ 3
△ 4
▲ 5
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