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Geo. C. Paffenbarger

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, 1955

Dental Research Laboratory

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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

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

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● Office of Basic Instrumentation ● Office of Weights and Measures

NATIONAL BUREAU OF STANDARDS REPORT

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4255

REPORT ON DENTAL RESEARCH AT THE NATIONAL BUREAU OF STANDARDS

Progress Report

January 1 to June 30, 1955

Dental Research Laboratory

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

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

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REPORT ON DENTAL RESEARCH
AT THE NATIONAL BUREAU OF STANDARDS

1. INTRODUCTION

Investigations of materials and equipment used in dentistry and of natural tooth structures have been carried on in the Dental Research Section of the National Bureau of Standards during the half year ending June 30, 1955. Lists of reports issued and papers published during this period and summaries of work now in progress are given below. Copies of the reports are appended.

2. REPORTS ISSUED

NBS Report 4129	Sulfinic Acid Derivatives as Accelerators in the Polymerization of Methyl Methacrylate.
NBS Report 4155	Preliminary Investigation of Color in Dental Resins.
NBS Report 4225	The Relationship Between Residual Monomer and Some Properties of Self-Curing Dental Resins.
NBS Report 4226	Development of Methods for Evaluation of Rotating Dental Diamond Abrasive Instruments.
NBS Report 4227	A Method for Measuring the Mucosal Surface Contours of Impressions, Casts, and Dentures.

3. PAPERS PUBLISHED

The Mechanism of Hygroscopic Expansion in Dental Casting Investments. I. C. Schoonover, H. W. Lyon, George Dickson. J. Den. Res. 34:44 Feb (1955).

X-ray Diffraction Studies of Tooth Structure. Aaron S. Posner. Norelco Reporter Vol. II, No. 2, Page 26, March-April (1955).

Factors Influencing the Cutting Characteristics of Rotating Dental Instruments. D. C. Hudson, J. L. Hartley, Robert Moore, William T. Sweeney. J.A.D.A. 50:377 April (1955).

Effects of Temperature and Degree of Polymerization on Sorption of Water by Polymethyl Methacrylate. G. M. Brauer and W. T. Sweeney. Mod. Plastics 32 (No. 9):138 May (1955).

Crazing of Acrylic Resins. W. T. Sweeney, G. M. Brauer and I. C. Schoonover. J. Den. Res. 34:306, June (1955).

4. WORK IN PROGRESS

4.1 Structure of Human Tooth Enamel and Dentin

The fluorophotomicroscopic studies of human enamel and dentin were continued. Specimens of tooth sections which had been demineralized with chelating agents and specimens which had been deorganized with potassium hydroxide-glycol and with ethylene

diamine were obtained from the National Naval Medical Research Institute. Fluorophotomicrographs of the deorganized specimens showed several interesting structual details. Series of lamella-like filamentous processes extending from the dentine-enamel junction to the outer surface of the enamel were present in many cases. Very prominent developmental lines (about 100 microns wide) in the enamel were observed in rare instances. The very low intensity of fluorescence in these lines suggests that organic matrix formation was interrupted during the period of their formation.

Ordinarily dentin, high in organic content, fluoresces brighter than enamel. However, in tooth sections which had been treated with ethylene diamine, fluorescence of the dentin was less intense than that of the enamel, indicating that more organic matrix had been removed from the dentin. This observation is consistent with the idea that the organic matrix of dentin is a collagen, whereas the organic matrix of enamel resembles the keratins and, therefore, is more resistant to hydrolysis.

Detailed studies were continued on the preparation of calcium phosphates. A need for a standard hydroxyapatite was finally filled by the growth of very pure, single crystals of this substance. This will serve as an X-ray diffraction standard to compare with the non-stoichiometric synthetic hydroxyapatites which resemble bone and tooth mineral. The study of these precipitated hydroxyapatites not having the hydroxyapatite chemical analysis but yielding the X-ray diffraction pattern of apatite, was continued. X-ray methods are being devised to characterize their structure. Single crystals of lead apatite $[Pb_{10}(PO_4)_6(OH)_2]$ were prepared in a hydrothermal system. This is part of a program in which many lead apatites of differing stoichiometry are being studied crystallographically. It is felt that the apatite structure with lead ions missing to lower the Pb/PO_4 ratio would offer a more radical change in the X-ray diffraction data and lend itself to solving the existence of a low Ca/PO_4 ratio in the (calcium) hydroxyapatites.

4.2 Low Temperature Alloys

Additional gallium alloys were investigated for possible use as tooth restorative materials. Alloys of gallium, copper and beryllium attained their maximum compressive strength rapidly (one hour) but the strength, 20,000 lb/in^2, is low compared to dental amalgams. The setting expansion of these alloys like that of almost all of the gallium alloys studied is also high, approximately 50 μ/cm. Alloys of gallium and cobalt exhibited a slight contraction, about 3 μ/cm and a low strength 13,000 lb/in^2. Addition of 10% cobalt to a gallium-nickel alloy reduced the setting expansion from 130 to 50 μ/cm. The low strength of gallium-

cobalt alloys, however, may limit the usefulness of cobalt as a modifying agent to reduce expansion. Gallium-nickel-silicon alloys retained their compressive strength on elevation from room temperature to 50°C whereas the strength of ordinary dental amalgams was reduced approximately 40% at the higher temperature.

4.3 Resins

(a) Polymerization of Resins.

Studies of the kinetics of decomposition of benzoyl peroxide in the presence of dimethylaniline were initiated. The rate of free radical formation in benzene was determined colorimetrically with diphenyl picrylhydrazyl. The reaction is of the 0.4th order with respect to dimethylaniline. Determination of the order of reaction with respect to benzoyl peroxide and diphenyl picrylhydrazyl have been started.

The Ultraviscoson instrument which uses a vibrating reed to determine the viscosity-density product of solutions was investigated to determine the possibility of using it for determination of the molecular weight of polymethyl methacrylate. The observations so far obtained indicate that the viscosity-density relation is concentration-dependent but may not be sufficiently sensitive for molecular weight determinations with the specimen cell ordinarily used. A new specimen cell is being built which will allow more accurate positioning and better temperature control to increase the precision. This method, if successful, will make a simple and fast technic available for following changes in molecular weight of resins of the methyl methacrylate type.

(b) Properties of Dental Resin Cements.

Many of the dental resin cements were found to have about the same solubility in water as do the zinc phosphate cements. However, the resin cements are not attacked by sulfides as are the zinc phosphate cements. The effects of acetic, citric and lactic acids and ammonium hydroxide on the cements was determined. The most notable effect was observed in the materials using carbonate fillers. Gas bubbles formed on the surfaces of the specimens and the color and optical opacity of the specimens were changed as the reaction took place between the carbonate and the acidic solutions.

4.4 Chromium-Cobalt Alloys

The chemical compositions and melting points were determined for the series of chromium-cobalt alloys previously tested for mechanical properties. On the basis of the results of these tests a proposed tentative specification has been drafted and circulated for comment to all manufacturers, agencies, and groups

known to have an interest in the dental application of these materials. The final report on the project and the specification are being prepared for publication.

4.5 High-Speed Handpieces

A testing procedure for dental handpieces was devised. On the basis of clinical observation a running period of one-half hour was selected as an approximation of one day of clinical usage. A one-eighth inch round-ball burnisher was chucked in the handpiece in place of a bur and a load of 100 grams was applied to the burnisher. During the first 30 hours of running the handpieces were immersed and run forward and backward in carbon tetrachloride and in oil for 30 seconds after each half hour and were disassembled and lubricated after each $2\frac{1}{2}$ hours. Between 30 and 100 hours the periods before immersion oiling and disassembly were increased to one and five hours respectively. After 100 hours the handpieces were run without further cleaning or lubrication until a total of 200 hours running time had elapsed or failure had occurred. Temperature rise, backlash, runout and lateral play were measured during the testing period.

In general the results obtained indicated that temperature rise was higher in new than in worn instruments, that contra-angle handpieces were more likely to fail at high speeds than were straight handpieces, that handpieces operated at speeds above those recommended by the manufacturer gave consistently poor service and that care and attention devoted to maintenance were more significant factors in the failure of the handpieces than were differences in design.

4.6 Panoramic X-ray Investigation

Several improvements have been made in the prototype panoramic X-ray machine for taking exposures of the entire dental arch on a single film. Changes have been made in the film-drive mechanism to secure smoother film movement. Gears and racks have been replaced by a cable-drive system which is simple and smooth in operation. Film loading has been simplified so that the cassette is now positioned from beneath the film carrier rather than from the front where it interfered with patient positioning. A simplified master-drive mechanism has been designed and is being installed to increase the flexibility of operation of the machine and at the same time improve the overall appearance. Further improvements in devices for positioning the patient have been made.

X-ray tube improvement has been secured through cooperation with a tube manufacturer. It appears that a satisfactory X-ray source is now available with a small 0.8 mm focal spot which gives better definition in radiographs produced with the machine.

4.7 Motion Pictures

The motion picture, "Dental Materials: Specification and Certification," showing how a specification is formulated and used was completed. The photography has been completed and the narration written for the picture, "Porcelain Jacket Crowns: A Rapid Precise Technic for the Dentist." A script was prepared for a motion picture on the hydraulic contra-angle handpiece.

4.8 Hydraulic Turbine Handpiece

Designs have been made for diamond cutting tools suitable for use with the hydraulic turbine contra-angle handpiece. Because of the high rotary speed and unique cutting characteristics of this instrument fewer tools are needed than with conventional handpieces. However, the tools must be more accurately balanced and more precisely centered in the chuck than is required for conventional instruments. Clinical evaluation of the hydraulic turbine handpiece is being carried on in five private offices.

4.9 Zinc Oxide-Eugenol Materials

Setting times of zinc oxide-eugenol mixtures using different particle size zinc oxide and varying powder-liquid ratios were determined. No correlation was found between particle size and setting time.

Difficulties were encountered in water sorption studies of Hyperfine zinc oxide due to the unexpected presence of ammonia in the material. Analysis showed that the material contains about 1.2% of ammonia. This ammonia is incorporated during the manufacture of zinc oxide from zinc carbonate in an ammonia atmosphere.

4.10 Agar-Agar Materials

A study of the causes of deterioration of agar-agar duplicating materials was initiated. These materials, on continued reuse, show changes in physical properties which make them unsuitable for further service. Heating a 2% aqueous agar-agar solution to 100°C caused a considerable decrease in pH (from 5.7 to 3.0) within 10 days. Solutions stored at this elevated temperature turned dark and did not form gels at room temperature.

4.11 Inlay Casting Wax

An investigation of the basic properties of waxes especially those of the synthetic type has been undertaken with the objective of developing an improved inlay casting wax because it is considered that the wax is the source of greatest error in precision casting process at present.

4.12 Evaluation of Materials

Materials evaluated for the Federal dental services and the American Dental Association by specification or special test methods included denture base resins, impression compounds, inlay casting gold alloys, inlay casting investments, inlay casting waxes, pliers, separating mediums, and wrought gold wire alloys.

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

NATIONAL BUREAU OF STANDARDS REPORT

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0708-10-0707

June 6, 1955

NBS REPORT
4129

Progress Report

SULFINIC ACID DERIVATIVES AS ACCELERATORS IN THE POLYMERIZATION OF METHYL METHACRYLATE

by

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and
F. R. Burns[1]

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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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SULFINIC ACID DERIVATIVES AS ACCELERATORS IN THE POLYMERIZATION OF METHYL METHACRYLATE

Abstract

A study was made of the efficiency of amine salts of p-toluene sulfinic acid as accelerators in the polymerization of methyl methacrylate. These compounds are readily synthesized by addition of amine to the ether solution of the sulfinic acid. Most of the salts are stable in air. Salts of secondary and tertiary aromatic amines such as the methyl aniline or dimethyl-p-toluidine salts are very efficient accelerators in the benzoyl peroxide initiated polymerization. However, colored products are formed. Aliphatic amine salts as well as the free acid give colorless polymers, but the setting time is increased considerably. Heterocyclic amines show reduced activity as polymerization accelerators.

The setting times of monomer-polymer mixtures containing some of these accelerators have been determined. Physical properties of the polymers have been evaluated by measuring their resistance to indentation and recovery.

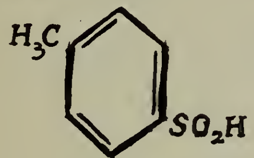
1. INTRODUCTION

In 1948 the use of organic sulfinic acids to promote rapid polymerization was advocated for a number of reasons, one of which was to decrease the color of the polymeric product [1-9]. These compounds proved to be excellent accelerators for the emulsion or bulk polymerization of methyl methacrylate and other vinyl monomers. Colorless polymerization products were readily formed. This is a big advantage over the colored products which are usually formed when methyl methacrylate is polymerized with a benzoyl peroxide-amine system. Furthermore, sulfinic acid shows no induction period. The polymerization starts immediately even when hydroquinone stabilized monomer is used. The sulfinic acid does not oxidize the hydroquinone inhibitor or react with any quinone present.

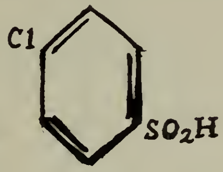
Unfortunately, sulfinic acids are rather unstable in air. In the presence of air they readily oxidize to sulfonic acids and other oxidation products which do not act as polymerization activators. One method of improving the storage life of these materials consists of dissolving the sulfinic acid in a silicone oil in a capsule. Before polymerization the capsule is

added to the monomer in which it dissolves and the sulfinic acid is liberated. Commercial products of this type have met some success. Obviously, monomer to which sulfinic acid has been added must be used within a short period of time.

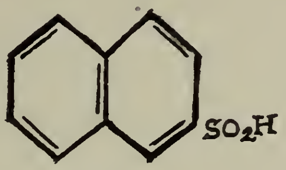
The sulfinic acids most commonly suggested as accelerators are p-toluene sulfinic acid (I), chlorobenzene sulfinic acid (II), 2-naphthalene sulfinic acid (III) or anthracene sulfinic acid (IV).



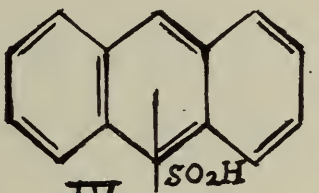
I



II



III



IV

The presence of an aromatic or condensed ring system increases the stability towards oxidation.

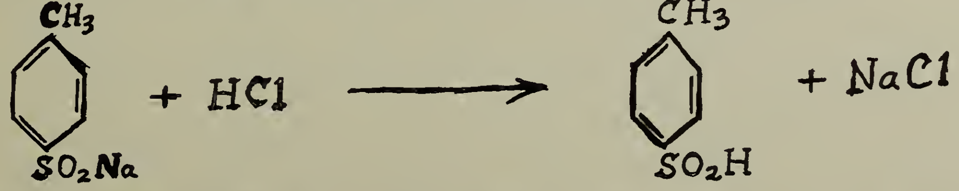
Recently Bredereck and Bäder [10-11] have synthesized derivatives of sulfinic acid such as oxysulfones, α-aminosulfones and sulfinic acid salts. Some of these compounds had good storage stability and were efficient accelerators for the polymerization of monomer-polymer mixtures at room temperature, especially after the addition of primary alcohols [12-13]. In the present investigation a more detailed study of the use of amine salts of p-toluene sulfinic acid as possible accelerators in the polymerization of methyl methacrylate was undertaken.

2. EXPERIMENTAL PROCEDURE AND RESULTS

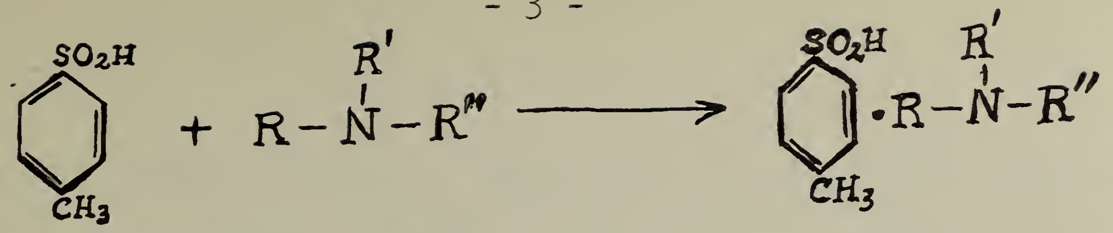
2.1 SYNTHESIS

The sodium salt of p-toluene sulfinic acid was used as starting material. This salt is stable and can be obtained commercially.

In order to prepare various p-toluene sulfinic acid salts which might have long storage life and good accelerating properties, the sodium salt was acidified in water.



The free sulfinic acid was difficult to dry without partial conversion into the sulfonic acid and thiosulfonic ester. The free acid was dissolved in ether solution according to the method suggested by Bredereck [10] and an ether solution of a very slight excess of the respective amine was added. The following reaction takes place:



p-toluene sulfinic acid

p-toluene sulfinic acid salt

R = C_nH_{2n+1} = aliphatic

= C_6H_5 = aromatic

R' = aliphatic, aromatic or H group

R" = aliphatic or H group

If a salt crystallized out, it was filtered off. Sometimes, on partial evaporation of the solution, an oily layer separated. This oil was removed and extracted with ether. If the material did not crystallize, the remaining solvent was removed at room temperature at approximately 60 mm pressure. The material was then heated to 60°C at 2 to 4 mm pressure, cooled and stored at 2 to 4°C until crystallization occurred. The yield of impure solid or oil was nearly quantitative.

Solids were purified by repeated recrystallization, usually from ether to which small quantities of methanol had been added. Recrystallization was continued until a colorless crystalline material with a sharp melting point was obtained. Those compounds which had been reported in the literature were identified by their melting points. The composition of all other solids was determined by analysis for carbon, hydrogen, sulfur or nitrogen. Considerable difficulty was encountered in purifying oily products, which had high boiling points, even in high vacuum. These compounds were tested for their accelerator efficiency without further purification.

Table 1 gives the melting points obtained in this study and those found in the literature. Analysis of the crystalline compounds not previously reported is also given. It will be seen that most salts of tertiary amines are oils. Salts of most primary and many secondary aliphatic amines are solids. The p-toluene sulfinic acid salts of di-iso-butylamine, N-methylcyclohexylamine, N,N-diethylcyclohexylamine and piperidine were unstable in ether solution and the corresponding sulfonic acids crystallized on standing. On repeated recrystallization, the dicyclohexyl and dibenzylamines also oxidized to the sulfonic acid.

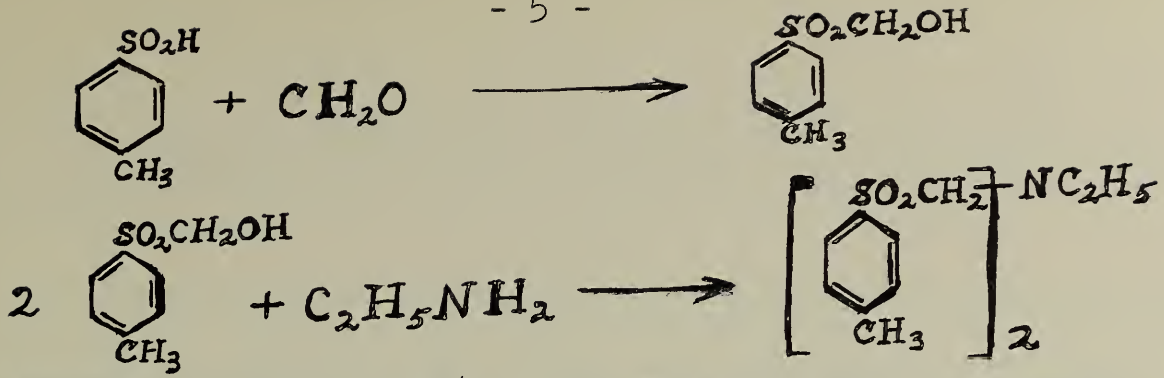
2.2 POLYMERIZATION

The effectiveness of these salts as accelerators of the peroxide catalyzed polymerization of methyl methacrylate was determined. Monomer containing 2% benzoyl peroxide and 0.006% hydroquinone inhibitor was prepared and varying concentrations of sulfinic acids were added. The polymerization reaction at 37°C was followed by means of an Ultra-Viscoson ultrasonic viscosity apparatus in the manner previously reported [14].

Results of the polymerization studies are given in Table 2 and Figure 1. The salts of the aromatic amines are the most efficient accelerators encountered in this study. In the presence of N-methyl aniline salt, a 1000 cps value was reached in less than 12 minutes. In comparison, the time necessary to reach 1000 cps for the commercially-used benzoyl peroxide-di-β-hydroxyethyl-m-toluidine and benzoyl peroxide-dimethyl-p-toluidine systems as determined in a previous study were 21 and 36 minutes respectively. Salts of naphthylamines showed a much reduced activity. No attempt was made to synthesize the N-methyl-p-toluidine salt which, based on experiments in the peroxide-amine system, should show an even greater activity than the N-methyl aniline salt. The polymerization products of all aromatic amines were yellowish or red. It may be possible to decrease somewhat the color of these products by careful purification of the raw materials and possibly by distillation of the amine salts in a molecular still. In agreement with Bredereck [10], it was found that the storage stability of the aromatic amines was much better than that of the free p-toluene sulfinic acid. The N-methyl aniline salt showed no decrease in activity after storage at room temperature for 5 months. The crystalline m-toluidine salt showed a faint yellow color within 10 months.

Salts of aliphatic amines showed a much decreased activity. The oily tertiary amine salts were somewhat faster acting than the crystalline secondary amines. Tri-n-hexylamine appeared to be the best accelerator in this series. Increase in chain length of the hydrocarbon radical decreased the accelerating activity. The isomeric di-n-butyl and di-iso- butylamines had approximately the same accelerating efficiency. The di-sec-butylamine was a less effective accelerator. Amines of cyclic hydrocarbons such as dicyclohexylamine are only slightly soluble in monomer and do not accelerate the polymerization appreciably. Salts of heterocyclic amines show only slightly improved accelerating efficiency as compared to the aliphatic amine salts.

Bredereck, in his paper [12], shows the high efficiency of α-oxy and α-amino sulfones. He reported that the latter compound is stable in air. Derivatives from p-toluene sulfinic acid were prepared according to his synthesis [10].



Monomer containing 2% of the α-oxysulfone or α-aminosulfone and 2% benzoyl peroxide polymerized rather slowly. After 1 hour, the solutions showed a viscosity of 6.5 and 24 cps, respectively.

Phosphinic acids have also been suggested as accelerators and their use has been patented by Loritsch [15]. The di-n-propylamine and methyl aniline salts of phenyl phosphinic acid were prepared by methods similar to those used for sulfinic acid salts. The salts are oily liquids. The di-n-propylamine salt gave an analysis of C=59.1, H=9.2% (calculated values C=59.2%, H=9.0%). Neither phenyl phosphinic acid nor its di-n-propylamine or methyl aniline salts showed any appreciable effects on the polymerization rate. Use of a hydroperoxide such as tertiary-butyl hydroperoxide instead of benzoyl peroxide as suggested by Loritsch did not decrease the setting time.

2.3 HARDENING OF MONOMER_POLYMER MIXTURES

In order to determine the setting time of monomer-polymer mixtures containing various amines, a penetration test was employed. The test method chosen was a modification of the A.S.T.M. penetration test for bituminous materials [16]. This method employs a standard needle mounted on a dial gage graduated in 1/1000 in.

One gram of ground polymer powder containing 1% benzoyl peroxide was mixed according to the established dental procedure with 1 ml of hydroquinone-inhibited monomer containing the various amine salts. Additional peroxide, methanol or hydrogen peroxide were also added to the monomer. The mix was placed in a brass ring 0.5 cm high and 1.1 cm in diameter, which was on a glass plate. A piece of polyethylene was placed on top of the ring before a second plate and a 100 g weight were positioned on it. At 2-1/2 minutes from the start of mix, the top plate and the weight were removed and the ring was placed in a 37°C air bath. The needle attached to the dial gage and under 100 g load, was lowered into the ring at 3 minutes from the start of the mix and left for 5 seconds. A reading was made and the needle was removed. The procedure was repeated every minute until the material could no longer be

penetrated. Penetration was begun in the center of the ring and continued in a clockwise direction around the ring with the final readings being made around the outside edge. Final readings made near the center of the specimen would not give accurate results.

It will be seen in Table 3 that mixtures containing the methyl aniline salt as well as the N-ethyl-bis-(p-tolylsulfone-methyl)-amine showed a very short setting time. The mixture hardened much slower when di-n-hexylamine salt was used as accelerator. Under the experimental condition no appreciable decrease in setting time on addition of methanol or a trace of hydrogen peroxide as reported by Bredereck was observed. Setting times as short as 2 to 4 minutes as reported by Bredereck and co-workers [12] for the polymerization of methyl methacrylate in the presence of the α-aminosulfone, benzoyl peroxide, 16% methanol and a trace of hydrogen peroxide were not obtained in these experiments. The preparation of the polymer, particle size and the exact monomer-polymer ratio which were employed are not given by Bredereck. In the absence of more complete data it is not possible to explain these variations in setting time. Since Bredereck followed the course of the polymerization by the rise in temperature only, his results do not make it possible to draw any conclusions concerning the physical properties of his polymeric products.

In order to obtain information on the physical characteristics such as hardness and elastic properties of the polymerized materials their indentation and recovery were measured using the Rockwell superficial hardness tester. Details of the procedure have been described by Sweeney, Sheehan and Yost [17]. Results of the indentation tests and percent recovery are given in Table 3.

A good dental restorative material should have low indentation values and high percent recovery. Polymers prepared with the methyl aniline salt of p-toluene sulfinic acid showed such behavior. The salt of tri-n-hexylamine sets much slower. Addition of methanol considerably decreased the setting time, but the resulting polymer was too soft for most applications. Polymers prepared in the presence of this accelerator have physical characteristics similar to those of materials polymerized with amine accelerators such as di-β-hydroxyethyl-m-toluidine or dimethyl-p-toluidine. N-ethyl-bis-(p-tolylsulfone-methyl)-amine produced a softer material. Indentation and hardness were improved somewhat by the addition of 16% methanol and a little hydrogen peroxide. Substituting t-butyl hydroperoxide for a portion of the benzoyl peroxide catalyst brought about a slight improvement of physical properties.

3. SUMMARY

1. The use of amine salts of p-toluene sulfinic acid and α-aminosulfones as accelerators in the polymerization of methyl methacrylate has been investigated.

2. Salts of aromatic amines are very efficient polymerization accelerators. The polymerization products are usually colored.

3. Salts of aliphatic and heterocyclic amines show reduced activity as polymerization accelerators. Most of the products formed are colorless.

4. The stability of the amine salts and α-aminosulfones appears to be better than that of the free sulfinic acid.

5. The setting times of a number of monomer-polymer mixtures containing the amine salts have been measured.

Resistance to indentation and recovery were used to evaluate the physical properties of the polymeric products formed in the presence of the various accelerators.

BIBLIOGRAPHY

1. Hagger, O. New catalysts for the polymerization of ethylenes at room temperature. Helv. chim. acta 31:1624-1630, (1948).

2. Ibid. Utilization of the energy of swelling for the acceleration of the sulfinic acid promoted polymerization of methacrylate esters at room temperature. Helv. chim. acta 34:1872-1876, (1951).

3. Castan, P. and Hagger, O. Polymerization of vinyl compounds in the presence of a sulfinic acid catalyst. U. S. patent #2,567,803, Sept. 11, 1951 (to Gebr. deTrey), Swiss patent #255,978, Feb. 1, 1949.

4. Imperial Chemical Industries Ltd. Polymerization catalysts for ethylenically unsaturated compounds. Brit. patent #586,796, April 1, 1947.

5. Farbwerke Hoechst. Method for the preparation of polymers or mixed polymers of unsaturated compounds. German patent #861,156, December 29, 1952.

6. Ynfiesta, J. L., Yanes, J. F. and Sanchez, F. R. Sulfinic acids as catalysts in vinyl polymerization: I. Study of the velocity of polymerization of methyl methacrylate. Anales real soc. espan fis y. quim. 47B:53-60, (1951).

7. Hashihama, Y., Sumitomo, H. and Okabe, J. Acrylic polymers II. J. Chem. Soc. Japan, Ind. Chem. Sec. 56:25-28, (1953).

8. Taylor, P. B. and Frank, S. L. Low temperature polymerization of acrylic resins. J. D. Res. 29:486-493, (1950).

9. Schroder, A. and Santorik, St. New investigations on so-called self-polymerizing resins. Schweizerische Monatszeitschrift für Zahnheilkunde 60:937, (1950).

10. Bredereck, H. and Bäder, E. Preparation of α-oxy and α-aminosulfones and sulfinic acid salts of organic bases. Chem. Ber. 87:129-140, (1954).

11. Bäder, E. and Hermann, H. D. New methods for the synthesis of sulfonamines. Chem. Ber. 88:41-49,(1955).

12. Bredereck, H., Bäder, E. and Wohnhas, A. α-oxy, α-aminosulfones and sulfinic acid salts as polymerization catalysts. Makromolek. Chem. 12:100-109, (1954).

BIBLIOGRAPHY (Cont'd)

13. W. C. Heraeus G.M.B.H. and Deutsche Gold und Silberscheideanstalt vorm. Roessler, British patents #710,534 and #710,535, June 16, 1954; British patent #708,077, April 28, 1954; German patent #913,477, June 14, 1954; and German patent #916,733, August 16, 1954.

14. Davenport, R. M. and Brauer, G. M. Amine accelerators for the polymerization of methyl methacrylate. (unpublished data).

15. Loritsch, J. A. Polymerization in the presence of an organo-phosphorous compound as an activator. U. S. patent #2,543,635, February 27, 1951. (to G.E.)

16. American Society for Testing Materials. Standard method of test for penetration for bituminous materials. A.S.T.M. Designation D5-53T.

17. Sweeney, W. T., Sheehan, W. D. and Yost, E. L. Mechanical properties of direct filling resins. J.A.D.A. <u>49</u>: 513-521, (1954).

TABLE 1

PROPERTIES OF AMINE SALTS OF p-TOLUENE SULFINIC ACID

AMINE	MELTING POINT		COMPOSITION[g]			
	found	reported	found		calculated	
	°C	°C	%		%	
Aliphatic						
di-n-propyl	60		S=12.1	N=5.4	S=12.4	N=5.4
di-n-butyl	105	104-6				
di-iso-butyl[a]	120		C=59.7	H=9.1	C=60.1	H=9.0[b]
di-sec-butyl	oil					
di-n-hexl	119	119				
dicyclohexyl[c]	153		C=67.5	H=9.3	C=67.5	H=9.2
N-methylcylcohexyl[a]	138		C=58.7 N= 4.9	H=8.0	C=58.9 N= 4.9	H=8.1[b]
diethanol	oil					
tri-n-butyl	oil	40-43				
tri-n-hexyl	oil					
N,N-diethylcyclohexyl[a]	100		C=62.5	H=8.7	C=61.9	H=8.8[b]
Aromatic						
aniline	116	118				
N-methyl aniline	oil					
m-toluidine	117	120	C=63.4 N= 5.2	H=6.5	C=63.8 N= 5.3	H=6.5
dimethyl-p-toluidine	oil					
dibenzylamine	132[d]		C=70.8 N= 4.0	H=6.6	C=71.2 N= 4.0	H=6.5
dimethyl-α-naphthylamine	oil					
phenyl hydrazine	158	158				

TABLE 1 (Cont'd)

AMINE	MELTING POINT		COMPOSITION[g]			
	found	reported	found		calculated	
	°C	°C	%		%	
<u>Heterocyclic</u>						
pyridine	oil[e]					
morpholine	124-5		C=54.1	H=7.1	C=54.3	H=7.0
piperidine[a]	130	130	C=56.1	H=7.4	C=55.9	H=7.4[b]
pyrrole	solid[f]					
pyrrolidine	oil					

[a] Sulfonic acid salt.

[b] Calculated for sulfonic acid salt.

[c] On recrystallization oxidized to the sulfonic acid salt.
M.P. = 179°C composition % , C=64.0 H=8.7 (found).
C=64.5 H=8.7 (calculated).

[d] On recrystallization oxidized to the sulfonic acid salt.
M.P. = 162°C composition % , S=7.7 N=3.8 (found).
S=7.7 N=3.7 (calculated).

[e] Oxidizes to hygroscopic solid.

[f] No sharp melting point.

[g] Analyses were performed by R. A. Paulson of the Analytical Chemistry Section of the National Bureau of Standards.

TABLE 2

ACCELERATORS OF THE POLYMERIZATION OF METHYL METHACRYLATE AMINE SALTS OF p-TOLUENE SULFINIC ACID

Benzoyl peroxide concentration: 2%

AMINE SALT	SOLUBILITY IN MONOMER	AMINE CONCENTRATION	TIME	VISCOSITY	POLYMER COLOR
		%	min	cps	
Aliphatic					
di-n-propyl	s.	2.0	60	10	faint yellow
		2.0	163	1000	
di-n-butyl	sl.s.	<2.0	60	12	colorless
		0.5	60	19	
		0.05	60	1	
di-iso-butyl	sl.s.	<2.0	60	18	slight yellow
di-sec-butyl	s.	2.0	60	1.5	yellow
di-n-hexyl	sl.s.	<2.0	60	9	colorless
		0.2	60	no change	
dicyclohexyl	sl.s.	<0.5	60	no change	colorless
N-methylcyclohexyl	ins.	<0.2	60	no change	colorless
diethanol	ins.	<2.0	60	no change	colorless
tri-n-butyl	s.	2.0	60	5	faint yellow
tri-n-hexyl	s.	2.0	60	105	colorless
		2.0	101	1000	
		1.0	60	50	
N,N-diethylcyclohexyl	s.	2.0	60	8	slight yellow

TABLE 2 (Cont'd)

AMINE SALT	SOLUBILITY IN MONOMER	AMINE CONCENTRATION	TIME	VISCOSITY	POLYMER COLOR
		%	min	cps	
Aromatic					
aniline	s.	2.0	36	3600	yellowish red
		0.5	116	1000	
N-methylaniline	s.	2.0	12	1300	reddish yellow
		1.0	14	1000	
		0.5	60	72	
m-toluidine	s.	2.0	28	1000	reddish brown
		0.5	60	475	
dimethyl-p-toluidine	s.	2.0	17	1000	brownish yellow
dibenzylamine	sl.s.	<0.5	60	6	colorless
dimethyl-α-napthylamine	ins.	<0.5	60	no change	reddish orange
phenyl hydrazine	sl.s.	<2.0	60	21	yellow
		0.2	60	11	
		0.05	60	32	
Heterocyclic					
pyridine	s.	2.0	60	13.3	colorless
morpholine	ins.	<2.0	60	28	colorless
		0.2	60	no change	
pyrrolidine	s.	2.0	60	24	colorless
piperidine	s.	2.0	60	12	colorless
Other accelerators (Not amine salts)					
p-toluene sulfinic acid	s.	2.0	130	1000	colorless
		1.0	205	1000	
di-(β-hydroxyethyl)-m-toluidine	s.	1.0	21	1000	yellow
dimethyl-p-toluidine	s.	2.0	140	1000	yellow
		0.5	36	1000	

TABLE 3

SETTING TIME AND PHYSICAL PROPERTIES OF MONOMER-POLYMER SLURRIES

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

EXP. NO.	ADDITIVES IN MONOMER	SETTING TIME	INDENTATION			RECOVERY		
			30-min	1-hr	5-days	30-min	1-hr	5-days
		min	mm	mm	mm	%	%	%
1	2% A[a]	6-8	.24	.15	.10	29	46	73
2	2% B[b]	>30						
3	Same as 2 + 16% methanol	13			soft			soft
4	Same as 2 + 30% methanol	8			soft			soft
5	2% C[c]	8-9		soft	.24		soft	26
6	4% C +4% benzoyl peroxide	6-7		.25	.17		16	49
7	Same as 6 + 6% methanol	-		.26	.15		12	54
8	Same as 6 + 16% methanol	7		.17	.13		49	68
9	Same as 8 + 1 drop 30% H_2O_2	7		soft	.20		soft	65
10	Same as 8 + 1 drop 3% H_2O_2	7						
11	4% C +4% t-butylhydroperoxide + 16% methanol	7		.23	.12		30	63
12	Same as 11 + 2 drops 30% H_2O_2	-		soft	.27		soft	2
13	Same as 11 + 1 drop 3% H_2O_2	7		.19	.14		41	66
14	2% di-(β-hydroxyethyl)-m-toluidine	10		.13	.10		46	78
15	2% dimethyl-p-toluidine	8	.18	.13	.09	39	52	79
16	1% dimethyl-p-toluidine	12	.23	.15	.10	36	48	76

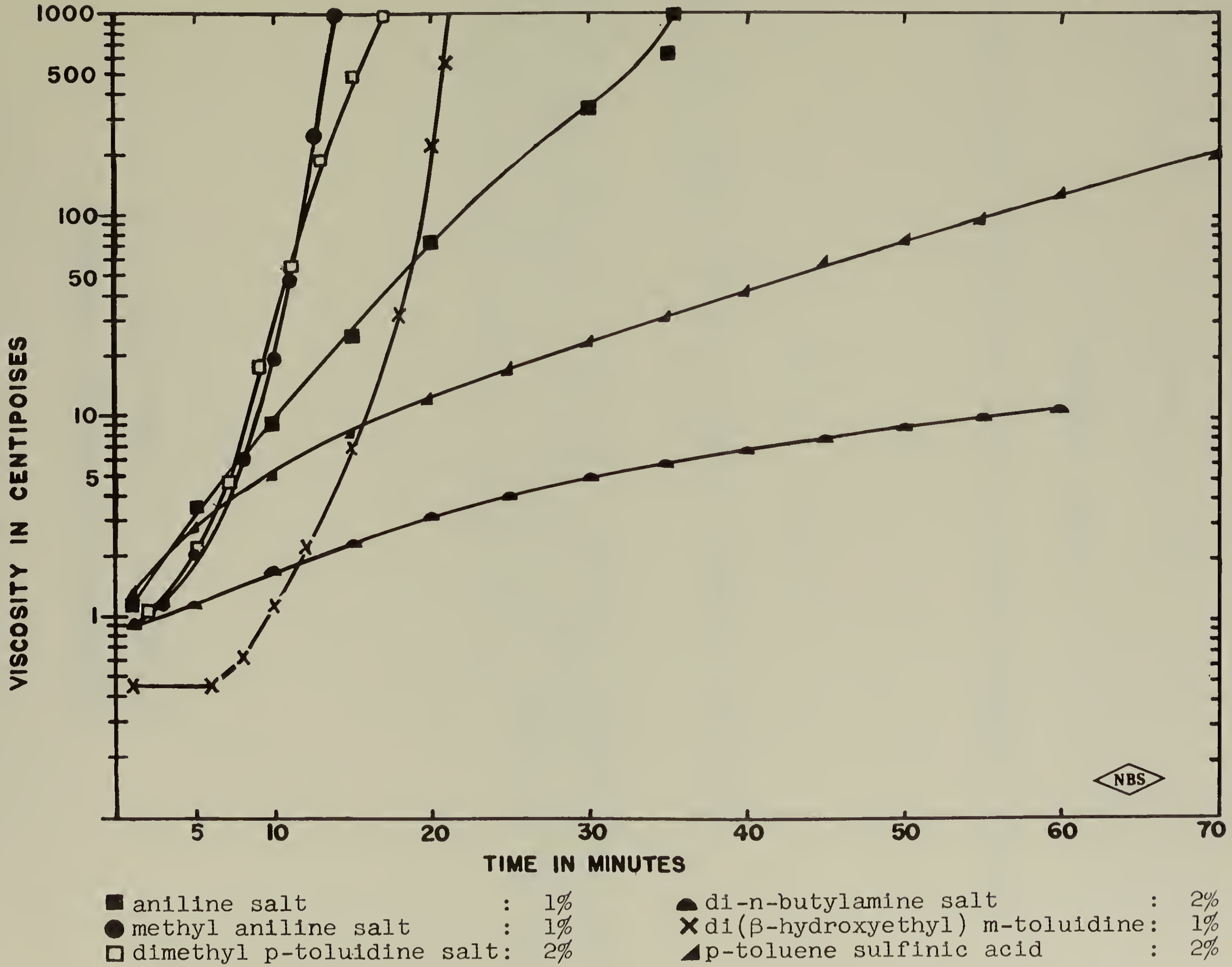
[a] A = N-methylaniline salt of p-toluene sulfinic acid.

[b] B = di-n-hexylamine salt of p-toluene sulfinic acid.

[c] C = N-ethyl-bis-[p-tolylsulfone-methyl]-amine.

Figure 1. Polymerization of methyl methacrylate in the presence of p-toluene sulfinic acid-amine salts.

Temperature 37°C. Benzoyl peroxide concentration: 2%.



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NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

PRELIMINARY INVESTIGATION OF COLOR IN DENTAL RESINS

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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PRELIMINARY INVESTIGATION OF COLOR IN DENTAL RESINS

Abstract

The color control of dental materials is of major importance to the dental profession. In this study several of the factors affecting the color of dental resins were investigated. The color of a translucent resin is the function of three light components. One component is the light reflected from the surface of the resin, another is the light diffused internally by the pigment, and finally the light which passes through the specimen, is reflected off a background and returns through the specimen. The color and intensity of the latter two components are affected by a change in thickness. A decrease in monomer to polymer ratio of these resins causes a small increase in opacity. In the normal range of monomer to polymer ratios this effect is relatively unimportant. With the color difference meter used in this study the precision of measurements of opacity and color is greater than is the precision of duplication of specimens.

1. INTRODUCTION

This report is a summary of initial findings in the field of color measurements of dental materials. A great amount of work has been done in the past in the field of color. Various systems of color specification [1,2] have been devised and a number of systems of measuring color [1,2] have been developed. However, little work has been done in applying the science of color to the field of dental materials.

In measuring the color of various dental materials a number of problems are encountered. All human structures exhibit the property of translucency (the ability to transmit light). If a dental material to be placed in the mouth is to appear life-like and match the substance which it is to represent, it must not only have the same color but must also have the same opacity. Opacity is used to designate different degrees of absorption of light.

Another factor involved in the color measurement of these materials is that of thickness. The thicker a material is, the greater is its opacity. In substances such as teeth the thickness is of such importance that minor variations will appreciably affect the color. In the tooth the thickness is not uniform, thus causing color variations throughout.

The background of any translucent material also has its effect on the color. The translucent material will usually tend to approach the color of the background. The more translucent the material the closer it will approach the color of the background.

A further complication is that structures such as teeth consist of two or more components of different colors and opacities. The observed color of a tooth is a function of both materials. Since each of these materials varies in thickness the composition of the ultimate observed color becomes complex.

Another factor involved is the thin layer of liquid which coats the oral cavity. The effect of this layer is to give a high gloss to the surface and also to intensify the color.

2. EXPERIMENTAL WORK

In this preliminary study, all efforts were concentrated on the evaluation of the effect of thickness and monomer-polymer ratio on the observed color and opacity of translucent heat-curing resin materials.

Various methods were attempted to determine the best method for producing color specimens. Dental flasks were used at first, but these were discarded because in the thicker specimens it was impossible to provide a sufficient reservoir to fill the voids created by the contraction of the monomer-polymer mix during polymerization.

The best method developed was curing in a Carver press with the mix under a constant positive pressure. It was felt that variations in curing time, temperature, and pressure would have negligible effect on the color and opacity of the specimens. However, in spite of this, great effort was made to reduce these variations to a minimum. The specimens were cured for one hour at 100 ± 10°C. About ten minutes of this hour were used to heat the specimen from room temperature to curing temperature. The pressure was held constant at 2,000 ± 200 psi.

Using the Carver press method, specimens of various thicknesses between 1/4 mm and 8 mm were prepared. Specimens were also prepared using different ratios of monomer to polymer. The range covered by these ratios was from 0.38 ml/gm to 0.68 ml/gm. The manufacturer's recommendation was for 0.56 milliliter of monomer per gram of polymer.

The specimens were measured by a tristimulus colorimeter (Gardner Automatic Color Difference Meter) to determine the color

relative to a standard. For each color a reflectance value "Rd" and two color coordinate values "a" and "b" are given. "Rd" is defined[3] as 100 times the amount of light reflected by a sample divided by the amount of light reflected by a perfectly diffusing sample when the light is incident upon the sample at an angle of 45° and the measuring device records the light diffused perpendicularly from the sample. A completely absorbing specimen would have an "Rd" value of zero, and a perfectly diffusing white would have a value of 100. "a" and "b" are [3] the rectangular coordinates of chromaticity in any plane intersecting the color solid perpendicularly to the white-black axis. Zero values of "a" and "b" indicate the color specimen is on the white-black axis, thus some shade of gray. A positive value of "a" indicates the color is on the red side while a negative value places it on the green side. A positive value of "b" indicates the color is on the yellow side and a negative value locates it on the blue side. Units of color difference for these three values are equivalent to NBS units of color difference. The NBS unit is approximately five times as large as the smallest difference perceptable to a skilled observer under the best experimental conditions.

All specimens were measured twice for color, once while using a white background and once while using a black background. The white background had the color coordinates, "Rd" 81.1, "a" -4.0, and "b" +2.9. For a black background no backing was used. The light was allowed to dissipate itself into a darkened room. Thus the black background was essentially a black body with the coordinates "Rd" 0, "a" 0, and "b" 0. A yellow color standard ("Rd" 60.3, "a" -0.2, and "b" +22.5) was used to standardize the colorimeter before each set of readings. The instrument was also checked

with the standard after the readings to determine any drift. The aperture of the colorimeter was 2½ inches in diameter. By measuring this large an area, any small local color inconsistancies were made relatively unimportant.

3. RESULTS

Figures 1, 2 and 3 show the effect of thickness on the color coordinates "Rd", "a", and "b", respectively, for #69 Hue-lon acrylic resin mixed with a ratio of 0.56 milliliter of monomer per gram of polymer. The results obtained for this resin were chosen as a representative of the group of ten resins tested.

An examination of the graphs shows that in the thicker specimens the "Rd", "a", and "b" readings for the white background approach those for the black background. With thick specimens (5 mm or more) there was no measureable difference in the readings with a change in background. The color of the thick specimens is the sum of two different light components. One component is the light which is reflected off the surface of the specimen and the other component is that one which is composed of the light which enters the specimen and is returned by diffusion from the individual pigment particles. These two components are not necessarily the same color.

In the thin specimens (1.5 mm and less) with a white backing the color approaches that of the background. The color of the specimen will never have the same color as that of the background because the main color component will always be diluted by a secondary color component. In this range of thickness the main color component is the color of the light passing through the specimen and being reflected by the background. This component will approach the color of the background. The secondary color component is that light which is reflected from the surface of the specimen. This

color component will have its own color. This component will not vary in color or intensity for different thickness specimens. In the case of a black background the main component is that light which enters the specimen and is reflected by the pigment. Its effect decreases with a decrease in thickness until it finally becomes negligible in relation to the surface-reflected light. With a black background the color of the specimen will approach the color of the surface-reflected light, rather than the background color.

In the range of 0.5 mm to 4 mm with the white background there is a deviation from the approach towards the background color. As the specimens decrease in thickness the intensities of the colors (both the "a" and "b" values) increase to a maximum, then reverse and begin to approach the color of the backing. The color of a specimen in this region is a function of three components. The first and least important component is the light which is reflected from the surface of the specimen. The second component, whose color intensity decreases with a decrease in thickness, is that light which is reflected internally from the pigment of the specimen. This component with increasing thickness approaches the color of an opaque specimen. The third component is the light which passes through the specimen and is reflected off the background and returns through the specimen. In very thin specimens this component is the dominant factor. Its color approaches that of the background as the specimens become thinner. As the specimens become thicker the light

of this component must pass through increasing amounts of pigment. The pigment acts as an absorber, removing certain portions of the light spectrum. Thus as the amount of pigment increases the greater is the absorbing action and the more intense in color is this light. As the thickness of the specimen continues to increase the magnitude of this component rapidly decreases. The rate of increase in color intensity of this component is much greater than that of the internally-reflected component. The combination of these two components causes the characteristic peak in "a" and "b" coordinates.

The colors at infinite thickness of the ten Hue-lon tooth-colored resins and one Vitacrylic pink-colored resin which were used in this study are listed in Table 1. The colors of the resins are averages of the prepared specimens. These coordinates should not be taken as the absolute colors of the resins because of the inability to accurately reproduce specimens. These figures indicate, however, the range of colors which were measured.

Table 1

Shade	"Rd"	"a"	"b"
No. 61 Hue-lon	45	+1	+18
No. 62 Hue-lon	45	+1	+16
No. 65 Hue-lon	45	+3	+19
No. 66 Hue-lon	45	+1	+19
No. 67 Hue-lon	38	+1	+20
No. 69 Hue-lon	38	0	+18
No. 78 Hue-lon	34	0	+19
No. 87 Hue-lon	32	+2	+19
No. C Hue-lon	49	0	+18
No. D Hue-lon	47	0	+20
Vitacrylic	24	+33	+15

Figures 4, 5 and 6 show the results of the color measurements of a series of specimens which were prepared using two different ratios of liquid to powder. The 0.68 ml/gm mix is a very thin mix while the 0.44 ml/gm is a very thick mix. Normally a mix would never be made that fell outside of these limits. For the preparation of these specimens No. 87 Hue-lon acrylic resin was used. Since opacity is the ratio of the black background "Rd" value to the white background "Rd" value, it can be seen from Figure 4 that there is a slight increase in opacity with a decrease in ratio of monomer to polymer. Such a change would be expected. A decrease in monomer per unit volume would necessitate an increase in pigment (contained in the polymer) per unit volume, thus increasing the opacity. The values for "a" and "b" shown in Figures 5 and 6 indicate that the ratio of monomer to polymer cause little change in color. In the range of normal variations of the ratio, the effect on color and opacity is negligible.

The reproducibility of readings on the colorimeter was checked by taking four sets of readings on 18 different specimens. The standard deviation for duplicating readings was 0.16 NBS units of color difference. Out of 144 measurements one value deviated between 0.6 and 0.5 NBS units, one between 0.5 and 0.4, three between 0.4 and 0.3 and all the rest by less than 0.3.

The ability to reproduce specimens is not nearly as good as the ability to measure their color. The standard deviation of prepared specimens was 1.06 NBS units of color difference.

4. SUMMARY

The color of translucent acrylic resins can be explained as the sum of three components. The first component is that light which is reflected from the surface of the specimen. The magnitude of this component is constant and is usually small compared to the sum of the three components. The second component is that light which enters the specimen, is diffused off the pigment and is returned. This component is always present and its importance along with its color intensity increases with an increase in thickness. The third component is the light which passes through the specimen and reflects off the background and is returned through the specimen. This component increases in color intensity with an increase in specimen thickness. In the case of thick specimens or those with a black background this component is absent.

A decrease in monomer to polymer ratio of these resins causes a small increase in opacity. In the normal range of monomer-polymer ratios this effect is relatively unimportant.

With the color difference meter used in this study the precision of measurements of opacity and color is greater than is the precision of duplication of specimens.

BIBLIOGRAPHY

1. Evans, Ralph M. *An Introduction to Color*, John Wiley and Sons, Inc., New York (1948).
2. Judd, Deane B. *Color in Business, Science and Industry*, John Wiley and Sons, Inc., New York (1952).
3. *The Gardner Automatic Color Difference Meter* (Instruction Pamphlet). Gardner Laboratory, Inc., Bethesda 14, Md.

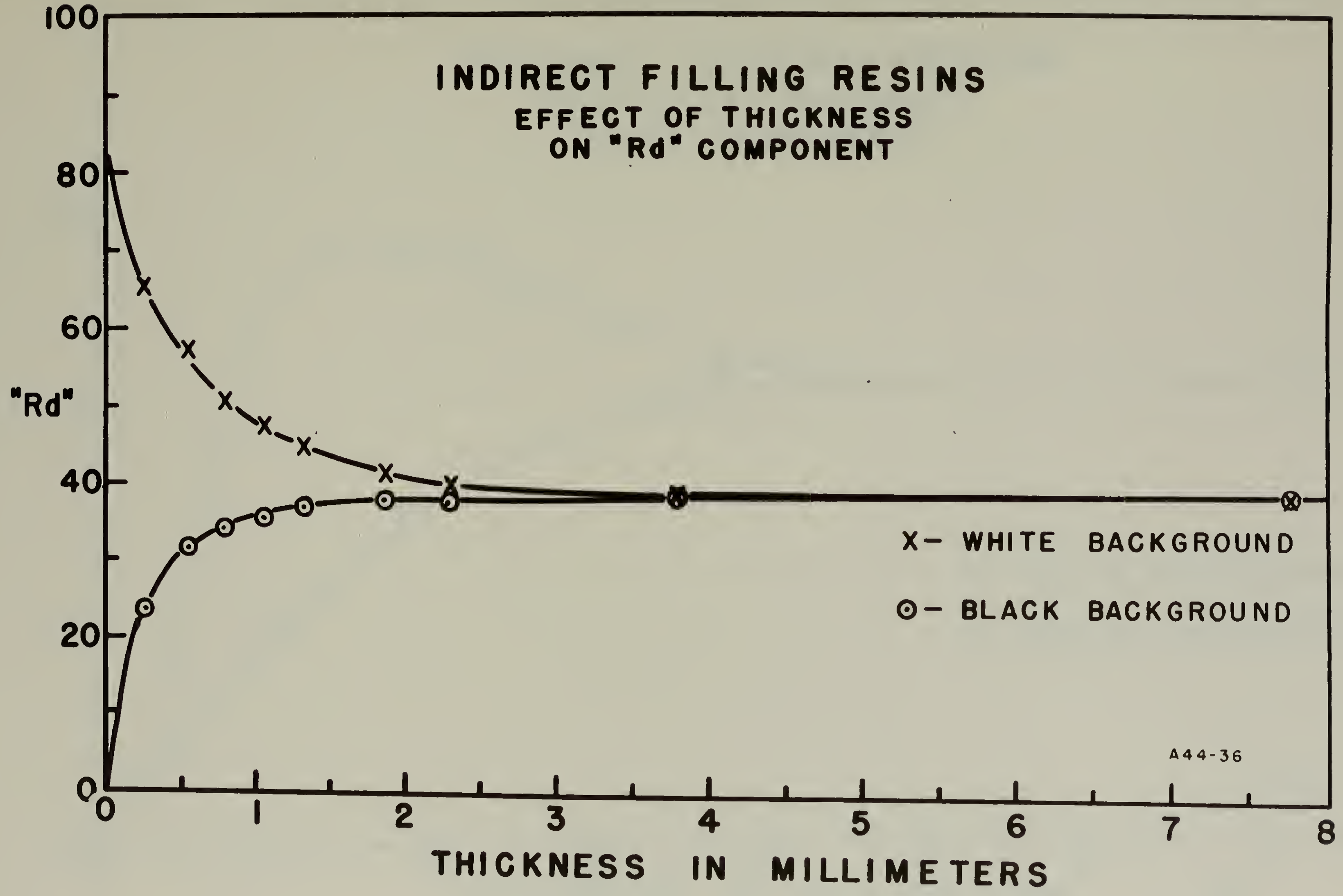

FIGURE NO. I THE CHANGE IN "Rd" COLOR COORDINATE OF A TRANSLUCENT RESIN WITH A CHANGE IN THICKNESS OF THE SPECIMEN

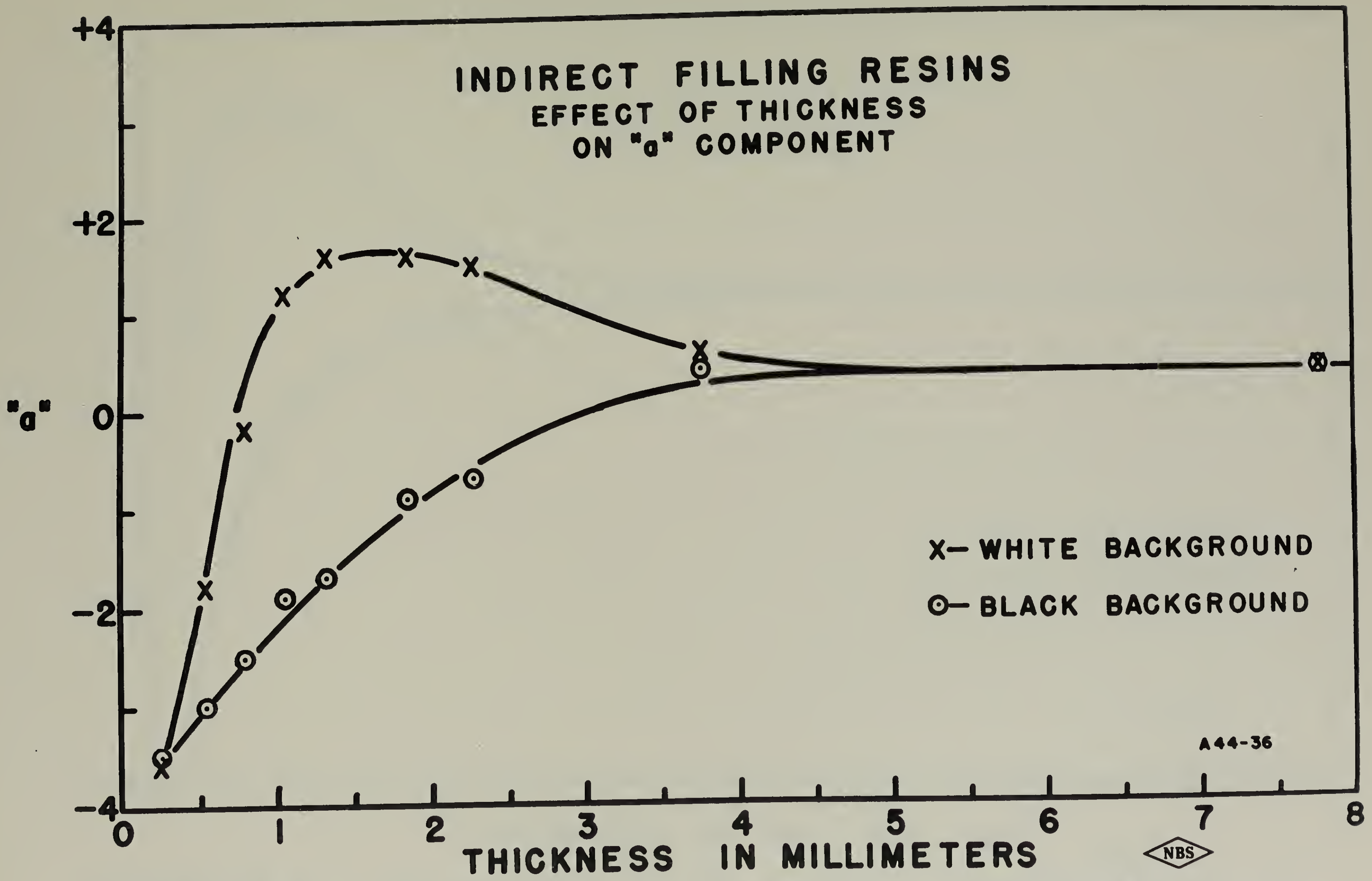

FIGURE NO.2 THE CHANGE IN "a" COLOR COORDINATE OF A TRANSLUCENT RESIN WITH A CHANGE IN THICKNESS OF THE SPECIMEN

[illegible]

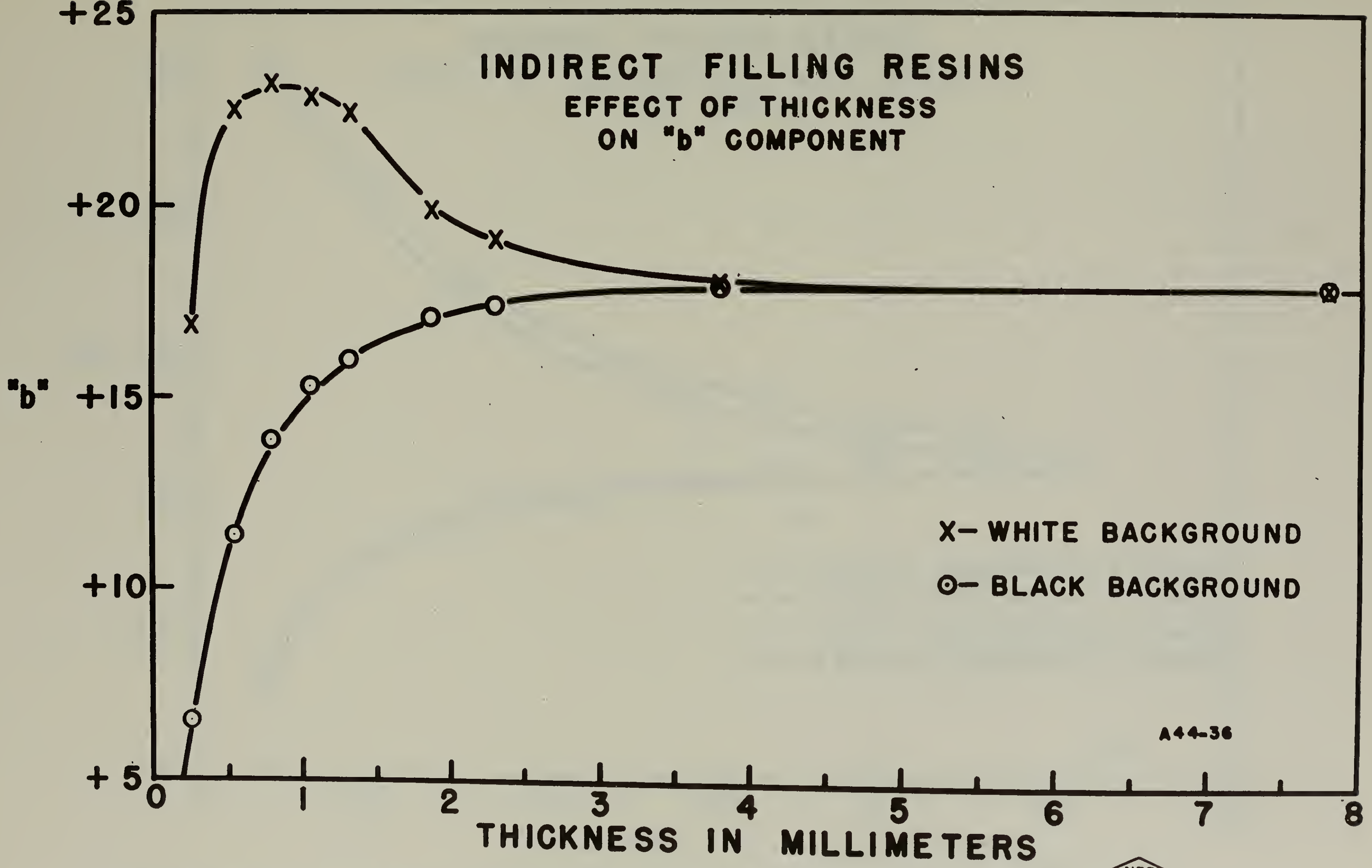

FIGURE NO. 3 THE CHANGE IN "b" COLOR COORDINATE OF A TRANSLUCENT RESIN WITH A CHANGE IN THICKNESS OF THE SPECIMEN

[illegible]

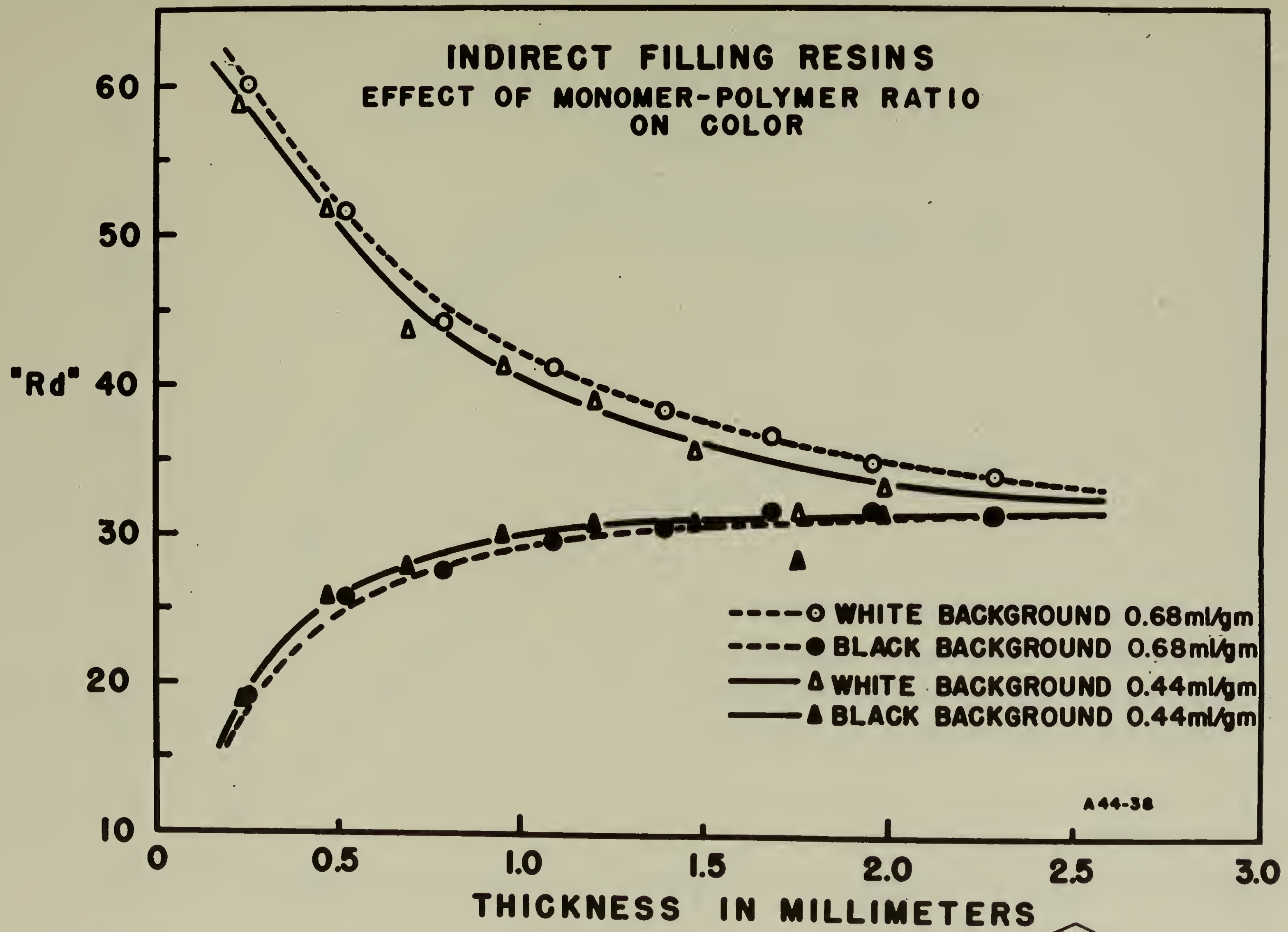

FIGURE NO.4 THE EFFECT OF MONOMER-POLYMER RATIO ON THE "Rd" COLOR COORDINATE OF A TRANSLUCENT RESIN

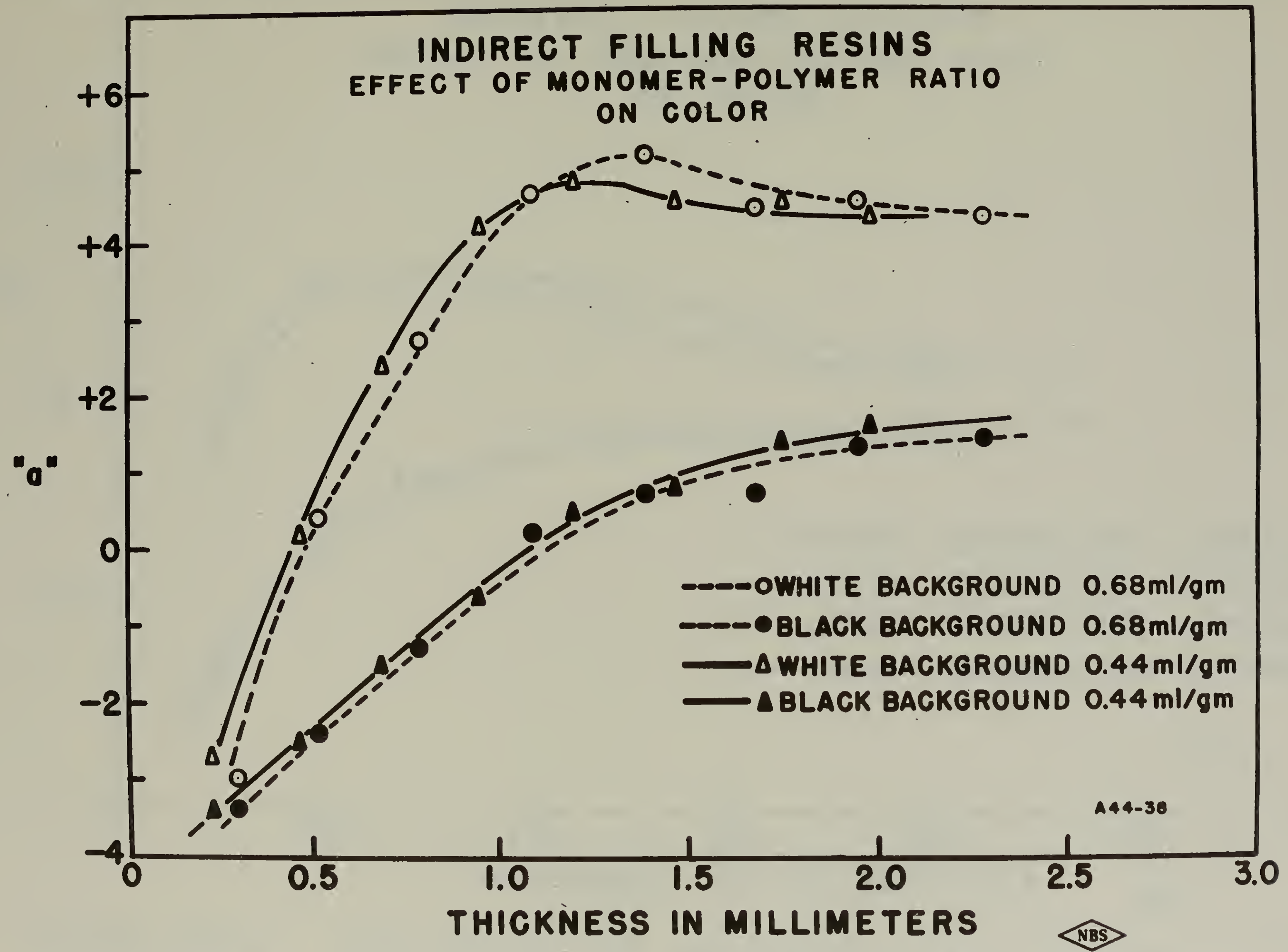

FIGURE NO. 5 THE EFFECT OF MONOMER-POLYMER RATIO ON THE "a" COLOR COORDINATE OF A TRANSLUCENT RESIN

[illegible]

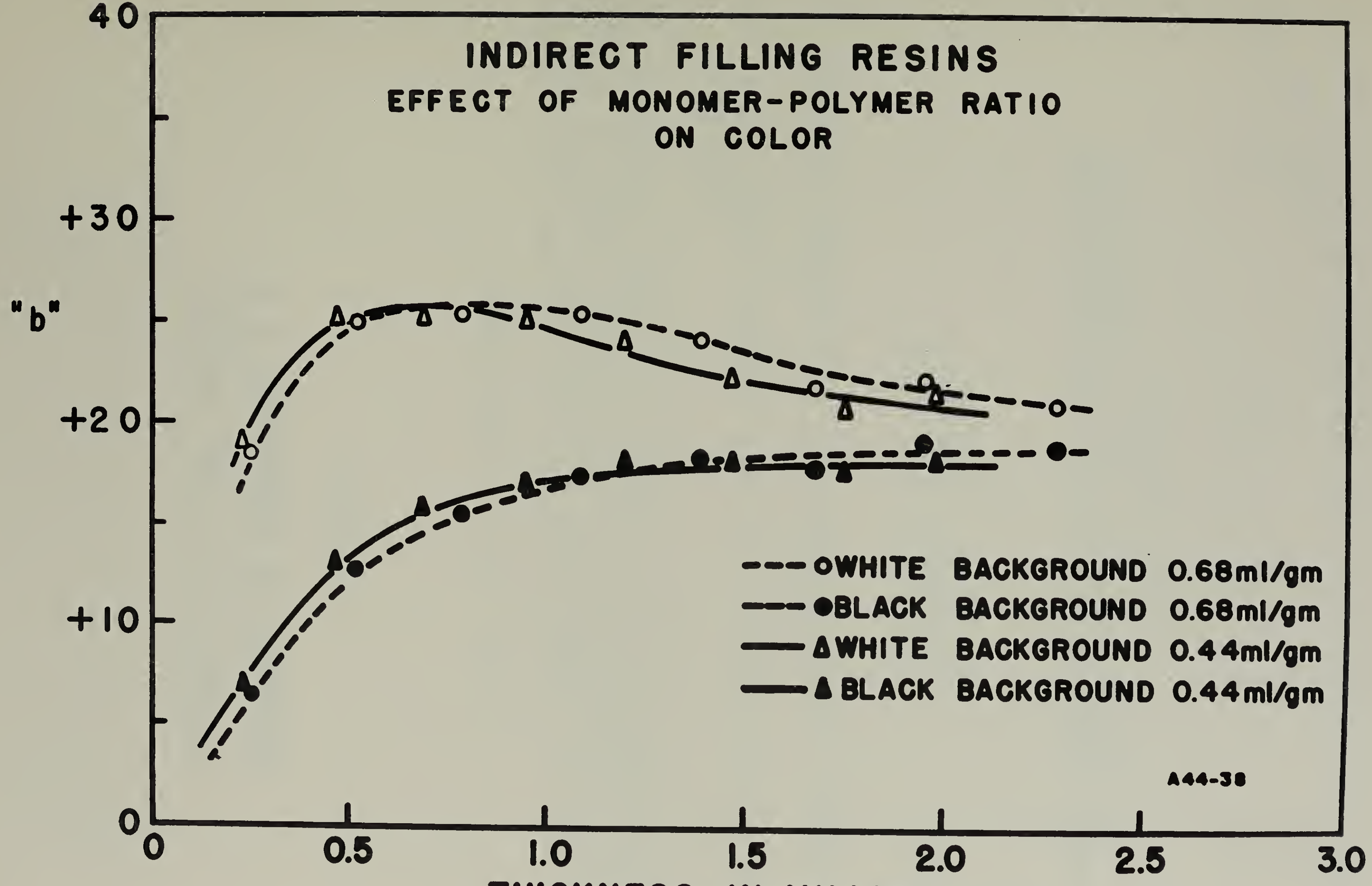

FIGURE NO.6 THE EFFECT OF MONOMER—POLYMER RATIO ON THE "b" COLOR COORDINATE OF A TRANSLUCENT RESIN

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

RELATIONSHIP BETWEEN RESIDUAL MONOMER AND SOME PROPTERTIES OF SELF-CURING DENTAL RESINS

by

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

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

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RELATIONSHIP BETWEEN RESIDUAL MONOMER AND SOME PROPERTIES OF SELF-CURING DENTAL RESINS

Abstract

The maximum temperature and the time to reach it during polymerization are reported for 15 brands of self-curing dental acrylic resins and for one of these resins to which known amounts of promoter were added. The promoter, dimethyl-para-toluidine, decomposes the benzoyl peroxide catalyst at room temperature and initiates the polymerization reaction of methyl methacrylate. The rate of polymerization and the maximum or peak temperature are dependent on the amount of promoter. Within the limits of promoter concentration used, increased promoter results in higher maximum temperature and reaction rate. When other factors are held constant the higher maximum temperatures, which exist for a matter of seconds, result in less residual monomer after the polymerization. Data are presented showing that as the residual monomer becomes less, physical properties such as strength and modulus of elasticity increase.

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1. INTRODUCTION

The self-curing acrylic resins are now offered to the dental profession for several purposes including uses as cements, denture bases, denture base liner and repair materials, and direct filling materials. These compounds contain various catalysts and promoters that have a pronounced effect on the polymerization reaction and the amount of monomer remaining in the cured resin.

It is generally accepted in polymer chemistry that larger molecules are produced as the temperature of polymerization is decreased. On the other hand, as the temperature of polymerization is decreased, the amount of monomer converted to polymer is decreased. Figure 1 shows that as the temperature starts rising due to the polymerization reaction, the maximum or peak temperature occurs in a matter of minutes. As the peak temperature increases, the time to reach it decreases.

This investigation was undertaken to determine the relationships between residual monomer content and the physical properties of the self-curing resins.

2. MATERIALS AND TEST PROCEDURES

The materials studied in this investigation grouped according to their use are listed in Table 1.

The peak temperature during polymerization and its time of occurrence were determined on cylindrical specimens (200 mm in volume) according to the procedure outlined by Wolcott, Paffenbarger and Schoonover [1].

The residual monomer content was determined by the method of Caul, Wall and Acquista [2], using the frozen benzene infrared method on specimens at least 2 days old.

The yield strength, indentation strength and modulus of elasticity were determined according to the methods outlined by Sweeney, Sheehan, and Yost [3]. Values of indentation strength are included in this report for two reasons. First, it is a very convenient method of measuring the strength of small specimens and, second, the value for indentation strength should be comparable to yield strength.

3. RESULTS AND DISCUSSION

Figure 2 shows the relationship between peak temperature and time to reach it for the materials investigated. This graph includes data from the Wolcott report as well as more recent data obtained by their technique. A single smooth curve cannot be used to cover all points since the results are too scattered.

As many of these materials contain different promoters, cross-linking agents, fillers, polymers and monomers, a single smooth curve would not be expected to fit the data.

The behavior of one material with various amounts of a promoter was investigated. Specimens were prepared with Duz-All polymer (a direct filling resin), methyl methacrylate monomer and dimethyl-p-toluidine (a promoter); the compositions are shown in Table 2. The peak temperature during polymerization and the time to reach it are shown as open circles in Figure 2. A smooth curve can be drawn through these data.

The monomer content, modulus of elasticity, yield strength, and indentation strength were determined for the specimens made with the various concentrations of promoter. These data are presented in Table 2. The interrelationships are shown graphically in Figures 3 and 4.

Figure 3 shows the relationships between the amount of promoter and (1) and the peak temperature, (2) time to reach peak temperature, and (3) the amount of residual monomer. Increased amount of promoter results in higher peak temperature, but shortens the time to reach it. The higher temperature peaks force the polymerization more nearly to completion and reduce the residual monomer content.

Figure 4 shows that as the amount of residual monomer increases the modulus of elasticity and yield and indentation strengths decrease.

4. SUMMARY AND CONCLUSIONS

When a direct filling resin polymer is mixed with methyl methacrylate monomer containing dimethyl-para-toluidine promoter, polymerization will occur at room temperature in a relatively short time.

The peak temperature during polymerization and the time to reach this temperature are reported for 15 brands of self-curing dental resins and for a self-curing resin containing known amounts of dimethyl-p-toluidine.

Values for residual monomer, peak temperature, time to reach peak temperature, modulus of elasticity, yield strength, and indentation strength were determined on samples of resin prepared from one polymer with monomer containing different amounts of promoter. It was shown that all of these factors and properties are interrelated.

As the amount of promoter is decreased, the temperature rise during polymerization decreases while the residual monomer and time to reach peak temperature increase. As the residual monomer increases, such physical properties as modulus of elasticity and yield and indentation strengths decrease.

BIBLIOGRAPHY

1. Wolcott, Robert B., Paffenbarger, G. C., and Schoonover, I. C. Direct resinous filling materials: Temperature rise during polymerization. J.A.D.A. 42:253, 1951.
2. Caul, Harold J., Wall, Leo A., and Acquista, Nicolo. The determination of monomer content of polymethyl methacrylate. Manuscript submitted to J.A.D.A.
3. Sweeney, W. T., Sheehan, W. D., and Yose, E. L. Mechanical properties of direct filling resins. J.A.D.A. 49:513, 1954.

TABLE 1

Identifying Number	Brand		Type
1	A-Thermoplast V-10		Direct filling resins
2	Dentafil		
3	Duz-All		
4	Fast Crown		
5	Kadon		
6	Plasto-filling pf 3		
7	Replica		
8	Sevriton		
9	Sweden		
10	Texton		
11	P.F.		
12	Dura Base		Denture base reliner
13	Dura Cement		Resin cements
14	Acrynamel		
15	Staweld		Denture base repair
	Duz-All polymer+ methyl methacrylate monomer	Amount of dimethyl-p-toluidine based on monomer	
16	"	0.50%	Experimental resins
17	"	0.25%	
18	"	0.20%	
19	"	0.15%	
20	"	0.10%	

TABLE 2

Properties of Acrylic Resins Prepared with Different Amounts of Promoter

Promoter*	Residual Monomer/	Temperature Rise≠ **	Time to Peak Temperature≠	Modulus of Elasticity ≠	Yield Strength≠	Indentation Strength/
%(based on monomer)	%	°C	min.	psi	psi	psi
0.50	1.7	30 ± 2.5	11.0 ± 0.3	3.1 ± 0.1x10^5	6.6 ± 0.1x10^3	10.6 x 10^3
0.25	2.6	23 ± 1.9	13.3 ± 0.4	2.7 ± 0.1	5.5 ± 0.4	9.6
0.20	3.1	17 ± 2.8	14.3 ± 0.5	2.5 ± 0.1	5.0 ± 0.4	9.4
0.15	3.5	14.5±2.1	16.2 ± 0.4	2.2 ± 0.2	4.1 ± 0.3	8.5
0.10	5.7	9.5±1.3	21.8 ± 1.8	1.6 ± 0.1	3.0 ± 0.4	7.2

* The values are the amount of dimethyl-para-toluidine present in the monomer (Rohm and Haas methyl methacrylate inhibited with 0.006% hydroquinone). The specimens were prepared by mixing 0.45 ml of monomer, containing the listed amount of promoter, with 1.0 g of the Duz-All polymer in powdered form.

/ These values are the average of 2 determinations.

≠ These values are the average of 5 determinations; the ± figures are standard deviations.

** Temperature rise = peak temperature -37°C.

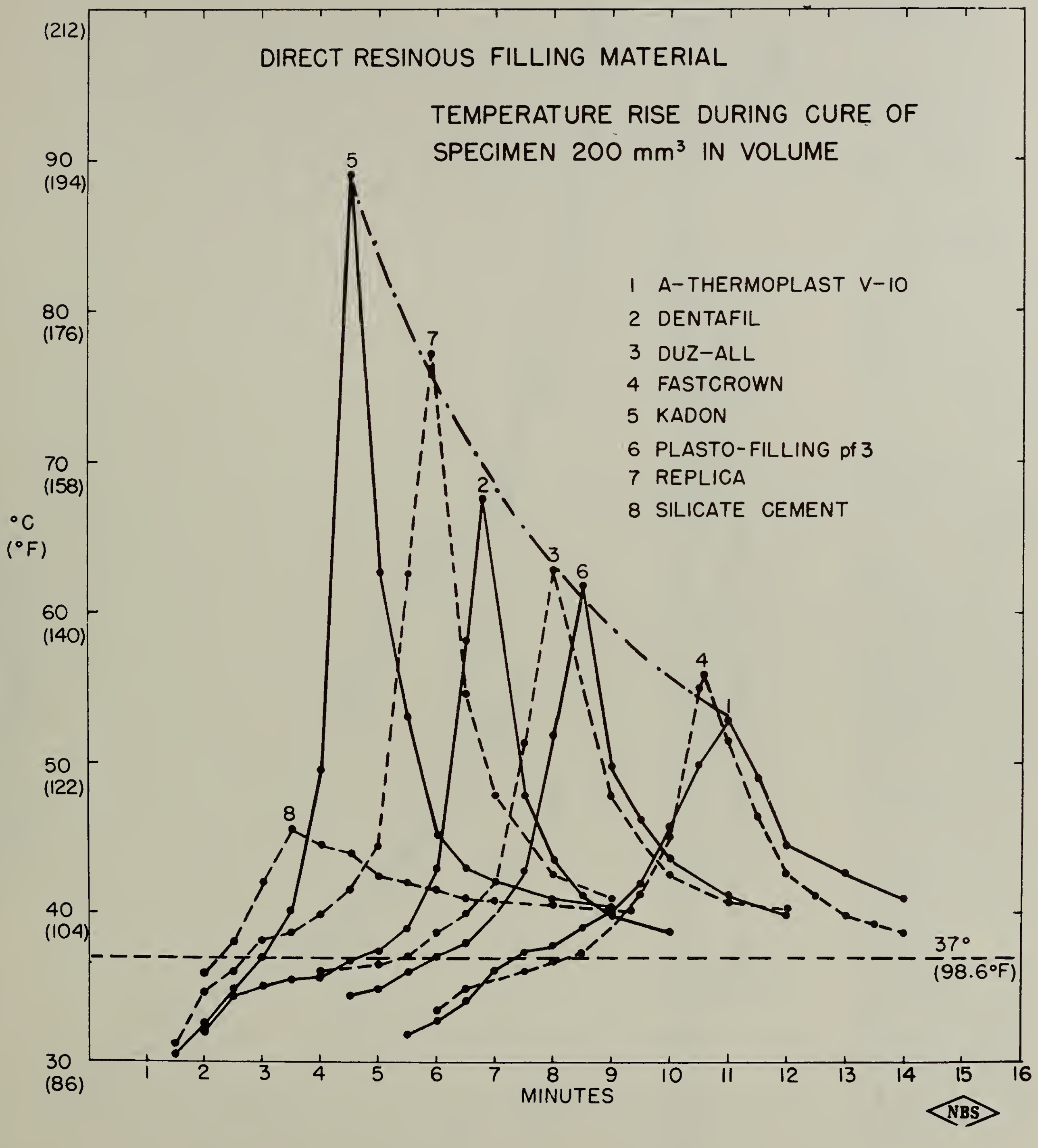

Figure 1. Relationship between temperature rise and curing time of self-curing dental filling resins.

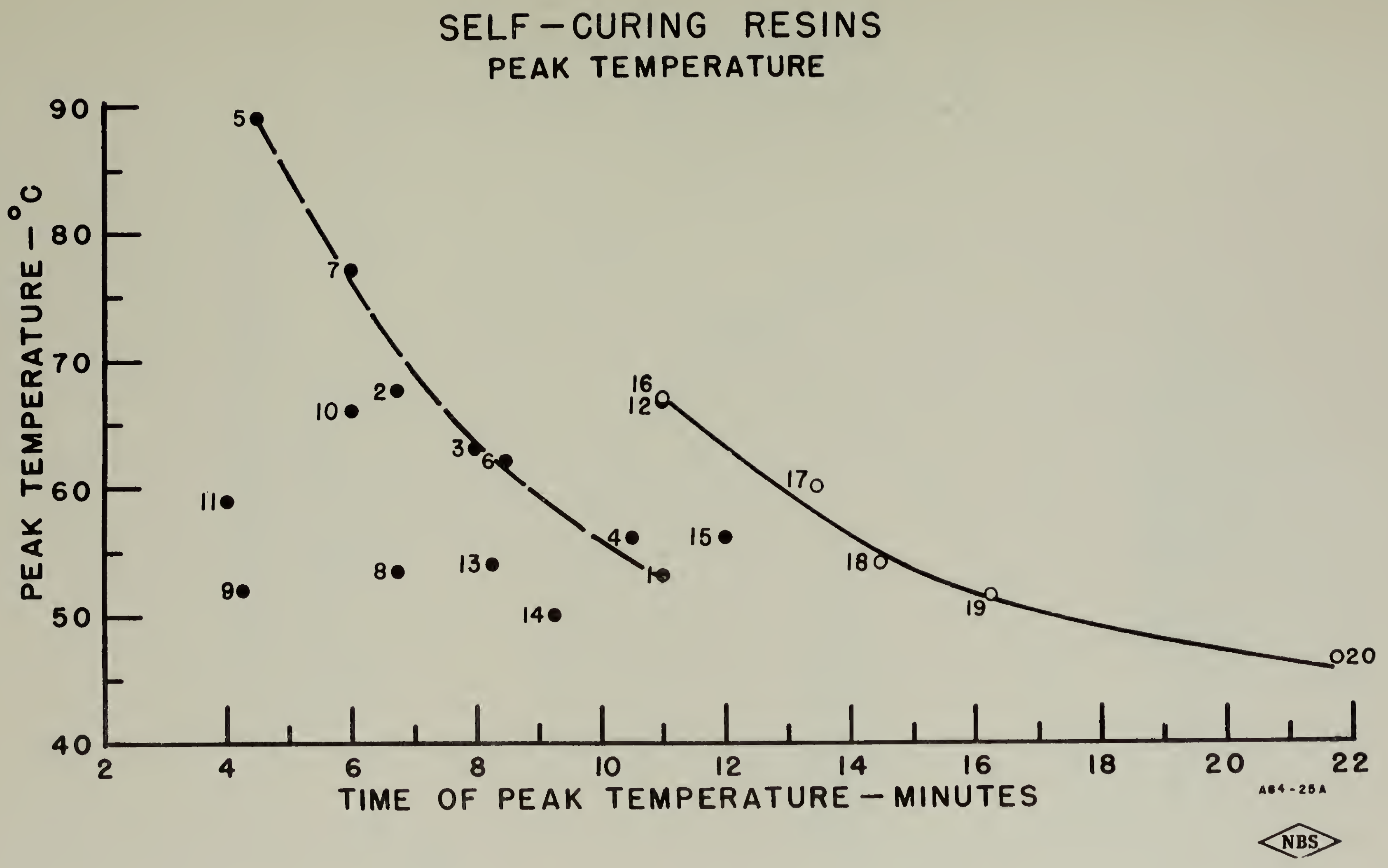

Figure 2. The broken curve is the same as that shown in Figure 1. The solid curve on the right shows the relationship between peak temperature and time of its occurrence for the experimental resins in which the promoter content was varied. Identifying numerals for each point are the same as those in Table 1. Solid circles are commerical brands of self-curing resins. Open circles are the experimental resins listed in Table 1.

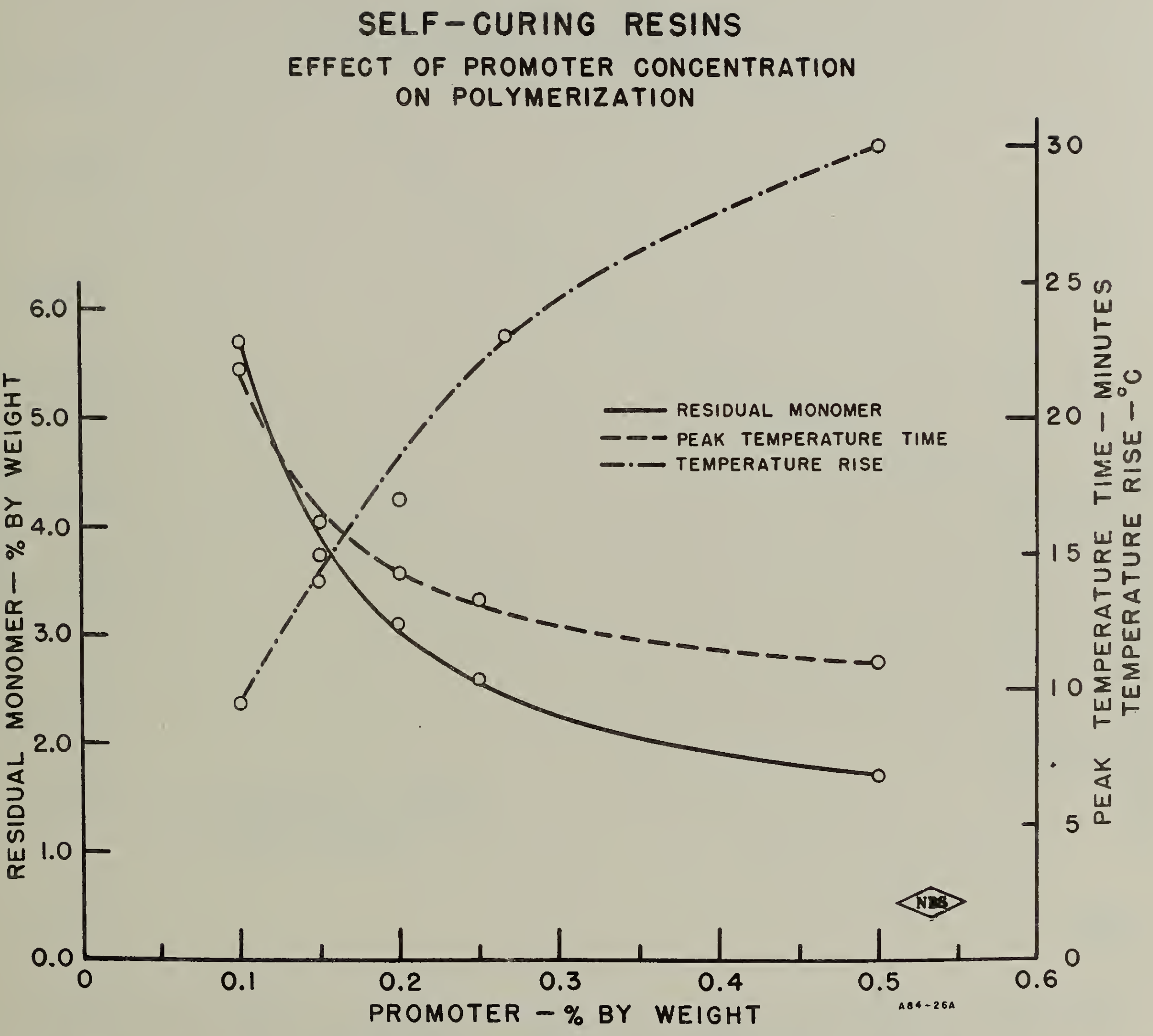

Figure 3. Effect of promoter concentration on the amount of residual monomer, peak temperature time, and temperature rise.

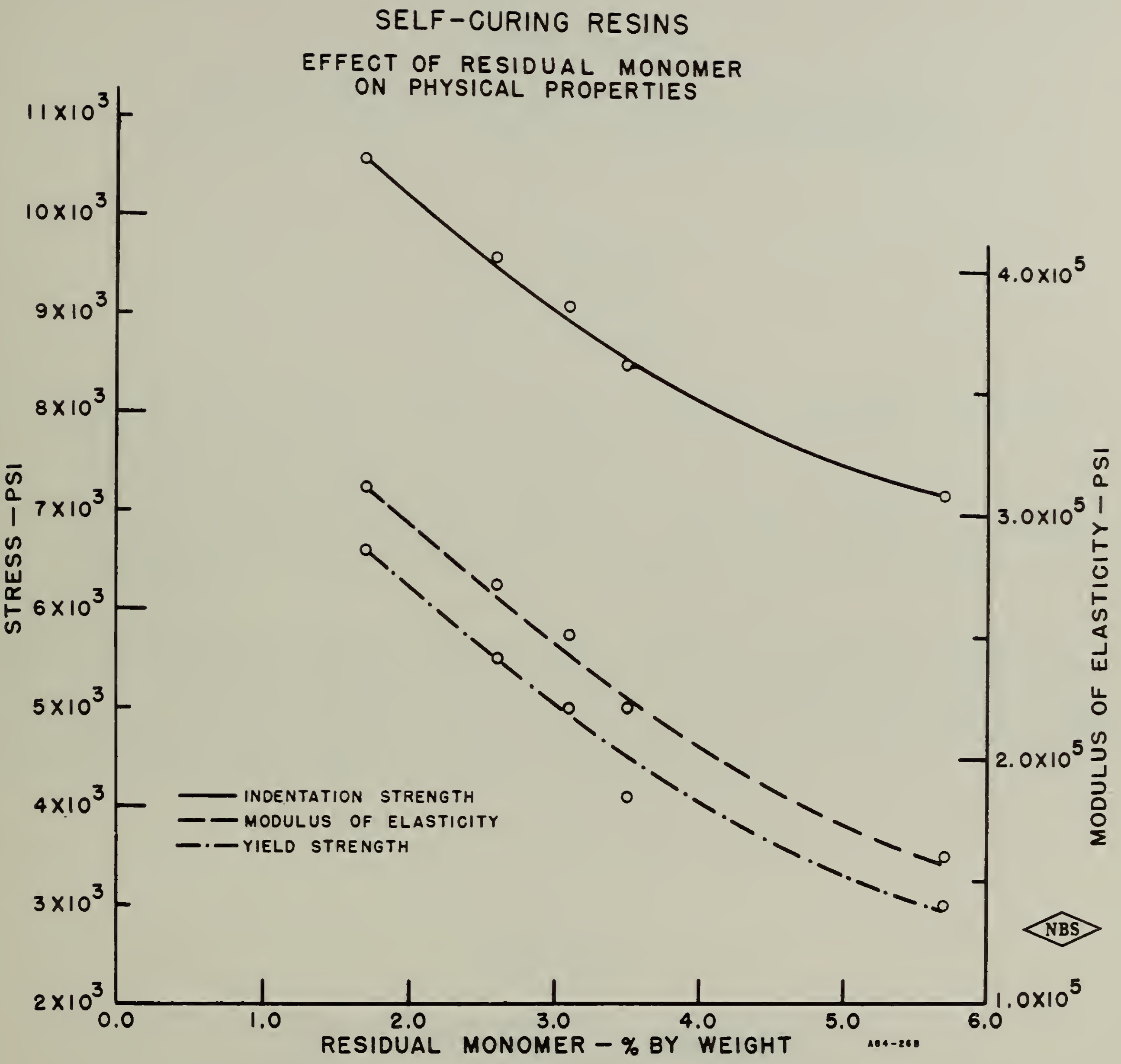

Figure 4. Residual monomer effect on the modulus of elasticity and indentation and yield strengths of self-curing resins.

NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

DEVELOPMENT OF METHODS FOR EVALUATION OF ROTATING DENTAL DIAMOND ABRASIVE INSTRUMENTS

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DEVELOPMENT OF METHODS FOR EVALUATION OF ROTATING DENTAL DIAMOND ABRASIVE INSTRUMENTS

Abstract

To determine the cutting effectiveness of rotating diamond instruments measurements were made of the rate of removal of material by these instruments from pyrex glass rods, common window glass and human enamel cut under controlled loads and speeds of rotation. Results obtained on enamel could not be closely correlated with those obtained on glass although it was observed that those instruments which were the most effective and those which were the least effective in cutting glass were also the most and least effective, respectively, in cutting enamel. Cutting in glass resulted in complete breakdown of the instruments through loss of diamonds in fifteen minutes or less, while the breakdown point was not attained in enamel although tests as long as one hundred and forty minutes were made. Examination of diamond points which had been discarded after clinical use indicated, however, that there is breakdown of critical areas of the instruments when used clinically in enamel. To evaluate diamond instruments it is essential to have a breakdown test capable of measuring the ability of bonding material to retain

the diamonds. The results obtained indicate that such a test can be based on cutting effectiveness in glass.

1. INTRODUCTION

A continuing program of research on the cutting characteristics of rotating dental instruments has been conducted at the Dental Research Laboratory of the National Bureau of Standards. This project has included studies of the cutting effectiveness of diamond instruments. There has been a widespread tendency toward the increased use of these instruments as a result of the higher handpiece rotational speeds now available to the dental profession. Recent work [1, 2], has indicated that diamond abrasive instruments operate more efficiently than steel or carbide burs in the removal of tooth enamel. Ingraham's work [3], provides a more efficient method for the rapid removal of hard tooth structures utilizing modern instrumentation. There have been, however, many reports from the field of unsatisfactory and inconsistant performance of these instruments. The work reported here was therefor undertaken for the purpose of developing laboratory methods for evaluating diamond abrasive instruments.

2. EXPERIMENTAL PROCEDURE AND RESULTS

In this study a weight-loss method was utilized to compare the cutting effectiveness of various brands of diamond instruments. A machine with accessory timing and controlling features which has been designed and constructed at the School of Aviation Medicine, Randolph Air Force Base, Texas, was modified for the diamond evaluation. A moveable platform which held the material

to be cut could be brought automatically under predetermined loads to a precision spindle and draw-collet chuck for the diamond instrument. Cutting application and release were accurately controlled by an electronic interval timer through an electro-magnet and spring mechanism.

Pyrex glass rods, one-quarter of an inch in diameter (Figure 1) were selected as the test material for the 3/32 inch cylindrical diamond points first evaluated. The measure of cutting rate was obtained by determining weight loss of the pyrex rod after a fixed interval of cutting time at a specific load. Speeds of 3, 5, 10 and 15 thousand revolutions per minute were employed.

The cutting cycle consisted of making a series of three five-second cuts in the same point on the rod, then shifting to a new area, where the cycle of three cuts was repeated. After four such cutting cycles or a total of one minute, the specimen (Figure 2) was removed and weighed. This procedure was repeated at the end of each minute of cutting for a total of five minutes. Beyond this point and up to a total of twenty-five minutes, weight loss was determined at the end of each five minutes of cutting. The weight loss during cutting time will hereafter be referred to as the rate of cut.

Five each of ten brands of 3/32 of an inch cylindrical diamond instruments were subjected to the test procedure. The load was 400 grams. The averages of the values for the five instruments of each brand, shown in bar graph form (Figure 3), are plotted in order of decreasing effectiveness

of the instruments and show the rate of cut per minute at five minute intervals for fifteen minutes. In all cases beyond this time, the instruments had deteriorated to the point where they were no longer effective in pyrex. These same data are plotted showing the total material removed in fifteen minutes of cutting at the four speeds (Figure 4). There is considerable variation in the performance of these instruments. The instrument group brand "I", for example, cut more material at the lowest speed (3,000 rpm), than all but one of the other brands at any speed. Those instruments in the higher performance group showed a general increase in cutting rate with the increase in speed; those in the low performance group did not, due to their more rapid deterioration.

A series of experiments was conducted with the intention of correlating the results of cutting human enamel and glass. The instruments were diamond wheels approximately one-quarter of an inch in diameter by one-sixteenth of an inch in thickness. The teeth were mounted so that they were at a 45 degree angle to the long axis of the grinding instrument (Figure 5). The load was 200 grams. These instruments cut more effectively than the cylindrical diamonds, because of their greater diameter. Reducing the load from 400 to 200 grams prevented cutting through the enamel into the dentin of the teeth during the cutting period. The diameter of the instruments varied somewhat from brand to brand. In order to provide a common basis for comparative results, rotational speed was adjusted to provide a constant

peripheral rate of travel for all brands. This was 450 feet per minute at approximately 5,000 rpm and 900 feet per minute at approximately 10,000 rpm. A different tooth was used for each minute of cutting. Twelve, five-second cuts were made, each in a new location. Each tooth was weighed before and after the cutting cycle of one minute.

There is no apparent breakdown of the bonding of the abrasive under the conditions of this experiment (Figure 6). The cutting rate remained essentially the same for a total of one hundred and forty minutes of cutting by two brands of instruments, brand "I", chosen from the outstanding performance group, and brand "B", from the low performance group, as determined by the performance of these instruments in pyrex glass.

In order to compare the relative cutting rates of several brands of diamond instruments, a series of experiments was performed on enamel. The total cutting time was ten minutes. Ten teeth were used for each instrument, the average weight of material removed per tooth was considered the cutting rate of that instrument. The load was 200 grams; the angle of cut was forty-five degrees. Twelve, five-second cuts were made in each tooth, each cut on a new area of the tooth surface. Results obtained at 5,000 rpm (450 feet per minute) and 10,000 rpm (900 feet per minute) are arranged in order of decreasing effectiveness of the instruments in Figures 7 and 8.

These same instruments were then re-run at 450 and 900 feet per minute in common one-eighth of an inch thick window glass.

The angle of cutting was forty-five degrees (Figure 9). The procedure consisted of making a series of three five-second cuts at a 200 gram load in each new location on the specimen. The glass was weighed before and at the end of each minute of cutting during the first five minutes, then every five minutes for a total of twenty minutes. The data were plotted for the first five minutes only because breakdown of all instruments occurred within this period (Figures 7 and 8). For purposes of comparison, the data for these instruments while cutting glass are also arranged in the order of relative cutting effectiveness in enamel.

3. DISCUSSION

It is believed that the peripheral speed attained by these instruments, because they are very small in diameter, is too low for optimum performance. Commercial grinding practice with industrial wheels [4], calls for a peripheral speed of from five to seven thousand feet per minute. Dental instruments only 3/32 of an inch in diameter have a peripheral speed of 360 feet per minute at 15,000 rpm. In order to obtain the recommended speed for commercial grinding practice, dental diamond abrasive instruments of this size would require rotational speeds of approximately 245,000 rpm.

There appeared to be very little correlation between the performances of diamond instruments in enamel and in glass. The cutting procedures in glass resulted in a rapid breakdown of the instruments, while this point was not obtained, under the conditions of this investigation, in enamel. Close correlation would not be expected unless this breakdown also occurred in enamel.

However, instrument brand "I", which was outstanding in pyrex glass when evaluated as a 3/32 of an inch cylindrical point at speeds of 3, 5, 10 and 15 thousand rpm, with a 400 gram load, was one of the best instruments in enamel when evaluated as a 1/4 inch wheel, with a 200 gram load. This was also noted when the instrument brand "I", 1/4 inch wheel cut common window glass. Under the same conditions instruments of brand "A" and brand "B" performed very poorly in both glass and enamel. All diamond instruments varied considerably in performance. Inconsistency of performance by individual instruments of the same brand was noted throughout the study.

It is to be emphasized that the cutting of glass results in an evaluation made under severe conditions of heavy loading upon a material that is unlike enamel in structure. Pyrex is homogenous, and is considerably harder than human enamel. Knoop hardness for this glass is 430, human enamel hardness was found to be Knoop 300 to 340. Analysis of the glass-cutting test indicates that it is, in effect, an accelerated breakdown test, wherein the material cut is considerably more destructive to the diamond instrument than is human enamel; this causes a loss of the diamond abrasive, and evaluates the strength of the bond between the diamonds and the head of the instrument.

Breakdown of the bonding medium, with resultant loss of the diamond abrasive, does occur in clinical use. Diamond instruments which had been discarded after clinical operative procedures were collected and examined. It was determined that loss of the abrasive occurred consistantly at the relatively small area or point

of the instrument which received the greatest loading in use. The other surfaces of the instruments showed little or no loss of the abrasive. A study of operative techniques in which diamond instruments were used, indicated areas on the instruments which would be repeatedly subjected to the greatest pressure per unit area (Figure 10). This breakdown in a limited area of the instrument occurs more frequently with diamond than with other abrasive instruments because the diamond instruments do not change shape, as long as they cut, and are used to cut exacting angles, grooves and bevels in operative or crown-and-bridge dentistry. These areas, A and B, (Figure 10) corresponded to the areas of greatest diamond loss noted on those instruments which had been discarded as being no longer of clinical value. The necessary use of small, specifically-shaped instruments results in low peripheral speeds, even at the higher rotational speeds available today. During the preparation of an exacting cut at these low peripheral speeds, the instrument is subjected to repeated high pressures in certain areas; thus, breakdown of the instrument in enamel occurs in clinical usage even though it did not occur under controlled laboratory conditions. Because of this breakdown, an instrument must be evaluated for its ability to resist loss of the abrasive. An accelerated test, using a material such as glass, should determine the ability of a diamond instrument to retain its abrasive particles under the harsh conditions necessarily encountered in clinical use. A specification for diamond instruments should also include a requirement for the removal of an established amount of a test material, possibly one which does not cause breakdown. This would eliminate an instrument

which cut ineffectively even though it did not lose its abrasive.

4. CONCLUSIONS

1. There is a wide variation in the cutting ability of diamond instruments under the conditions of this experiment.

2. Those instruments that performed in an inferior manner in glass, were those that deteriorated rapidly, losing a greater part of their abrasive during the first few cuts.

3. The more durable instruments removed a greater amount of material as rotational speed was increased. The less durable diamond instruments demonstrated little or no improvement in their performance at the higher speeds.

4. Close correlation of the relative cutting efficiencies of these diamond instruments in glass and enamel could not be obtained under the conditions of this experiment. The breakdown which occurred in glass was not produced in up to one hundred and forty minutes of cutting in enamel. Those instruments that were outstanding in cutting glass were in most cases also outstanding in enamel. The poorest instruments in glass were also relatively ineffective in enamel. All instruments were erratic in behavior.

5. Breakdown of these instruments does occur under clinical use possibly because of their small size which results in low peripheral speeds and high pressures on specific areas of the instruments. This breakdown is due to failure of the bonding medium with resultant loss of the diamond abrasive.

6. In the evaluation of the relative cutting effectiveness of dental diamond instruments, a test of the bonding medium should be included. Such a test can be based on cutting effectiveness in glass.

BIBLIOGRAPHY

1. Peyton, F. A., Temperature rise and cutting efficiency of of rotating instruments. New York Dent. J. 18:439 Nov., 1952.
2. Hudson, D. C., and Hartley, Jack L., et al., Some factors influencing the cutting characteristics of rotating dental cutting instruments. J.A.D.A. 50:377 April 1955.
3. Ingraham, Rex, and Tanner, H. M., The adaptation of modern instruments and increased operating speeds to restorative procedures. J.A.D.A. 47:311 Sept., 1953.
4. Kent, William, Mechanical Engineers Handbook, 12th ed., Vol. 2, Sec. 23. John Wiley and Sons, Inc., New York, N. Y. 1952.

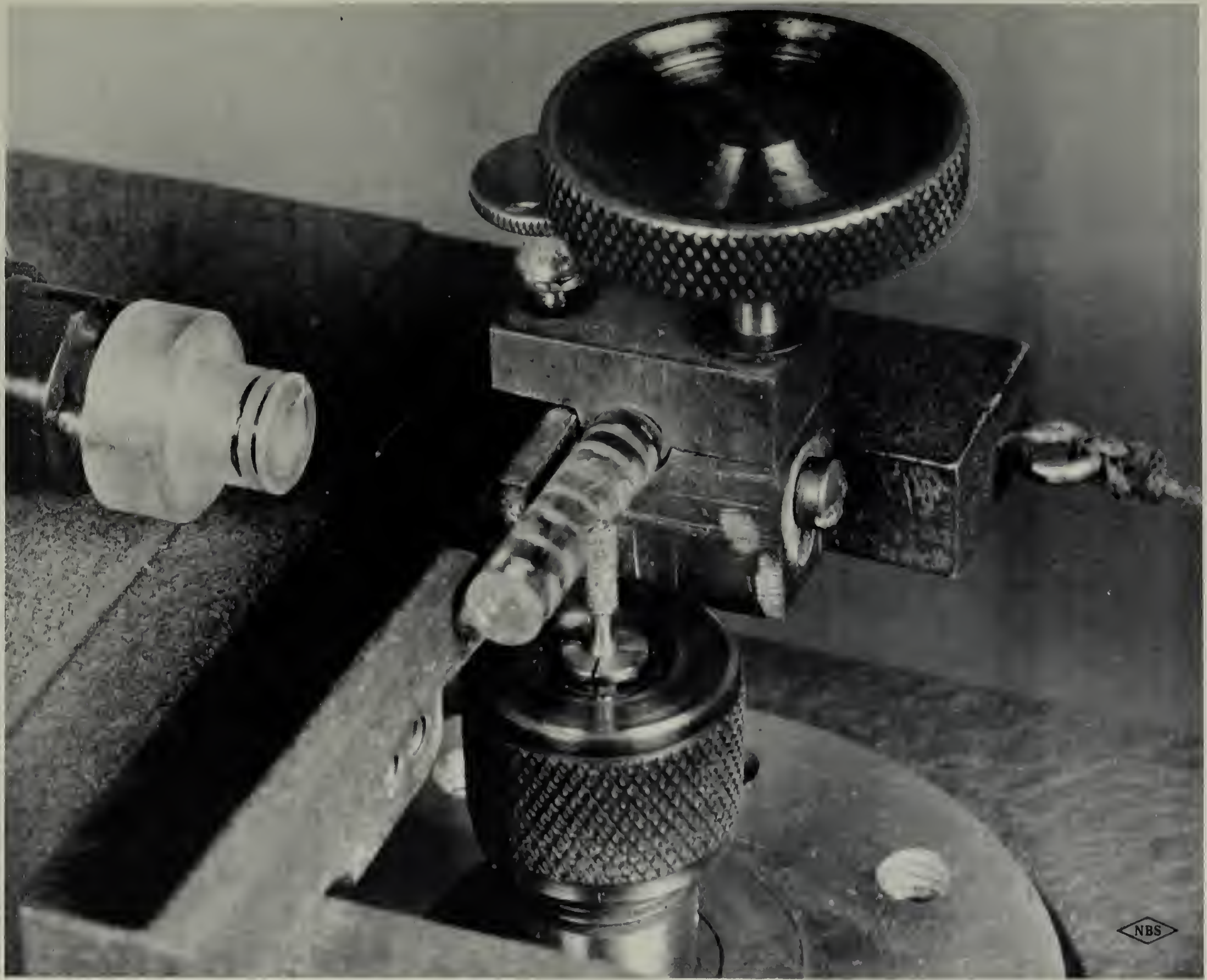

Figure 1. Specimen holder of bur-evaluating machine with pyrex rod specimen in place. A movable platform is electronically controlled to bring the specimen into contact with the rotating diamond instrument for a predetermined period with a known load.

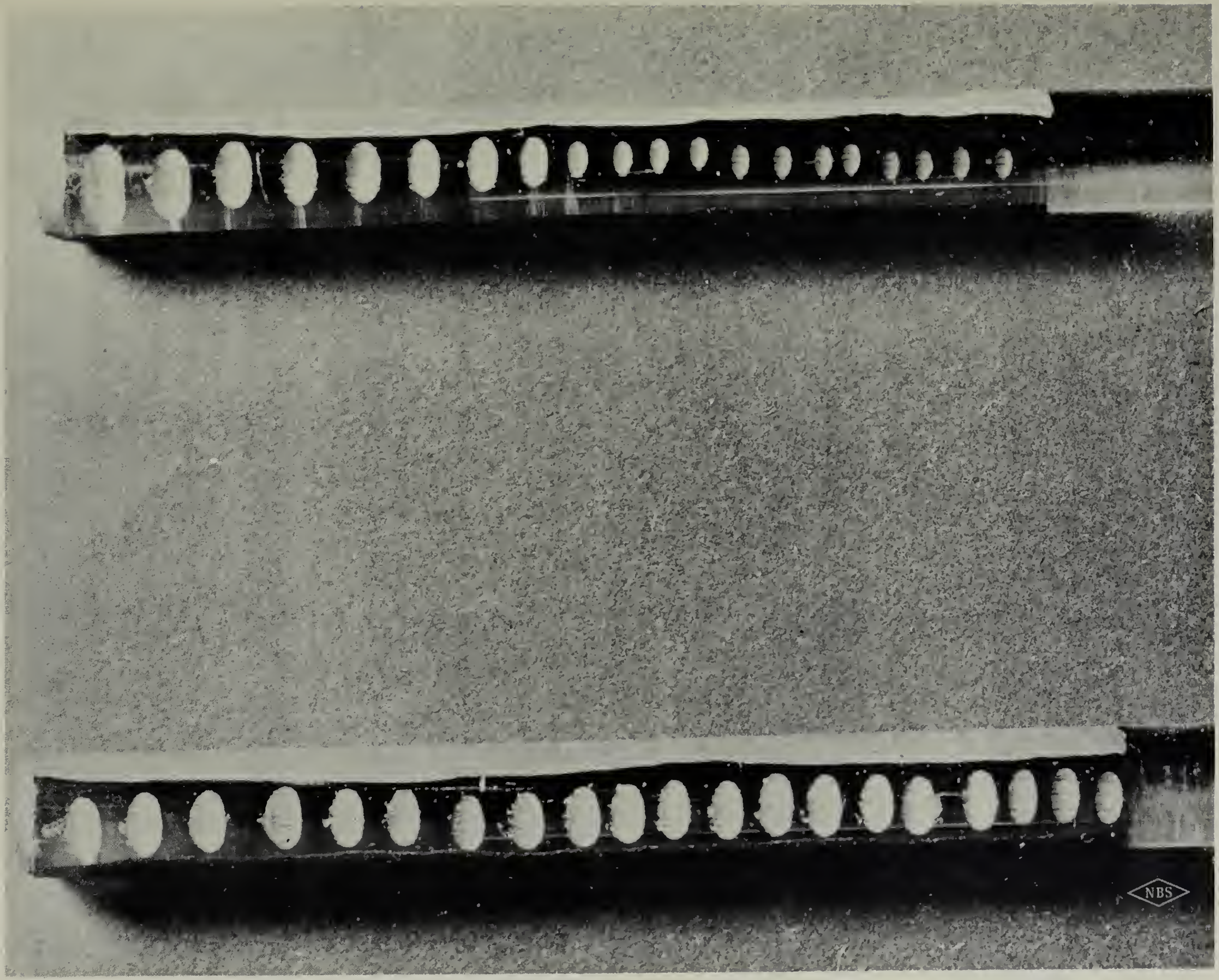

Figure 2. Pyrex rods used in evaluating cutting characteristics of 3/32-inch diamond points. Above: typical series of 15-second cuts by a diamond instrument which rapidly lost its abrasive within the five minutes of cutting shown on the rod. Below: typical series of 15-second cuts by an instrument which did not deteriorate rapidly in the five minutes of cutting shown. Speed, 5,000 rpm; load, 400 grams.

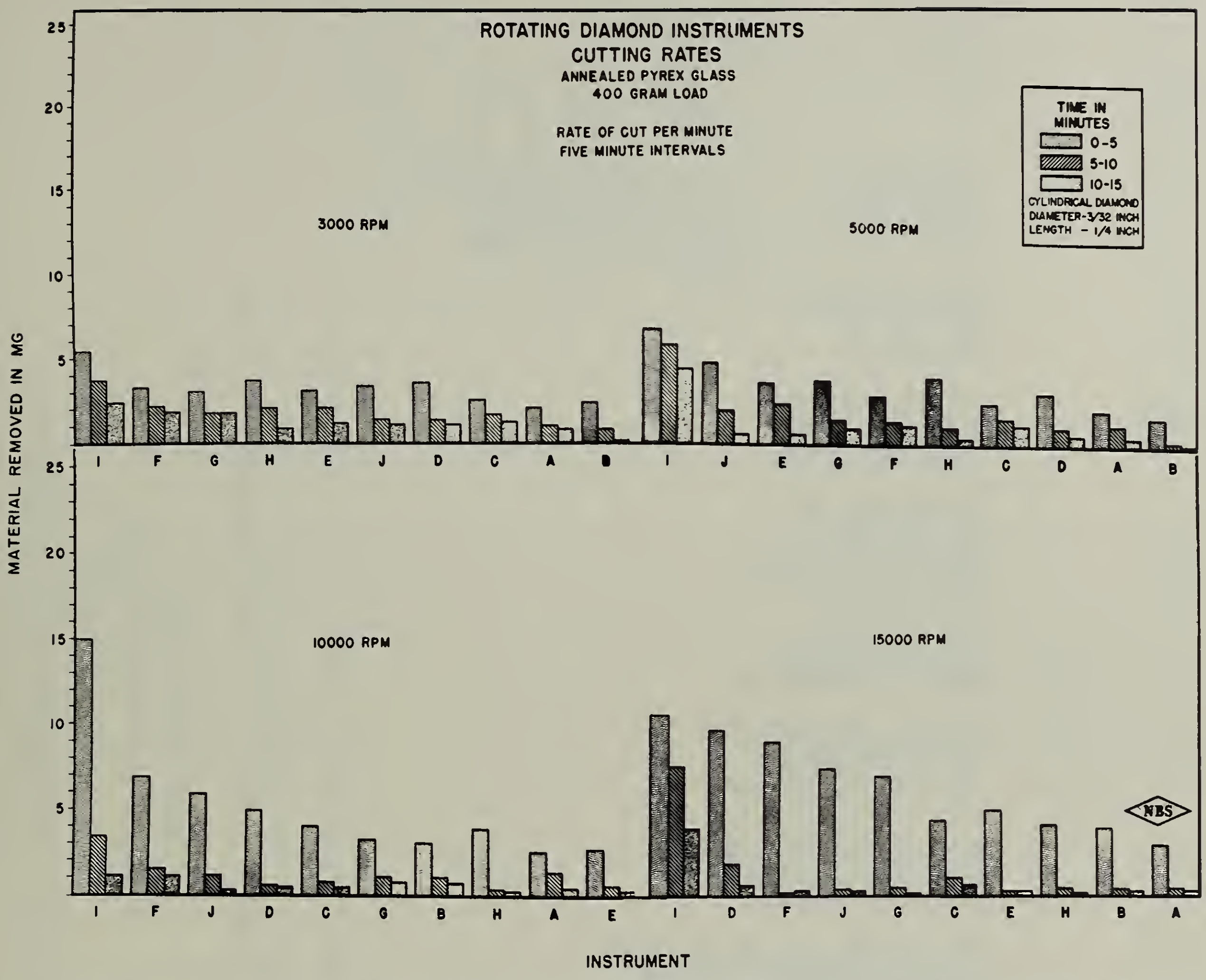

Figure 3. Cutting rates of ten brands of dental diamond abrasive instruments. Five instruments of each brand were evaluated. Note the high cutting rate of instruments of brand "I" at all four speeds, and the low rate of instruments of brands "A" and "B".

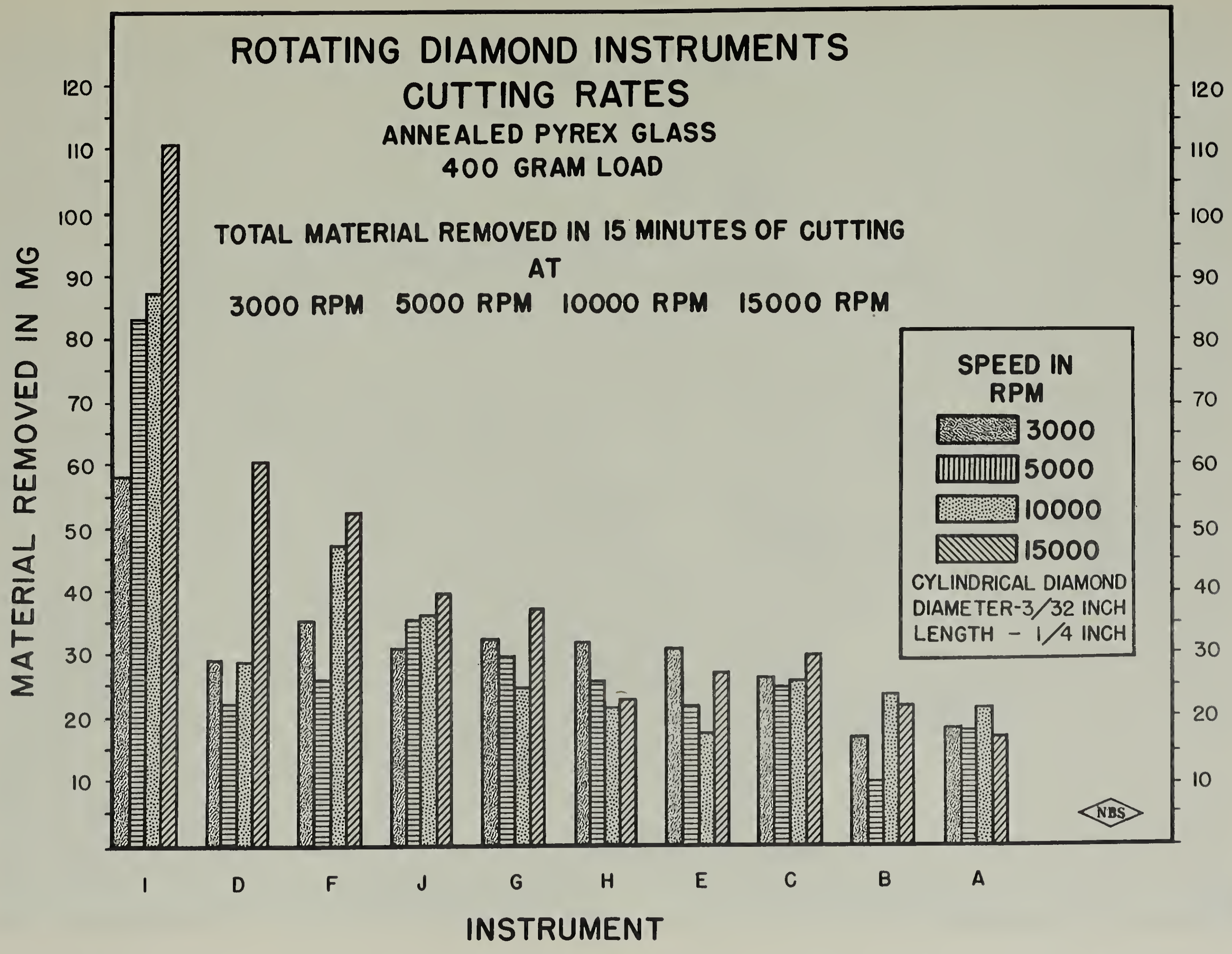

Figure 4. Cutting rates of the same instruments as in Figure 3, showing total material removed. Note that the high-cutting-rate diamond points at the left removed more material as the speed of rotation was increased, but that those instruments at the right did not.

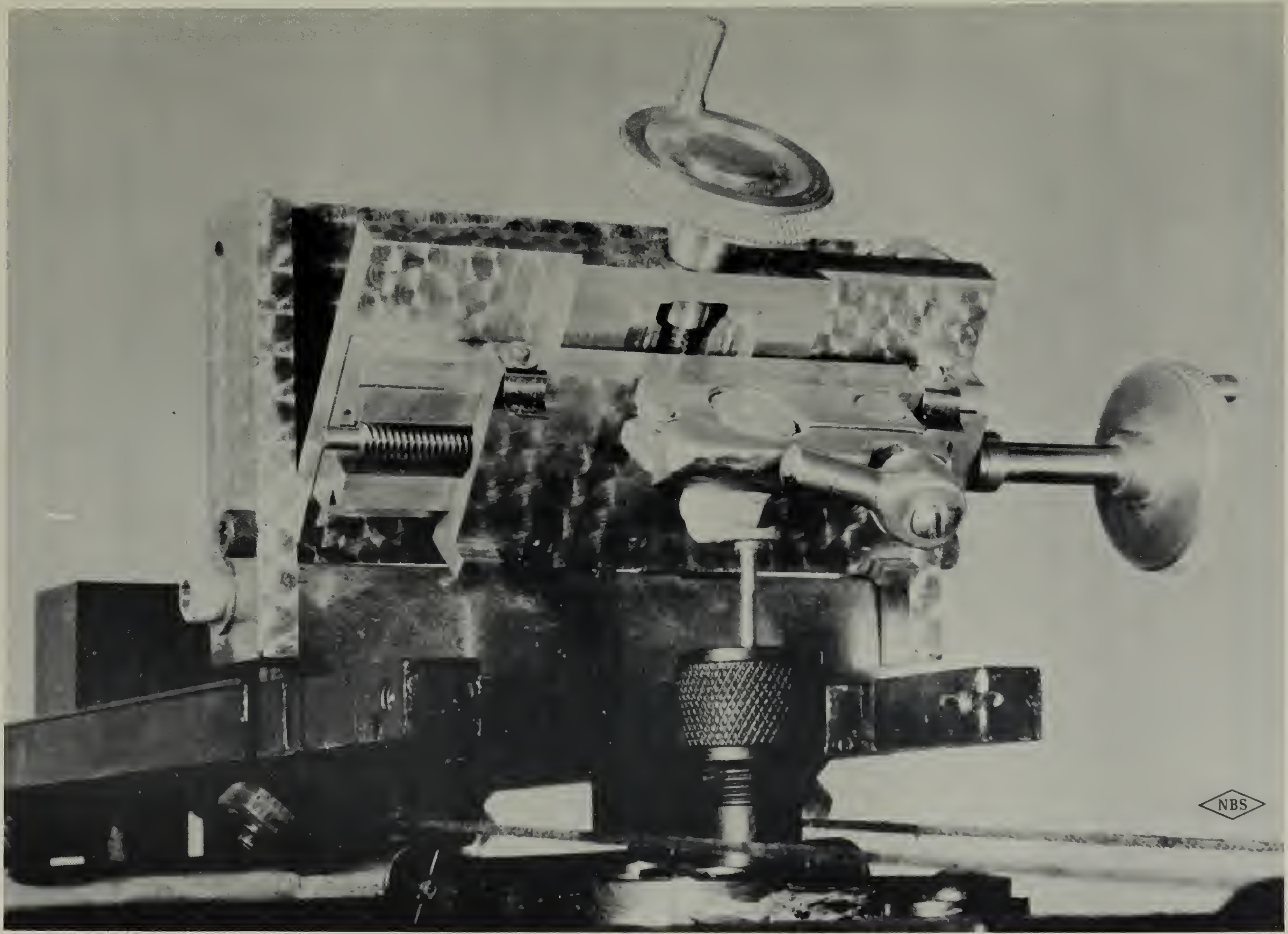

Figure 5. Apparatus on movable platform for holding and shifting human tooth specimens in weight-loss determination for relative cutting rates of one-quarter-inch diamond wheels. Controls adjust locking and horizontal and vertical movement of the tooth.

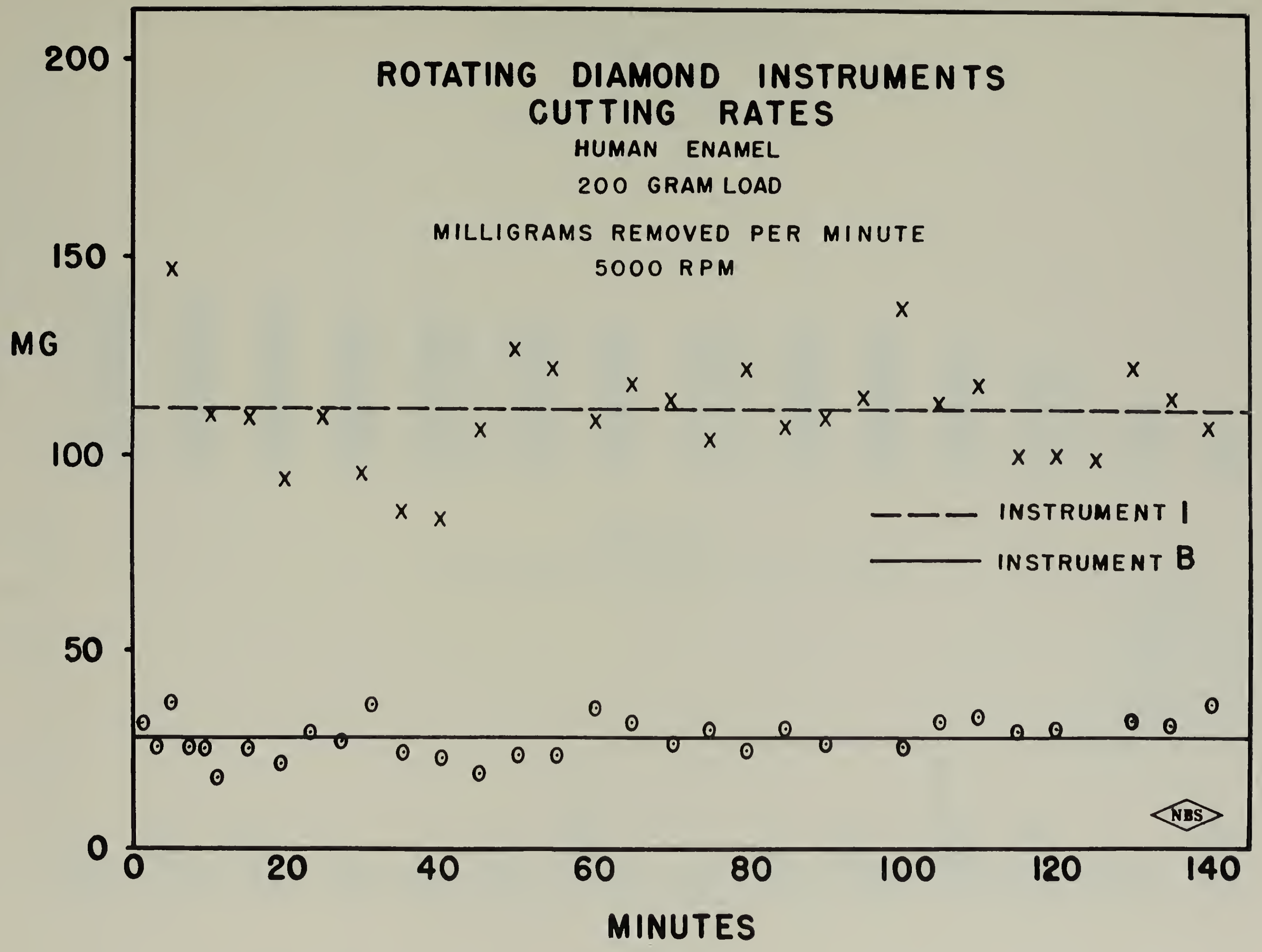

Figure 6. Comparison of cutting rates in enamel of two instruments of brands "I" which had a high cutting rate in glass, and brand "B", which had a low rate of cut. Neither instrument attained the breakdown point in enamel within this 140-minute period.

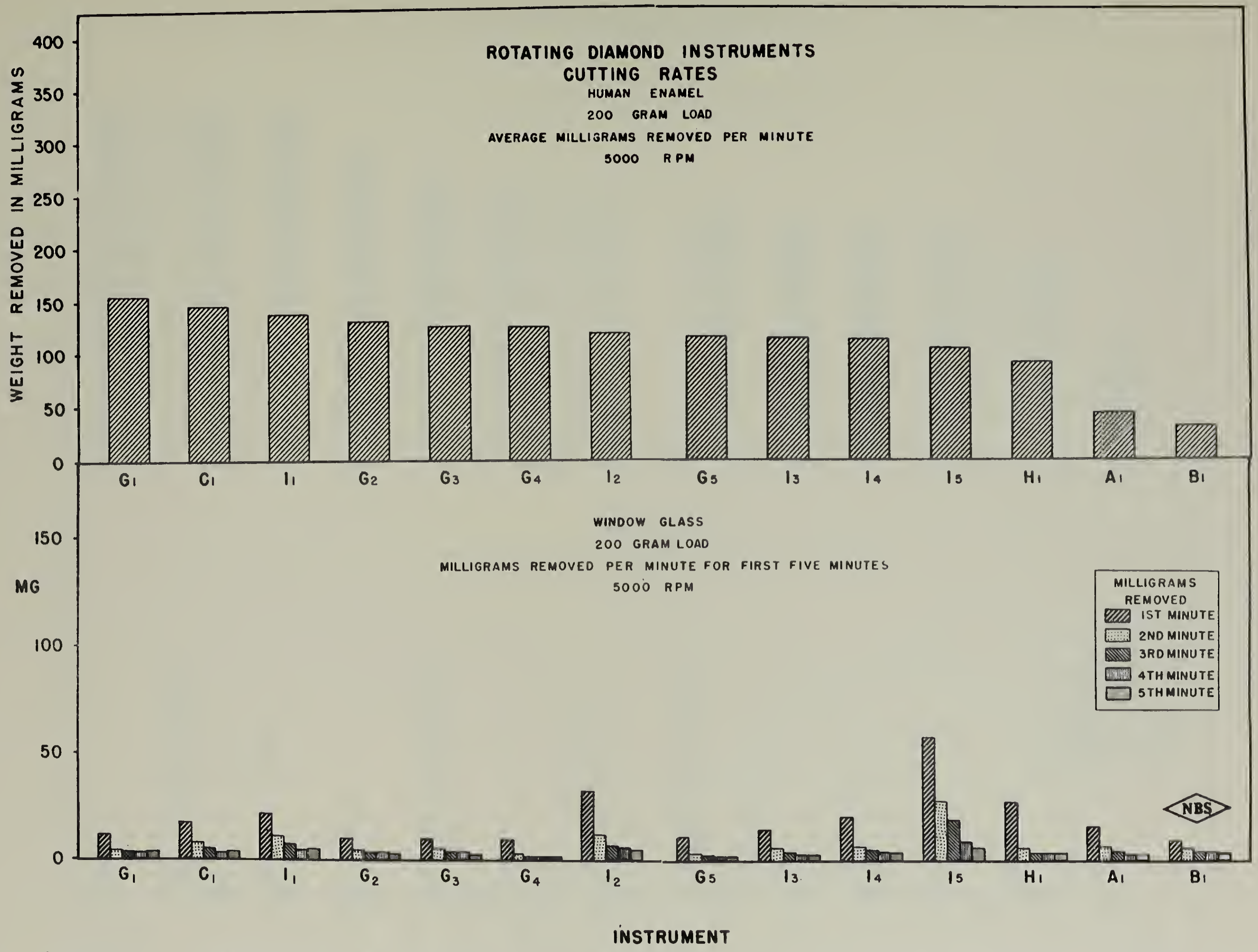

Figure 7. Comparison of cutting rates of one-quarter-inch diamond wheels in enamel at 5,000 rpm with the cutting rates of the same instruments in common window glass. Letters indicate brands, the subscripts indicate individual instruments of those brands.

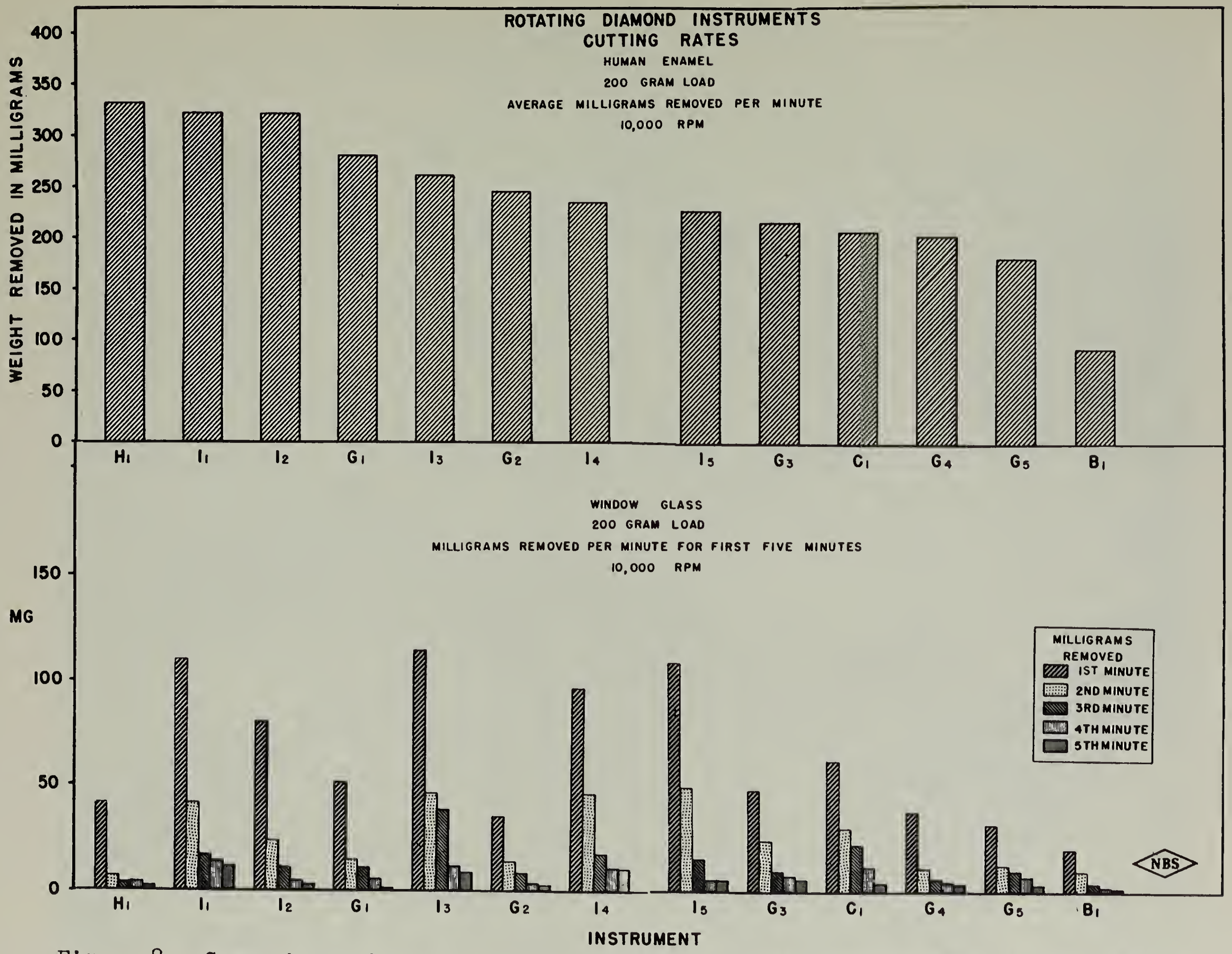

Figure 8. Comparison of cutting rates of one-quarter-inch diamond wheels in enamel at 10,000 rpm with the cutting rates of the same instruments in common window glass. Letters indicate brands, the subscripts indicate individual instruments of those brands.

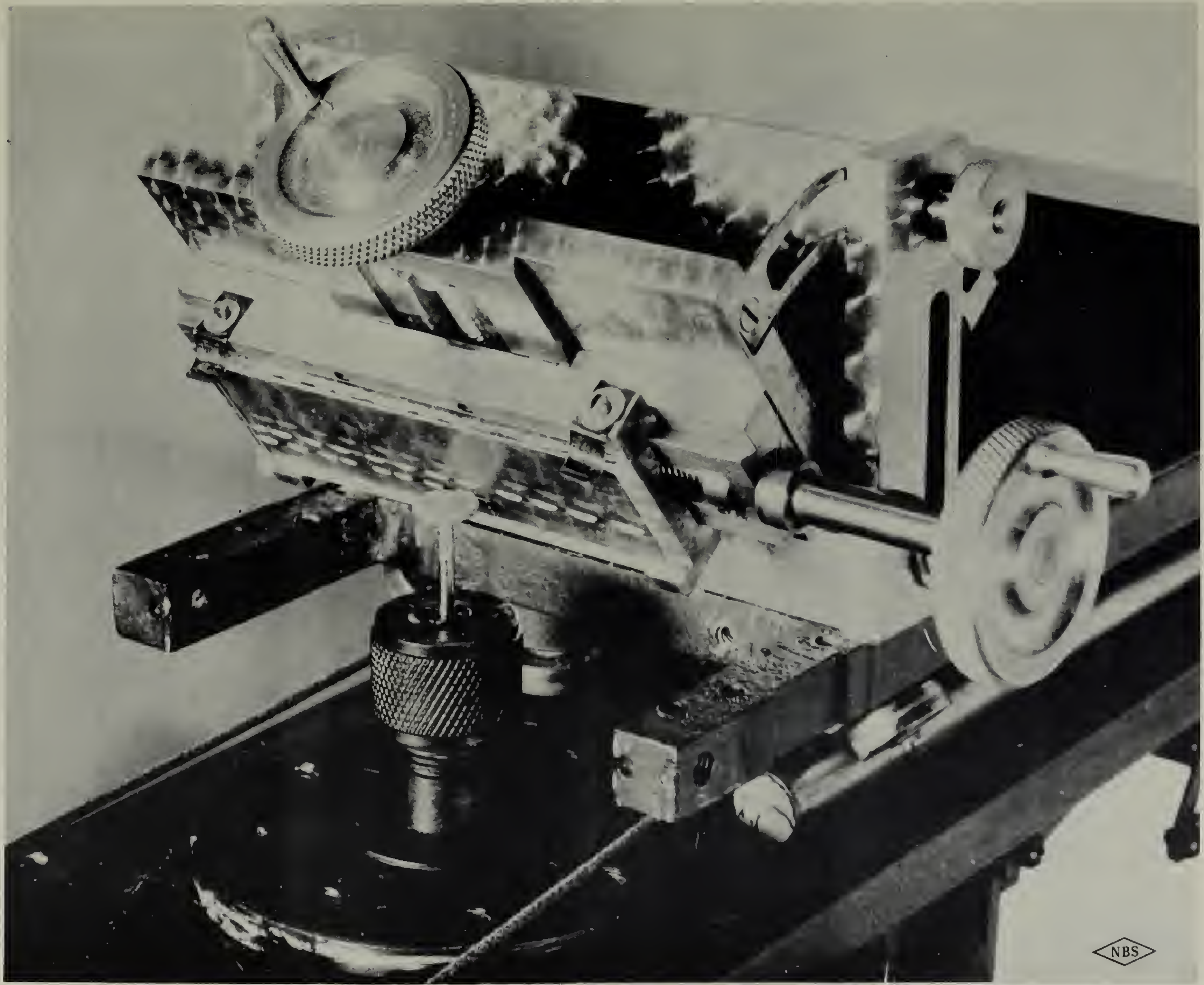

Figure 9. Specimen holder for one-by-three inch common window glass specimens, mounted on movable platform of rotating-instrument evaluating machine. Note 45-degree angle of cut.

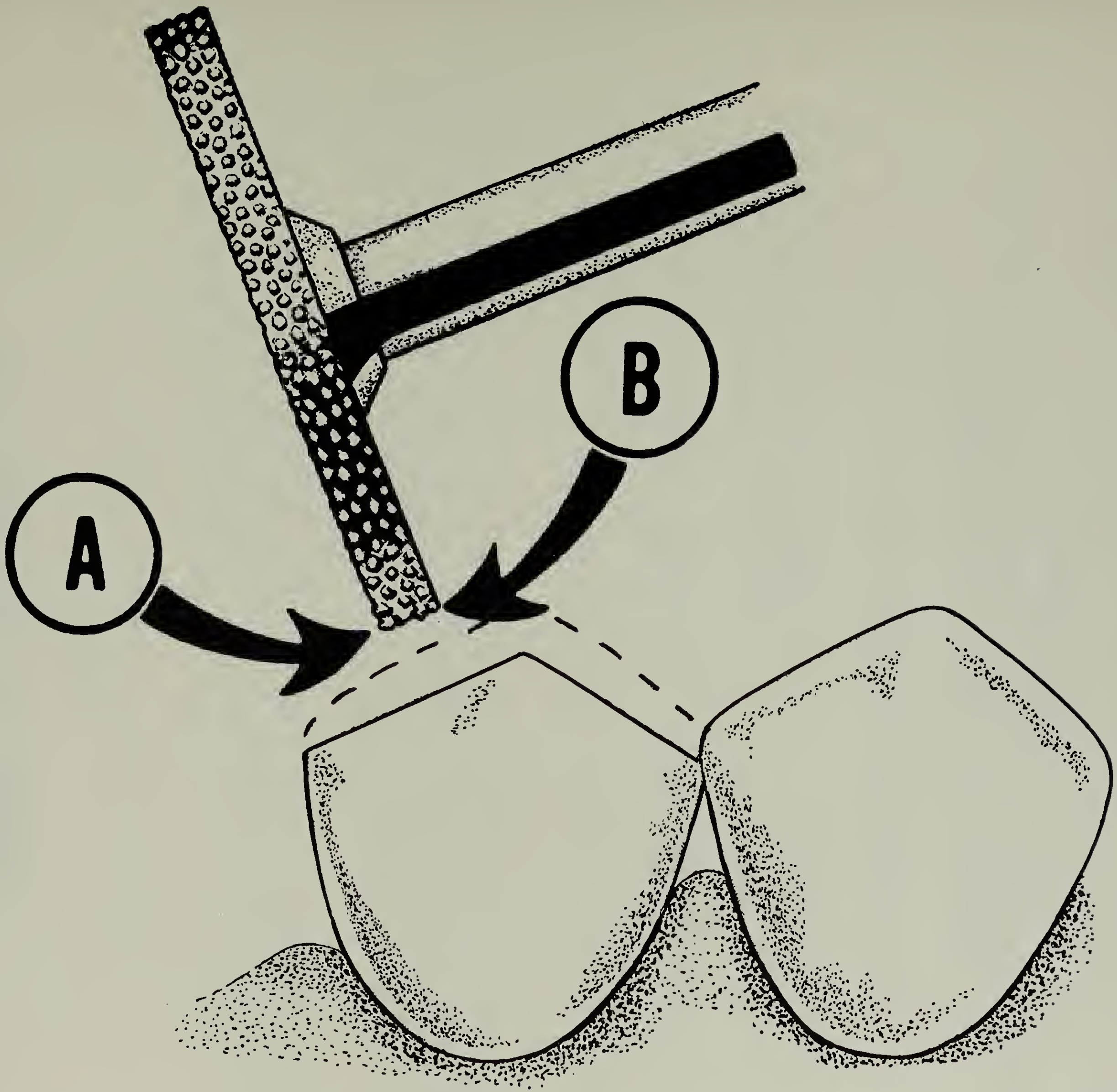

Figure 10. Clinical use of diamond wheels. Points "A" and "B" indicate areas of this diamond wheel which would receive the highest pressures per unit area resulting in breakdown of the bonding of the abrasive to the instrument.

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Progress Report

A METHOD FOR MEASURING THE MUCOSAL SURFACE CONTOURS OF IMPRESSIONS, CASTS, AND DENTURES

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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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A METHOD FOR MEASURING THE MUCOSAL SURFACE CONTOURS OF IMPRESSIONS, CASTS AND DENTURES

Abstract

A practical technique based on comparative measurements of identical areas of two precisely positioned surfaces has been developed for measuring the mucosal surface contour of impressions, casts and dentures. Using a pantographic type of comparator the dimensional differences between two surfaces are determined. These differences can be measured over an entire area to an accuracy of ±0.002 of an inch in less than an hour's time. With this method it is possible to make the following determinations: (1) relative accuracy of impressions; (2) growth or recession in the mouth as recorded on casts; and (3) effect of different techniques or materials on the dimensional accuracy of dentures.

---

1. INTRODUCTION

The accuracy with which dentures fit the oral mucosa has been the subject of many articles and discussions. The opinions expressed are usually based on clinical experience, or observations made on how well a denture fits a stone cast or on measurements in a horizontal plane between marks on the denture [1]. The method presented here for measuring the

mucosal contour provides quantitative data on the comparison of two surfaces whether they be of soft impression material, stone or denture base resin. Therefore, it is possible to determine the accuracy with which a denture reproduces the original impression, the patterns of growth or recession as reflected in casts, and the dimensional stability of different materials used in impressions and dentures.

A survey of the literature revealed only the Krogh-Poulsen [2] technique for measuring mucosal contour. In this method the positioning is difficult to reproduce accurately and the measurements tedious to make. A more accurate and convenient method was, therefore, sought. Thus this method using a pantographic type of comparator was developed [3].

2. DESCRIPTION OF THE COMPARATOR

The comparator, Figure 1, a modification of the Dentagraph [4]*, consists of a framework in the form of a parallelogram having one side fixed and the four corners hinged. When one of the two corners away from the fixed side is moved the other follows a similar path [5]. The framework is mounted on pivots so that it can be rotated with the fixed side as the axis. The whole unit is mounted on ways, or ball bearing tracks, so it can be moved forward and backward. Ball-shaped pointers with a diameter of 0.147 inch are attached to the corners of the free side. The pointer on the left is fixed and acts as

* Designed and Manufactured by G. R. Kern, 5525 23rd North, Arlington, Virginia.

a guide, Figure 2, b, while the pointer on the right moves up and down indicating the amount of movement in a vertical direction on a dial gage, Figure 2, y. These readings of the gage are recorded as the Y coordinates. At the mid point of the sweep of the gage the indicator point is in the same horizontal plane as the guide pointer. When the indicator is touching an area higher than the guide the gage will read plus; if lower, minus. Thus the mucosal contours on the two impressions, casts or dentures can be compared as to difference in height providing the pointers are touching corresponding points on the two objects.

In order to determine the distance moved laterally a dial gage is mounted on a telescoping rod across the diagonal of the parallelogram, Figure 2, X, this gage indicates the change in shape of the parallelogram as the guide is moved laterally. Multiplying the reading by a factor, 2.3, gives an approximation of the distance traveled in the lateral, or X axis. The pointers may be locked at predetermined points on the lateral, or X axis, by a set screw on the telescoping rod while readings are taken on the Y axis.

A lock plate, containing a series of fifteen holes, is mounted on the frame of the comparator, Figure 2, Z. The whole unit may be fixed on the ways at definite forward-backward, or Z axis, positions by dropping a pin thru a hole in a plate on the side of the parallelogram mounting into one of the holes on the lock plate.

The objects to be measured are mounted on two separate platforms on the comparator, Figure 3. The left platform has the following three adjustments: (1) four leveling screw legs, Figure 3, d, to make the plane of the left platform parallel to that on the right platform, (2) one set screw, Figure 3, e, on the base to lock the left platform after rotation into alignment with the right platform, (3) two screw-thread drives, Figure 3, f, for anterior-posterior or forward-backward, and lateral positioning.

The right platform has only one adjustment, a lock-nut arrangement, Figure 3, g, on a jack screw for raising and lowering the platform. By using all the adjustments with care it is possible to position precisely the objects to be measured.

3. PROCEDURE FOR USE OF THE COMPARATOR

3.1 Positioning of the Objects to be Measured

Before any measurements can be made the two objects to be compared must be positioned similarly on the platforms of the comparator. In principle the only requirements for positioning, if the objects are identical, are: (1) the objects must be so located that distances between corresponding points on the two objects are the same as the distance between the indicator points, and (2) the lines connecting corresponding points must be parallel to the line connecting the two indicator points when the Y, or vertical axis, dial indicator is in the zero position. In a practical case these conditions cannot be obtained since the objects to be compared are similar but not identical. Therefore, the objects are positioned so their planes of symmetry are

approximately perpendicular to the X axis. Corresponding points in these planes are placed so that the distance between them is the same as the distance between the indicator points on the comparator and lines connecting these and other corresponding points are made as nearly as possible parallel to the line connecting the indicator points when the Y axis dial indicator is in a zero position.

In positioning dentures, corresponding anterior and posterior reference points near the midline are first adjusted so that they fall below the indicator points. A bench mark placed near the midline at the posterior of the impression and reproduced in the denture serves as a posterior reference point. The posterior reference point is adjusted to a zero position in the Y axis and further adjustments are made until all points in the ridge area give as nearly the same reading as can be obtained. Simultaneous with this, opposing slopes are also adjusted so that Y axis readings as nearly similar as possible are obtained.

Considerable care must be exercised in making the positioning adjustments. Coarse adjustments of the planes of the dentures are made by using as an indicator a spirit level mounted on a tripod which may be placed on the dentures. Further adjustments are made using the indicator points of the comparator on flat surfaces of the denture. Final adjustments are made by using the Y axis dial indicator to determine when readings on opposite slopes of the denture are similar. Since a slight horizontal displacement of the dentures will result in a large difference

in the Y or vertical axis dial indicator readings on the slopes of the denture, this procedure makes possible a very precise location of the denture, or other object being measured.

3.2 Measurement of Differences

The bench mark is used as the fiducial point when measuring. If it is not practical to make bench marks, there are landmarks which can be used. After the pointers are placed in the marks on the dentures the Z axis lock plate, Figure 2, z_a is moved so the pin will drop into hole number three, four, or five and the number of the hole recorded. The plate is locked in position. Now, as the pin is moved from hole to hole the distance from the posterior bench mark forward is known. A reading of the X axis dial indicator, Figure 2, x, is recorded while the points are in the posterior bench mark. The pin is then removed from the lockplate, the pointers are moved to an anterior bench mark or landmark, and another X axis reading is made. These readings are recorded as shown on Table 1 so future mountings can be checked for alignment. If the alignment of each successive mounting in a series of measurements of dentures or impressions is not consistant, the arcs scanned will not be over the same paths. The method for alignment is described later in this section under remounting.

The pointers are moved back to the posterior bench mark and the pin is reinserted in the lockplate. The parallelogram is now free to move in only two directions, vertical and lateral. The movement of the points in these directions is in the paths of arcs which have a nine-inch radius. The pointers are moved

to the left buccal flange and the set screw tightened to prevent movement along the X axis. Now the pointers are brought carefully to the surface of the dentures and the readings on both the X and Y axes are recorded. An electronic device to indicate the moment the pointer touches the surface is attached to the right denture. The device registers the first contact of the pointer by completing a circuit which activates a relay to turn off a light, Figure 2, a. The next reading is made by loosening the X axis set screw and moving the pointers to the right and again securing the set screw. The pointers are lowered to the surfaces and another reading is made on both the X and Y indicators. As many readings as desired can be made at each setting of the Z axis. A series of eleven readings made at Z, number 5, is shown on Table 1. After this arc is completed the pin is removed from the lock plate and the parallelogram is moved along the Z axis to the point desired to make the next readings, such as Z at number 8 and Z at number 11 on Table 1. In this way the differences between the two surfaces in the vertical direction, or Y axis, are determined at definite points on the X and Z axes. Measurements at these points can be repeated since the X and Z readings at the posterior bench mark are known, and the positions of all the other readings are known relative to that point.

A device for recording the path of the guide point along the X and Y axes is mounted on the left platform, Figure 4. The stylus marks the different points where readings are made. This profile is not an accurate reproduction of the contour, because the pointers are ball-shaped and different sides of the ball touch

the surface when readings are made on different sides of the ridge. The tracing will, however, give an approximate profile of the surface and indicate on this profile the points at which differences in the surface height are recorded.

When a case is remounted, or another case compared, the case on the right platform must be replaced as closely as possible to the original position for a slight rotation will throw the arc scanned over a different area and the readings will be inaccurate. This repetition of position is done by the use of a key consisting of a plaster or compound impression made of the case while mounted.

A series of five remountings with one repositioning for each mount was analyzed statistically. The standard deviation of experimental error within a single mount was 1 thousandth of an inch. The standard deviation when differences due to remounting were included was 1.8 thousandths of an inch. It is recommended that one reset series of readings be made for each mounting. A comparison of the reset readings to the original series shows whether positioning is accurate.

A direct calibration of the Y axis indicator was made by using a series of millimeter gage blocks on the right platform. At each addition or subtraction of a gage block a reading was made on the Y indicator. Each comparator reading was within 5 ten-thousandths of an inch of the calculated value for that reading.

The X and Z axes readings are used to reproduce the points at which Y axis measurements are recorded. Readings along the

X and Z axes, therefore, although they are reproducible and make possible precise positioning, provide only approximate measurements of the distances on the dentures or other objects compared. The distance the points travel on the X axis was determined by measuring on a measuring microscope the distance between marks made by the pointers at different readings on the dial indicator. From these findings the factor, 2.3, to convert the dial readings to the distance moved by the points was determined to be accurate to ±0.01 inch. The distance from hole to hole on the Z axis was measured on the measuring microscope.

4. EXAMPLES OF RESULTS OBTAINED ON DENTURES AND IMPRESSIONS

4.1 Dimensional Accuracy of Two Dentures Cured by Different Techniques

Comparative measurements were made showing the effect of different curing cycles on the dimensional accuracy of dentures. The dentures were processed by different curing cycles and then compared to the common original impression. A metal impression was used in place of the usual impression material to eliminate as much as possible any change in the impression. The changes measured are those occurring from the impression to the completion of the curing cycle. One of the dentures was cured by the recommended slow cure. After placing the packed flask in a cold tank the temperature was raised slowly to 165°F and held for eight hours. The tank was then allowed to return to room temperature before the flask was removed and opened. The other case was placed in boiling water for one hour then placed under cold running water. The flask was opened as soon as it was cool

enough to handle. Figure 5 shows graphically the results obtained. The lower part is a profile of a portion of the denture measured and the upper part shows the plus and minus variation of the denture surface heights from the original impression. The plotted points can be projected down to the profile to see where the measurements were made. A pictoral representation of the changes occurring from the original impression to the cured denture processed by the slow cure is shown on Figure 6 where the differences are plotted from the profile curve.

4.2 Dimensional Accuracy of an Alginate Impression

An alginate impression taken of a stone case poured in a metal impression was compared to the original metal impression. The alginate impression was mounted within a plioform bag in the mounting ring to maintain one hundred percent relative humidity and minimize dimensional changes while the measurements were being made. The data are given in Table 2. The readings of 30 thousandths and 27 thousandths of an inch were on the buccal surface of the left alveolar ridge. When the impression material was removed from the tray a space, not noticeable previously, was found between the alginate and the tray at the point where this reading was taken.

5. CONCLUSIONS

A method for making comparative measurements of contoured surfaces has been developed. These measurements give the dimensional difference between two surfaces in the vertical direction, or Y axis, at different points in the horizontal plane, or X and Z axes. The precision of the measurements depends on the ability to position accurately the objects being compared. The components of

the comparator used make this positioning possible. A statistical analysis of the readings from a series of five remountings, with one resetting for each remount, shows the standard deviation to be 1.8 thousandth of an inch.

Two examples for the use of this method are presented: (1) measuring the changes due to the effects of different curing cycles on the dimensional accuracy of dentures, and (2) measuring the dimensional accuracy of an alginate impression.

Additional possible uses for this type of measurement are: determining the rate of growth or recession of oral tissues by measurements on a series of casts made over a period of time; evaluating the dimensional stability of different materials used in making impressions, casts, or dentures; and studying the resulting tissue displacement from different impression techniques.

BIBLIOGRAPHY

1. Sweeney, W. T., Denture base material. J.A.D.A. 26:1863 (1939).
2. Krogh-Poulsen, W. G., Paffenbarger, G. C., and Schoonover, I. C., Two methods of graphing the "mucosal" surface of plaster models. J.A.D.A. 36:397 (1948).
3. Whitehead, T. N., The design and use of instruments and accurate meachanism. Cover Publications Inc. (1954).
4. Lilley, G. A. Dental Laboratory Review, 36 May (1948).
5. Rolt, F. H., Gauges and fine measurements. McMillan and Co. 311-333 (1929).

TABLE 2

COMPARATIVE MEASUREMENTS OF ALGINATE IMPRESSION

Posterior	Bench Mark	.494 (Z at 5)
Anterior	Bench Mark	.500

Z at 7

	x	y	
		a* in.	b in.
1	.035	+.007	+.004
2	.105	+.030	+.027
3	.156	+.005	+.004
4	.241	+.002	.000
5	.500	.000	.000
6	.753	-.004	-.002
7	.867	+.004	+.006
8	.926	.000	+.002
9	.999	+.006	+.004

* a Original positioning.
b Reset positioning.

TABLE 1

MEASUREMENTS OF CHANGES FROM IMPRESSION TO DENTURE

Three different arcs scanned on the Z axis.

	a	b	
Posterior Bench Mark	.497	.497	Z at 5
Anterior Bench Mark	.508	.508	

Z at 5

	x*	y	
		a	b
		in.	in.
1	.025	+.007	+.006
2	.047	.000	.000
3	.091	-.016	-.014
4	.162	-.002	-.002
5	.270	+.007	+.005
6	.538	+.002	.000
7	.780	+.006	+.005
8	.885	-.002	.000
9	.973	-.010	-.014
10	1.160	+.002	.000
11	1.224	+.010	+.009

Z at 8

	x*	y	
		a	b
		in.	in.
1	.086	+.002	+.001
2	.153	-.015	-.016
3	.183	-.007	-.008
4	.270	+.005	+.004
5	.503	-.004	-.005
6	.771	+.008	+.010
7	.844	-.005	-.006
8	.906	-.015	-.016
9	.908	+.004	+.003

Z at 11

	x*	y	
		a	b
		in.	in.
1	.234	+.003	+.003
2	.380	-.019	-.018
3	.512	-.005	-.005
4	.668	-.018	-.018
5	.781	+.003	+.003

* These readings times 2.3 equal x dimension in inches.

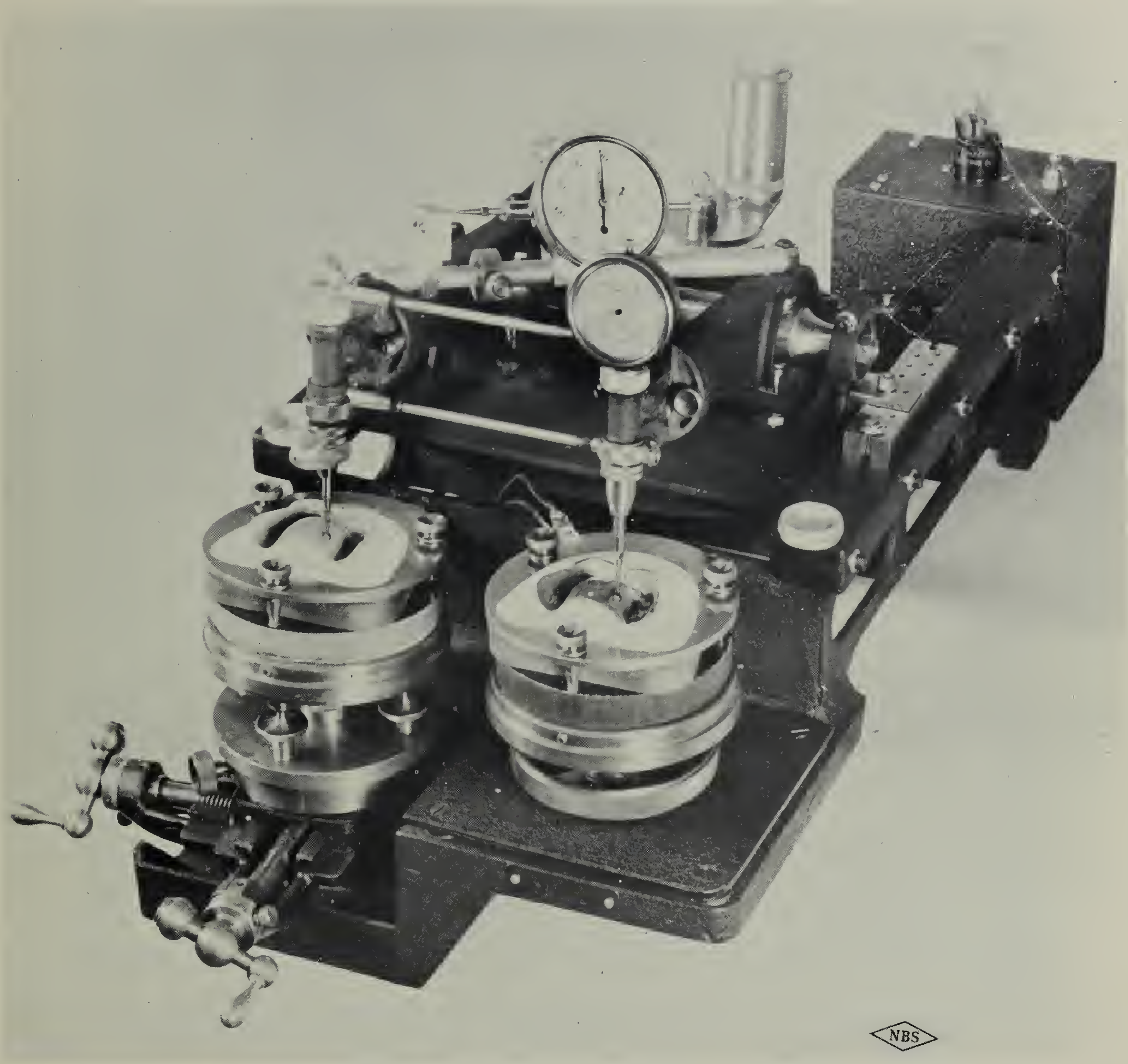

Figure 1. COMPARATOR FOR MEASUREMENTS OF MUCOSAL CONTOURS OF IMPRESSIONS, CASTS, AND DENTURES.

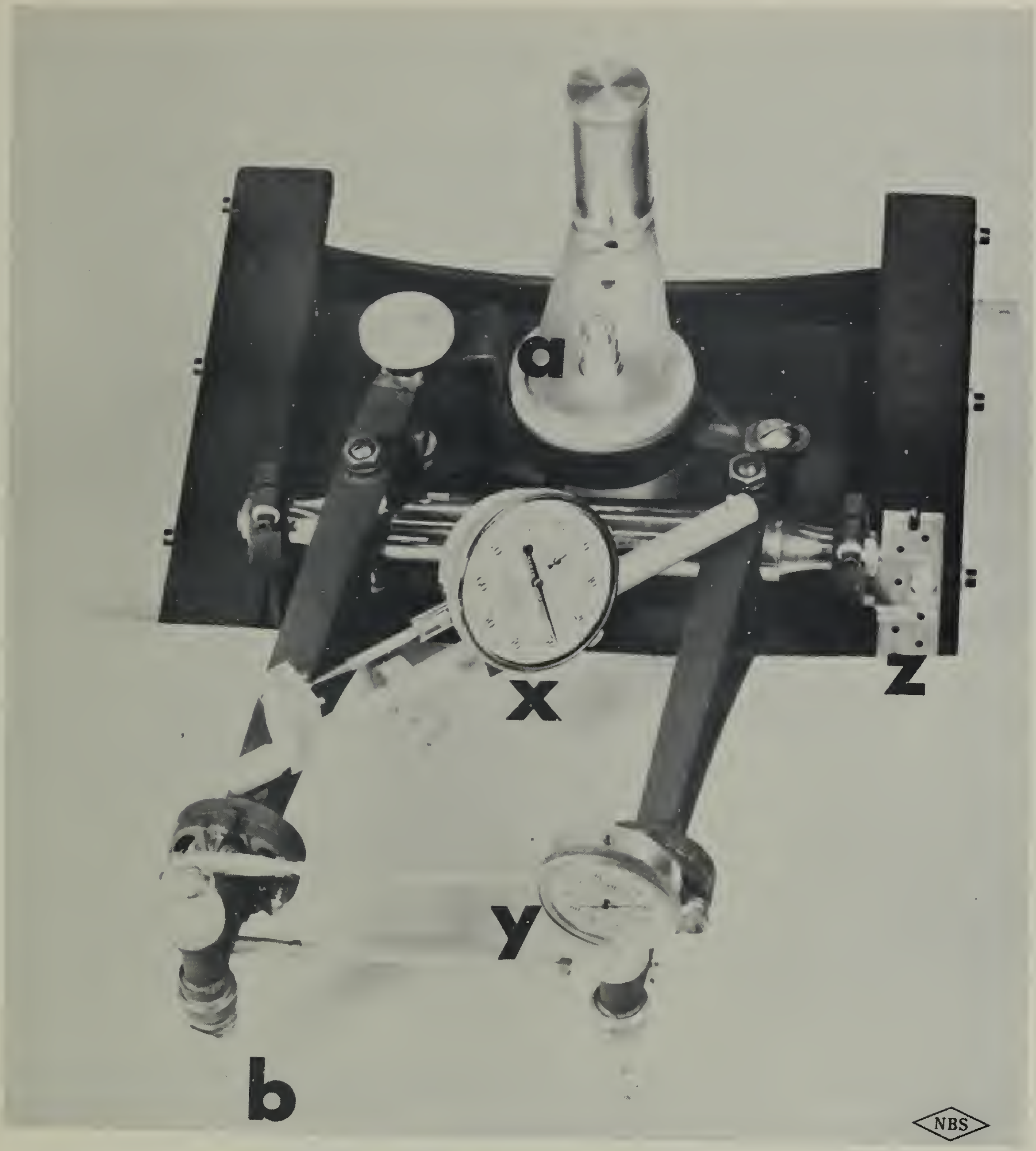

Figure 2. PARALLELOGRAM OF COMPARATOR.

a. Light, to indicate instant pointer touches surface being measured.
b. Guide pointer, permanently positioned.
x. Dial indicator, registers change in shape of parallelogram.
y. Dial indicator, registers change in vertical direction of the surface the indicator pointer touches in relation to the surface the guide touches.
z. Lock plate, holds parallelogram in a definite forward-backward position while measurements in the X and Y axes are being made.

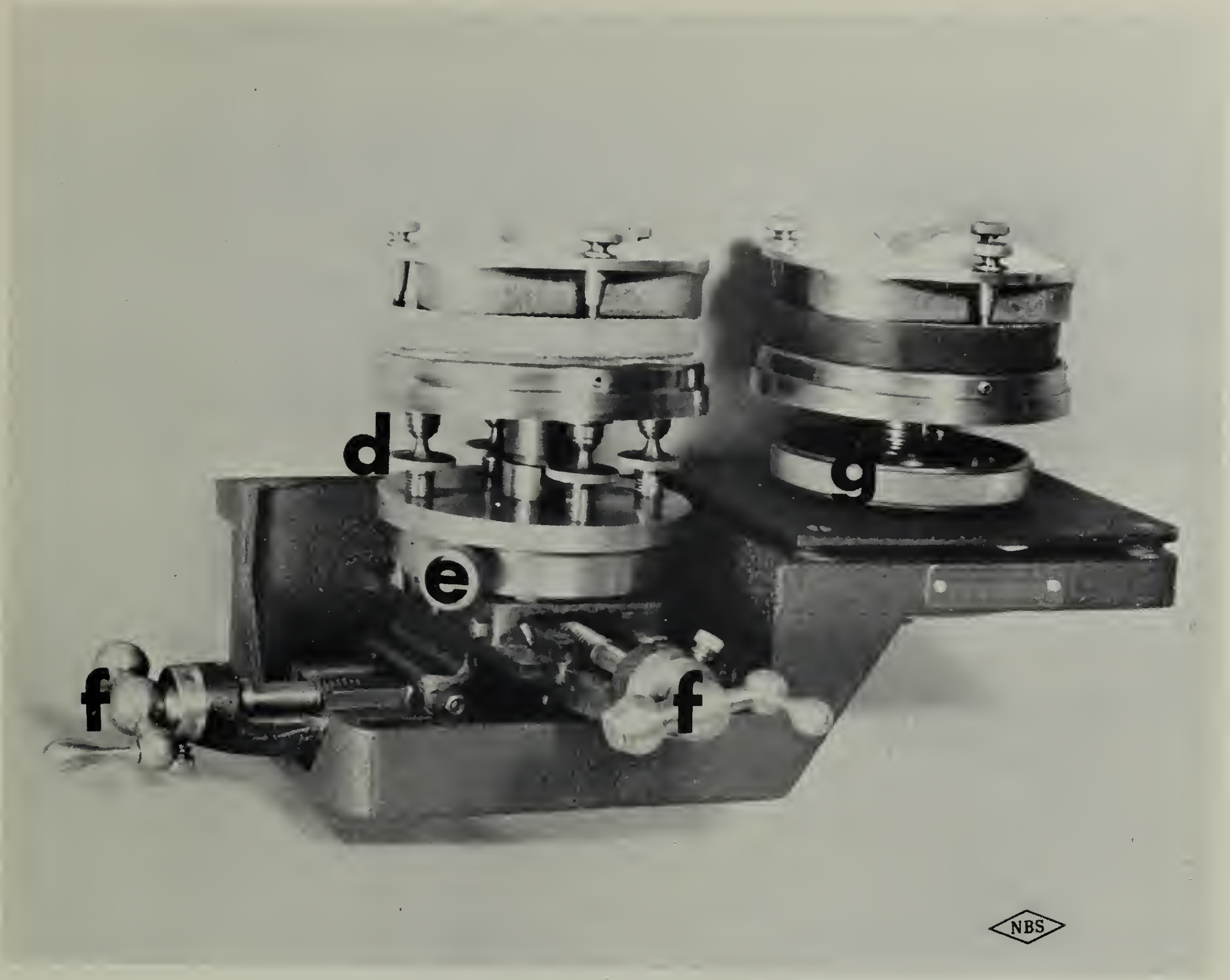

Figure 3. PLATFORMS OF COMPARATOR.

d. Tilting adjustment, four screw legs to adjust the plane of the left platform.
e. Rotating adjustment, set screw to control rotation of the left platform.
f. Screw thread travel, two lead screws to control lateral and forward-backward position of the left platform.
g. Lock nut, controls the vertical height of the right platform.

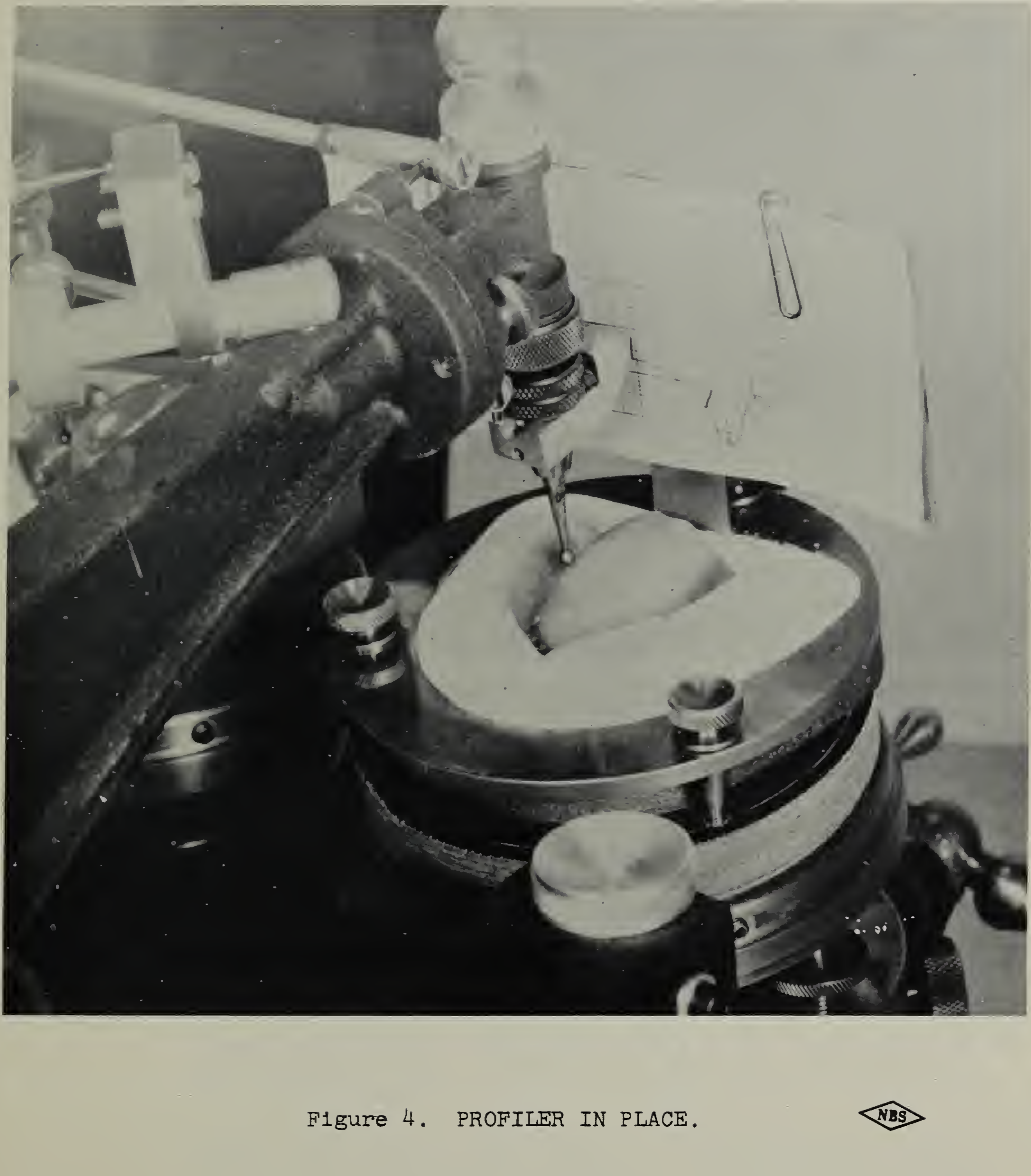

Figure 4. PROFILER IN PLACE.

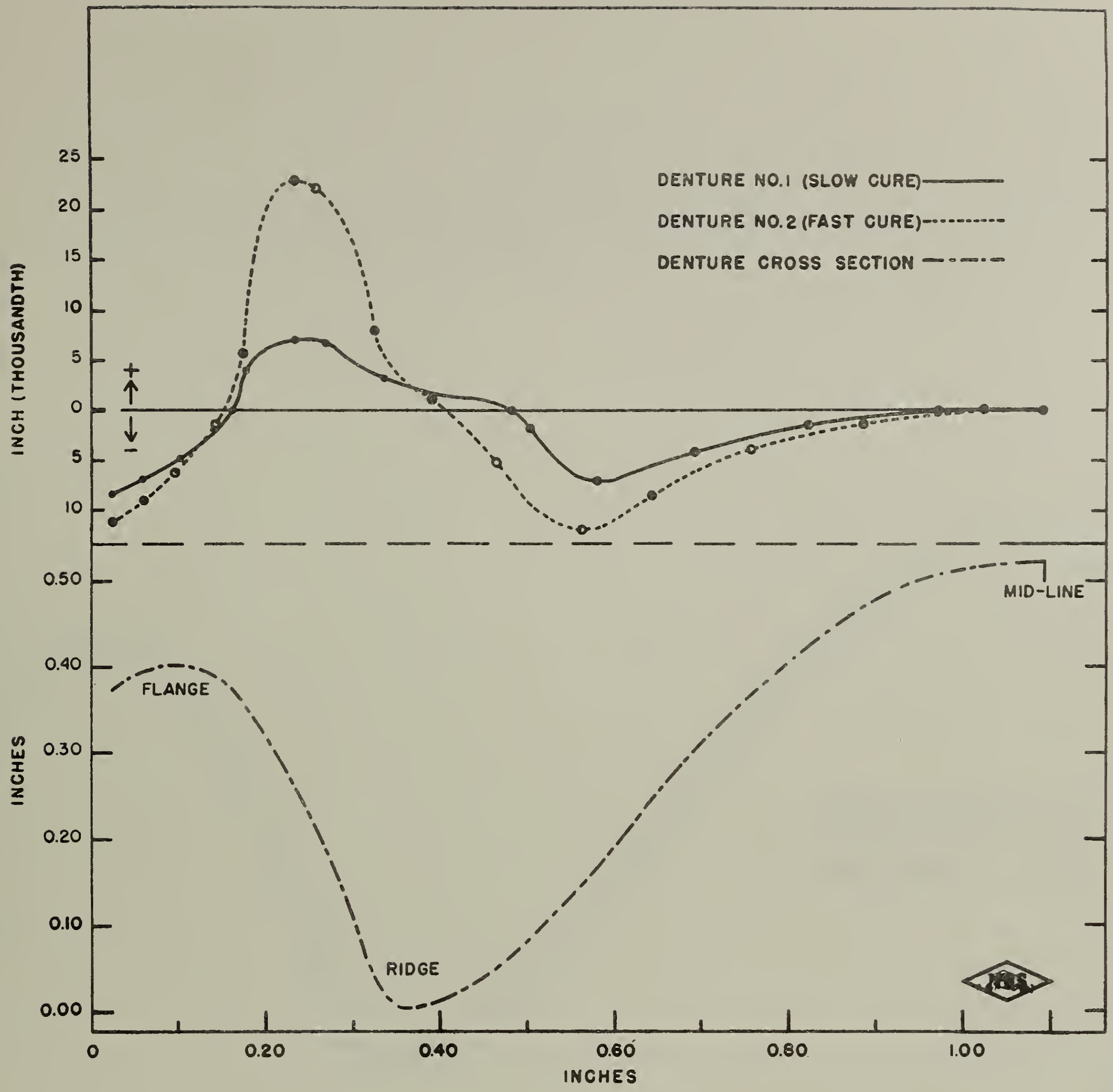

Figure 5. COMPARISON OF DIMENSIONAL CHANGES RESULTING FROM DIFFERENT CURING CYCLES.

Both dentures were compared to the original metal impression.

Upper portion of the graph shows the plus and minus deviation of the surface heights as indicated by the comparator.

Lower portion of the graph is a profile of part of the denture area measured. The plotted points on the upper portion can be projected down to the profile to show where the changes took place.

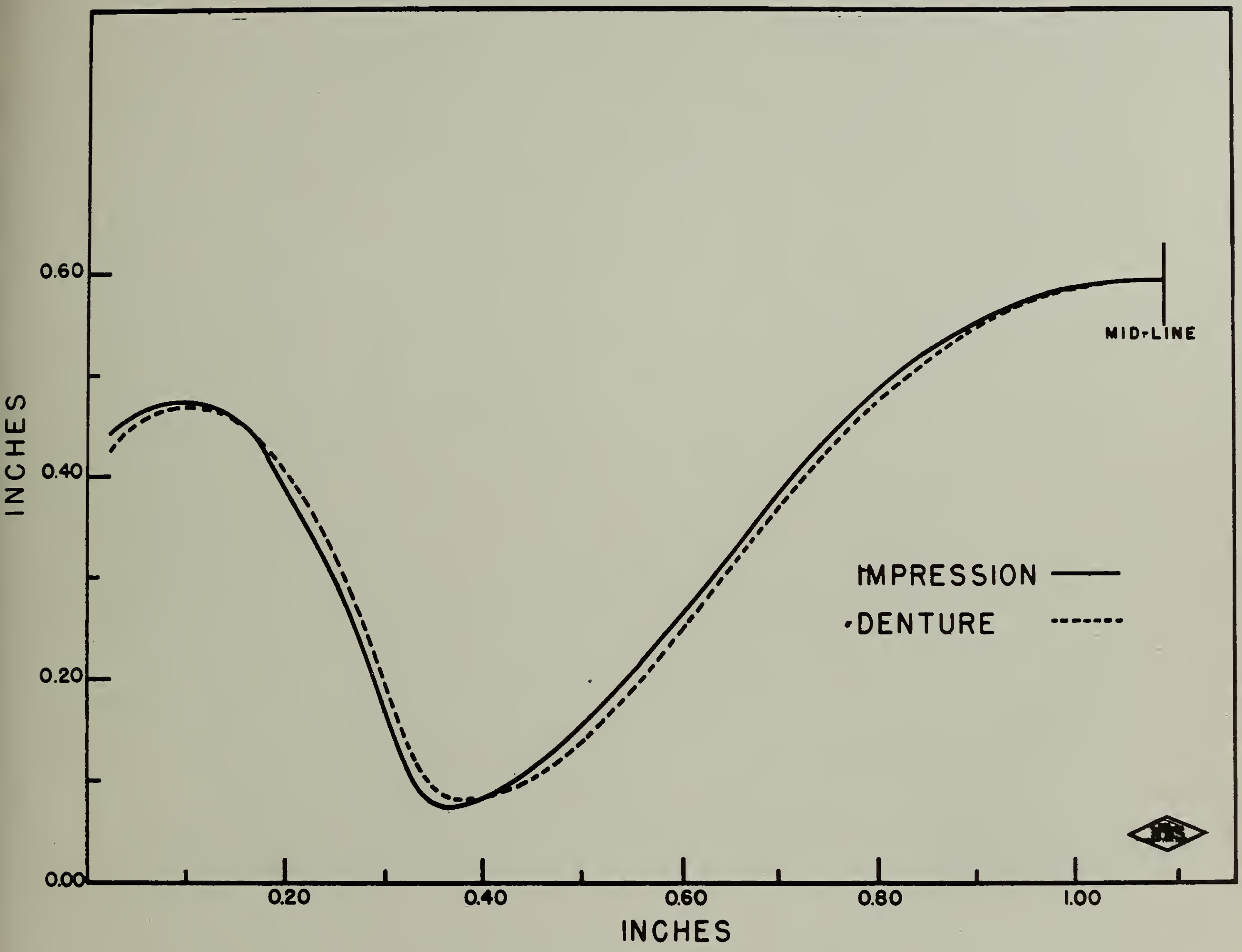

Figure 6. DIMENSIONAL CHANGE FROM IMPRESSION TO DENTURE.

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