

NATIONAL BUREAU OF STANDARDS REPORT

9983

Progress Report
on
A FILLED COLD-CURING
ACRYLIC RESIN AS A SPLINTING MATERIAL



U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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A FILLED COLD-CURING ACRYLIC RESIN AS A SPLINTING MATERIAL

by

E. F. Huget,* G. M. Brauer,⁺ J. W. Kumpula⁺⁺ and S. Civjan**

* Research Dental Officer, Division of Dental Materials,
U. S. Army Institute of Dental Research.

⁺ Research Chemist, Dental Research Section, National Bureau
of Standards, Washington, D. C.

⁺⁺ Mechanical Engineering Technician, Dental Research Section,
National Bureau of Standards, Washington, D. C.

** Chief, Division of Dental Materials, U. S. Army Institute
of Dental Research.

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A Filled Cold-Curing Acrylic Resin as a Splinting Material

E. F. Huget, G. M. Brauer, J. W. Kumpula and S. Civjan

INTRODUCTION

The stabilization of alveolar fractures and avulsed, subluxated and reimplanted teeth by acrylic splinting devices has been described by numerous authors.^{1,2,3,4} The use of auto-polymerizable acrylics presents an intriguingly simple and rapid means of achieving the required degree of stability for fixation purposes. The excessive heat evolved during the polymerization of these substances and the accompanying patient discomfort and soft tissue damage have, however, limited their use. The "rebound" tendency of acrylics in dough form and intraoral manipulation problems related to the use of more fluid mixes have also limited the scope of acceptance of auto-polymerizable acrylic splints.

In this study, a number of acrylic formulations were evaluated. A poly(methyl methacrylate) (PMMA) resin admixed with the appropriate inert inorganic filler and mixed with methyl methacrylate (MMA) monomer containing a low percentage of amine accelerator yielded a material with desirable physical

and mechanical properties. This product also exhibited highly desirable manipulation and setting characteristics that precluded the difficulties associated with materials currently used for direct splinting procedures.

MATERIALS AND METHODS*

A series of commercially available methacrylate polymers and copolymers were evaluated for potential use as direct splinting materials (Table 1). Inorganic fillers consisting of Al_2O_3 **, dental stone***, CaCO_3 **** or ZnO^+ were added to selected polymer powders. The Al_2O_3 was passed through a No. 325 sieve prior to use. All other inorganic fillers were

* Certain commercial materials and equipment are identified to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards or the Dept. of the Army, nor does it imply that the material or equipment is necessarily the best for the purpose.

** T61 Tabular Alumina, Aluminum Co. of America, Bauxite, Ark.

*** Kerr Rapid Stone, Kerr Mfg. Co., Detroit, Michigan

**** Precipitated calcium carbonate, 1-10 μ particle size, NON-FER-AL, USP, Diamond Alkali Co., Cleveland, Ohio.

+ Zinc oxide, USP, J. T. Baker Chemical Co., Phillipsburg, N. J.

used as supplied by the manufacturer. Polymer and filler powders were mixed by tumbling weighed amounts of the constituents in glass jars. Some powders were blended with benzoyl peroxide⁺⁺ by suspending the polymer and filler in a solution of the polymerization initiator in ethyl ether, followed by evaporation of the solvent.

The polymer or polymer-filler blend was mixed with methyl methacrylate monomer⁺⁺⁺ containing 0.2-0.5% amine accelerator, N,N-dimethyl-p-toluidine.⁺⁺⁺⁺ At ambient temperature the monomer-polymer slurries reached the dough stage of polymerization in less than one minute after mixing. The dough was removed from the jar and held in the palm of the hand until peak polymerization temperatures were reached. Cylindrical segments of dough (approximately 20 mm in length and 4 mm in diameter) derived from formulations evolving quantities of

⁺⁺ Fisher Reagent, Fisher Scientific Co., Pittsburgh, Pa.

⁺⁺⁺ Methyl methacrylate, inhibited with 35 ppm butylated hydroxytoluene, Rohm and Haas Co., Philadelphia, Pa.

⁺⁺⁺⁺ Eastman Organic Chemicals, Rochester, N. Y.

heat well tolerated by the skin of the palm of the hand were then placed in the muco-buccal folds of volunteer patients for more definitive evaluation of heat tolerance. Ratios of 1.5-1.7 gm. of polymer or blended polymer powder to 1.0 ml liquid provided practical amounts of material for evaluation of dough stage manipulative characteristics, hardening time and heat evolution.

The polymer powder used in the most promising formulation was analyzed microscopically for further characterization. Sorption, solubility and color stability, were determined according to American Dental Association Specification No. 12 for denture base polymer⁵; transverse deflection by American Dental Association Specification No. 13 for denture cold curing repair resin⁶; hardening time and temperature rise by American Dental Association Specification No. 17 for denture base temporary relining resin⁷. Ultimate compressive strength was determined as prescribed by American Dental Association Specification No. 9 for dental silicate cement⁸. Tensile strength was measured by the diametral method using disc shaped specimens 1/4 inch in diameter and 1/16 inch in thickness without platen modification as recommended by Civjan and de Simon⁹. Shear strength was determined by the

"punch" method described by Taylor and Margetis¹⁰ using disc shaped specimens 1/2 inch in diameter and 1/16 inch in thickness. All strength determinations were performed using with an electric strain gauge load cell a universal testing machine/operated at a crosshead speed of 0.02 in/min.

RESULTS

Polymerization characteristics of the 14 formulations evaluated are presented in Table 1. Three monomer-polymer slurries (No. 1, 2, 3) did not polymerize. Hardening time the (from the time/dough stage had been reached) of three mixtures (No. 4, 12, 13) exceeded 10 minutes. Most mixtures that hardened in 10 minutes or less at room temperature evolved excessive amounts of heat (formulations No. 7-9, 14). One mixture that evolved a tolerable amount of heat yielded an elastic dough that was not readily adaptable to the labial and buccal surfaces of the teeth (formulation No. 6). Formulation 5 containing 2% of accelerator gave a slightly yellow product. Two formulations (No. 10 and 11) exhibited desirable gross polymerization characteristics. The doughs resulting

from these mixtures were readily formed into ropes and easily adapted to the labial and buccal surfaces of the teeth of volunteer patients. Hardening of cylindrical segments of dough (formulation No. 11) approximately 20 mm in length and 20 mm in diameter (vol. $\sim 63 \text{ mm}^3$) occurred in 6-8 minutes.

Substitution of aluminum oxide, dental stone or zinc oxide for the calcium carbonate filler in the most promising formulations resulted in inferior products that were usually chalky and friable.

Microstructure analysis of the polymer constituent of the most promising formulation revealed spherical particles ranging from $1\mu\text{m}$ to $150\mu\text{m}$ in diameter with the largest portion of the particles having diameters of $25\mu\text{m}$ to $75\mu\text{m}$.

The physical and mechanical properties of the most desirable filled acrylic mixture used in all further evaluation procedures are given in Tables 2 and 3.

DISCUSSION

Physical Properties of Filled Splinting Resin

The physical and chemical characteristics of the polymer powder as well as the type and amount of inorganic filler affected the molding quality of the resultant dough. Poly(ethyl methacrylate) and copolymers of methyl methacrylate and ethyl acrylate yielded rubbery reaction products when reacted with methyl methacrylate monomer. Two methyl methacrylate polymers also produced very elastic doughs when reacted with methyl methacrylate monomer. A slurry of high molecular weight poly(methyl methacrylate) homopolymer powder with monomer did not harden (formulation 11). A small particle size powder appeared to be beneficial as a splinting material. Increasing the benzoyl peroxide initiator or dimethyl-p-toluidine accelerator concentration shortened the hardening time.

Enough residual peroxide is apparently present in the polymer powder normally used in dental applications to act as a polymerization initiator. Addition of 0.2% peroxide, however, yielded mixtures that hardened more rapidly.

The presence of 50% CaCO_3 filler prevented the temperature rise from exceeding clinically tolerable limits, thus rendering these materials suitable for splint fabrication.

Only two of the fifteen formulations evaluated in this study demonstrated potential for use as a direct splinting material (Nos. 10 and 11). The powder component of formulation 11 included a 49.8% finely ground poly(methyl methacrylate) polymer powder with 0.2% benzoyl peroxide and 50.0% CaCO_3 filler. The monomer portion was methyl methacrylate with 0.2% N,N-dimethyl-p-toluidine. The mixing of 1.5 gm of the filled-polymer powder with 1.0 ml of monomer produced a non-sticky easily managed dough within less than one minute. The hardening of relatively large cylindrical segments approximately 90 mm in length and 6 mm in diameter (vol. $\sim 2500 \text{ mm}^3$) occurred in the mouth within 6 minutes without any appreciable rise in temperature. If a slower hardening material is desired, formulation 10 should be used which has the same composition as formulation 11, but does not contain any added peroxide.

The CaCO_3 filler not only serves as an efficient attenuant for the heat evolved during the polymerization of a mixture of acrylic polymer (SR-120) and methyl methacrylate monomer, but also imparts a "dead-fall" characteristic to the dough

stage. The dough does not rebound from the affected portion of the dentition after initial adaptation.

The relatively low exothermic heat of polymerization allows border molding and smoothing of the material after adaptation by direct contact and movement of the mucosa of the lips and cheeks over the intact segment of material.

Physical and mechanical properties of the CaCO_3 filled acrylic were determined to more completely characterize the material. The hardening time of 12 minutes (Table 2) reflects the influence of the geometry of the polymerizing mass (required in the specification test) on polymerization characteristics. Disc shaped specimens 60 mm in diameter and 2 mm in thickness required twice as much time for polymerization as cylindrical specimens approximately 90 mm in length and 6 mm in diameter. Rupture of transverse deflection specimens at loads of 2500-2600 gm was the result of the high percentage of inorganic filler. For clinical use, the CaCO_3 filled acrylic has demonstrated adequate rigidity and strength for splint fabrication. With the exception of the fracture of the material in the transverse deflection test, this material possesses properties similar to those associated with denture cold-curing repair resins.

Clinical Application

The advantages of the preferred material over previously suggested products are its low heat of polymerization, as well as its ease of manipulation. This material should therefore be the material of choice for the stabilization of alveolar fractures and avulsed, subluxated and fractured teeth. It can also be used for the stabilization of implants and reimplants. Initial clinical results of these applications have been most encouraging.

The filled acrylic could also be used with preformed, non-corrosive metallic pins (Fig. 1 and Fig. 2) for the maxillo-mandibular fixation and stabilization of mandibular fractures (Fig. 3). The acrylic material prevents lingual displacement of the metallic pins that serve as anchor points for interarch elastics.

The characteristics and properties of the filled acrylic suggest its usefulness in nondental as well as dental procedures. Nondental applications may possibly include:

(1) the fabrication of orthopedic appliances, (2) the stabilization of surgical implants, and (3) a replacement for portions of the calvarium following craniotomy procedures.

SUMMARY

The reaction products of a series of filled and unfilled acrylic polymer-monomer mixtures were evaluated for use as splinting materials.

Polymer powder particle size, type and amount of inorganic filler and amine concentration in the monomer influenced the polymerization characteristics of the mixtures and the properties of the resultant products.

Two formulations demonstrated potential for use in splinting procedures. The powder component of the preferred formulation contained 49.8% finely ground poly(methyl methacrylate), 50.0% CaCO_3 , and 0.2% benzoyl peroxide. If a slower cure is desired, the peroxide can be omitted. The monomer portion was methyl methacrylate with 0.2% N,N-dimethyl-p-toluidine. The dough produced by this reaction mixture polymerized in the mouth within 6 minutes without the evolution of excessive amounts of heat. The physical and mechanical properties of the polymerized product render this material suitable for the fabrication of short span intraoral splints.

The material, because of its low exothermic heat of polymerization, may also be useful for the fabrication of small

orthopedic splints, the stabilization of surgical implants, and as a replacement for portions of the calvarium following craniotomy procedures.

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TABLE 1

Polymer and Copolymer Mixtures Evaluated for Use as Direct Splinting Materials

No.	Powder		Accelerator		Benzoyl Peroxide %	Hardening Time Min	Heat Evolved	Characteristics of Material
	Acrylic Resin %	Calcium Carbonate %	N,N-Dimethyl-p-toluidine In methyl methacrylate %	Min				
1	100.0*	----	0.5	d.n.h.**	---	----	---	---
2	49.0*	50.0	0.2	d.n.h.**	1	----	----	---
3	49.0*	50.0	0.5	d.n.h.**	1	----	----	---
4	100.0***	----	0.2	17	---	tolerable	tolerable	rigid product
5	100.0***	----	2.0	9	---	tolerable	tolerable	rigid product, slightly yellow
6	79.0***	20.0	0.2	8	1	tolerable	tolerable	mass easily rolled into rope, dough elastic and rebounds, rigid product
7	79+	20.0	0.4	<10	1	excessive	excessive	dough elastic and rebounds, rigid product
8	99.5++	----	0.2	7	0.5	excessive	excessive	rigid product
9	69.5++	30.0	0.2	8	0.5	excessive	excessive	rigid product
10	50.0++	50.0	0.2	10	---	minimal	minimal	dough readily formed into rope adaptable to teeth. No rebound. Rigid product.
11	49.8++	50.0	0.2	6	0.2	excessive	excessive	very rubbery
12	49.8+++	50.0	0.2	25	0.2	excessive	excessive	very rubbery
13	49.8†	50.0	0.2	>30	0.2	excessive	excessive	very rubbery mass
14	100.0††	----	0.5	10	---	excessive	excessive	very rubbery mass

* Fisher Scientific Co., Pittsburgh, Pa. ** d.n.h.: dough did not harden.

*** Of grade, Liquid Nitrogen Processing Co., Malvern, Pa.

+ Fine acrylic (minus 270 sieved), Liquid Nitrogen Processing Co., Malvern, Pa.

++ SR 120, Sartomer Resins Inc., Essington, Pa.

+++ K 120N copolymer, Rohm and Haas Co., Philadelphia, Pa.

† KM 228 copolymer, Rohm and Haas Co., Philadelphia, Pa.

†† HG-42 poly(ethyl methacrylate), E. I. duPont de Nemours and Co., Wilmington, Del.

TABLE 2

PHYSICAL PROPERTIES OF A CaCO_3 FILLED RESIN*

Sorption	Solubility	Color Stability	Peak Temperature	Hardening Time
mg/cm^2	mg/cm^2		$^{\circ}\text{C}$	min
0.4	0.02	no perceptible change	50.5	12

* Powder: 49.8% PMMA copolymer (SR-120) with 0.2% benzoyl peroxide and 50.0% CaCO_3

Liquid: MMA containing 0.2% N,N-dimethyl-p-toluidine

Powder-liquid ratio 1.5 gm/1.0 ml

Values are averages obtained from 2 specimens

TABLE 3

MECHANICAL PROPERTIES OF A CaCO_3 FILLED RESIN*

Transverse Deflection	Shear** Strength	SD	Tensile** Strength	SD	Compressive Strength**	SD
mm deflection 1500 to 2500 gm load***	psi	psi	psi	psi	psi	psi
1.1	5700	160	2450	200	8850	350

* Composition: Same as reported in Table 2; values are averages obtained from 5 or more specimens.

** Determined after 24 hours.

*** Determined after one week. Specimens broke before 4000 gm load was reached.

SYNOPSIS

A polymeric material suitable for the rapid fabrication of splint-type appliances has been developed. The dough-like product formed on mixing a powder and liquid can be readily adapted to the cervical third of the intact teeth. Auto-polymerization occurs in the mouth within 6 minutes at peak temperatures not exceeding 50°C. The polymerized product exhibits sufficient strength, rigidity and dimensional stability to function as a splint.

This material may also find application for the fabrication of orthopedic splints and other medical uses.

Fig. 1. Preformed interproximal pins.

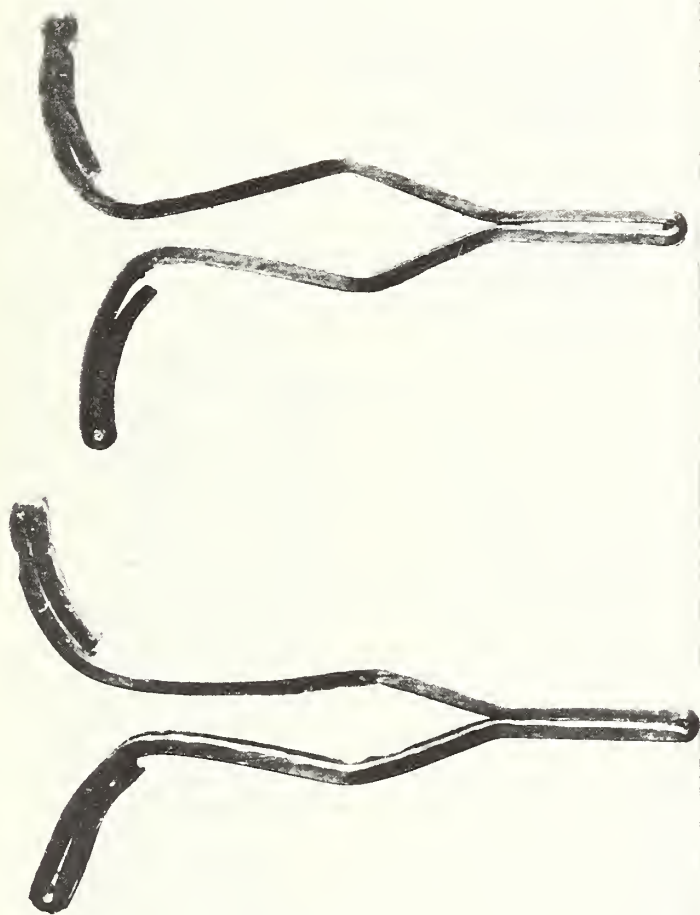




Fig. 2. Preformed interproximal pins provide anchor points for interarch elastics.

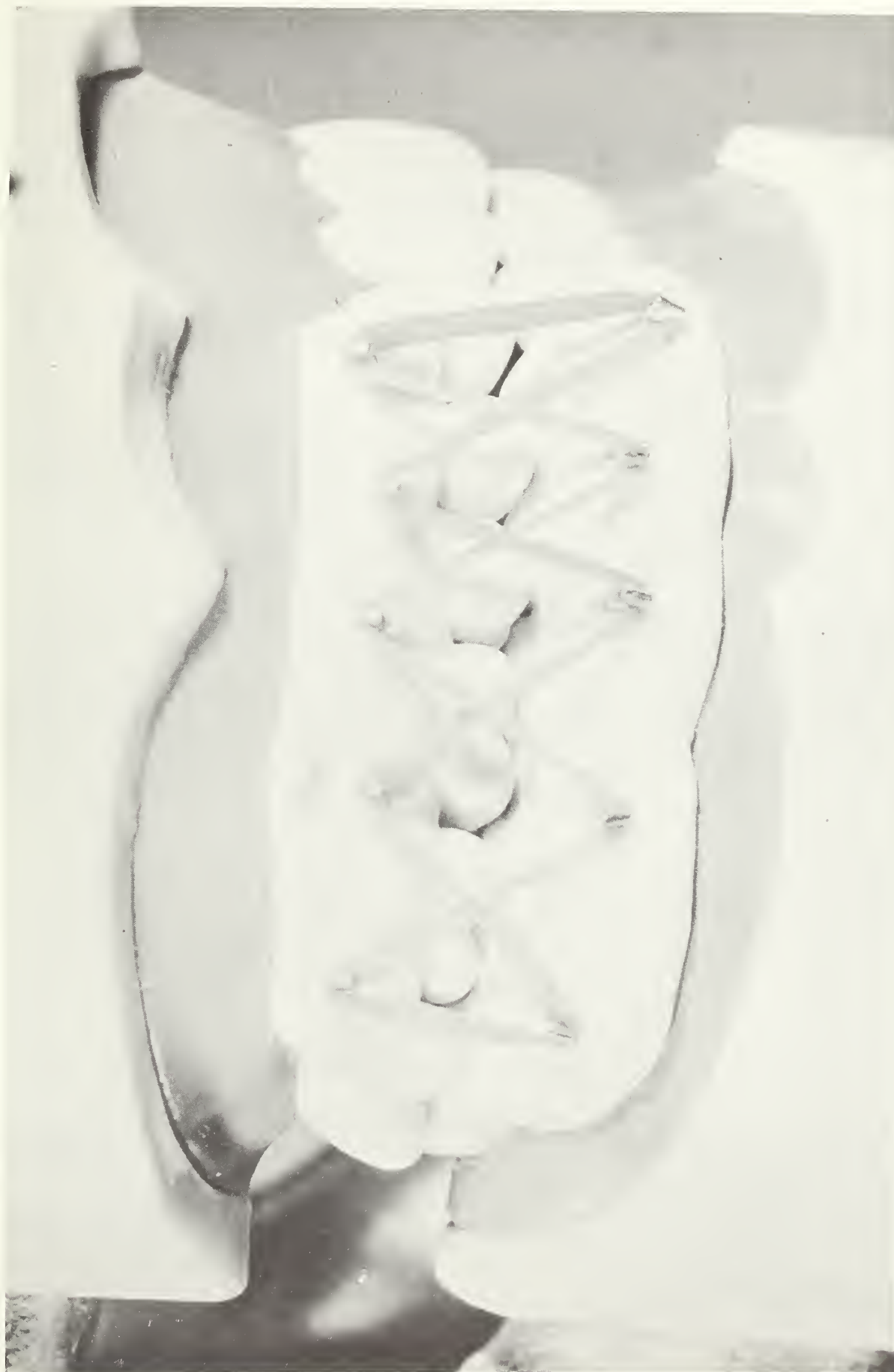


Fig. 3. Maxillomandibular stabilization achieved by use of interarch elastics.



