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DEVELOPMENT OF A RADIOPAQUE DENTURE BASE MATERIAL

by

H. H. Chandler,* R. L. Bowen+ and G. C. Paffenbarger+

* Research Associate, American Dental Association Research Program in the Dental Research Section, National Bureau of Standards, Washington, D. C. on a two-year leave of absence from The Ohio State University College of Dentistry, Columbus, Ohio 43210.

+ Research Associates, American Dental Association Research Program in the Dental Research Section, National Bureau of Standards, Washington, D. C. 20234.

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DEVELOPMENT OF A RADIOPAQUE DENTURE BASE MATERIAL

ABSTRACT

Radiopaque glass-resin composites were made for evaluation as denture base materials.

The addition of silane-treated, radiopaque, powdered glass to clear poly(methyl methacrylate) resulted in composites that had greater optical translucency than commercially available pink denture base resins. These formulations could be pigmented and opacified to produce materials that simulated oral soft tissues in color and translucency.

Other composites were made using various monomer, polymer and glass combinations. Those made from mixes of BIS-GMA, methyl methacrylate, poly(methyl methacrylate), and radiopaque glass had excellent translucency but handling characteristics were less than ideal.

Removal of very small glass particles (less than a few µm) appeared to improve optical translucency.

A radiographic survey of 12 specimens that contained from 29 to 57% of the radiopaque glass, indicated that all had sufficient radiopacity to aid in localization of swallowed or aspirated dentures made from such materials.

Finishing procedures on composite specimens were more difficult and time-consuming and did not produce surfaces as smooth as those obtained on poly(methyl methacrylate). The finished surfaces felt smooth to the tongue but might stain more easily in the mouth.

Introduction

In a previous paper, the need for radiopaque denture base materials was demonstrated by a review of 123 cases of swallowed or aspirated dentures or denture fragments.[1] The difficulties and time involved in locating and orientating the missing materials would, in many cases, have been decreased if they had been sufficiently radiopaque to be discernible in radiographs.

Previous methods of making denture base resins detectable on radiographs have been either the addition of certain salts of heavy metals to the polymer powder of the placement of radiopaque inserts into the mixed material during the molding procedure.[2-5] Neither has had wide acceptance. The addition of salts of heavy metals tends to decrease the optical translucency of the cured material, as well as cause a deterioration of certain physical properties.[3,5] Addition of radiopaque inserts causes a concentration of stresses at the interface between the insert and the resin which sometimes results in fracture of the base material.

In this study, several experimental radiopaque composite denture base materials were made from mixtures of a silane-treated radiopaque powdered glass and various monomer or monomer-polymer combinations. The mixes were evaluated for general handling, working, and molding characteristics; the polymerized specimens were evaluated for optical translucency, radiopacity, surface finis and overall suitability as a denture base.

One formulation, based on the addition of silane-treated radiopaque glass to poly(methyl methacrylate) (PMMA), was selected for measuring some pertinent physical properties and for constructing a number of technic dentures. The results will be reported in subsequent papers.[6,7]

Materials and methods*

An x-ray opaque glass was previously developed for use as a filler in dental restorative materials.[8] This glass has been used as one of the fillers in an experi-

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* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of S Standards or that the material or equipment identified is necessarily the best available for the purpose.

mental anterior filling material, and the radiopacity of the finished restorations was useful in dental radiographic diagnosis.[9] The batch formulation of the glass was SiO_2, 44; BaF_2, 28; B_2O_3, 16; and Al_2O_3, 12, in mole percent.[8] The density of the glass was about 3.5 Gm/cc and its refractive index n_D^{25} was 1.535. The powder particle sizes ranged from about 1 to 50 μm.

For reasons of expediency this glass powder was the primary one investigated in this study as an x-ray opacifying agent for denture base materials. Other glass and resin compositions, especially formulated for use in denture base materials, would probably yield better overall results.

The glass powder was slurried with 0.5% (with respect to the powder) 3-methacryloxypropyltrimethoxysilane in a solution of 95% acetone. After intermittent stirring, the mixture was dried in a vacuum oven at 120°C and about 33.7 kN/m^2 (250 mm Hg) and passed through a U. S. Standard Sieve No. 100 (maximum opening 149 μm). Silane treatment can significantly increase the bonding between a filler and a resin matrix[10] and can make the powder hydrophobic. This glass, unless otherwise specified, was used in making the specimens in this study.

Initial testing indicated that glass particles of very small size (less than a few μm in diameter) caused a large reduction in optical translucency of the cured specimens. Therefore, another powder was prepared like the foregoing, except that before silane treatment, the glass was mixed about 8 times with 95% ethanol and all but the last mixture was allowed to stand undisturbed for 2 to 16 hours, after which the cloudy supernatant liquid was decanted and discarded. The silane was added to the last glass-ethanol mixture. Microscopic examination of the dried powder revealed that the range in particle size remained about the same, but presumably there was a decrease in the number of the smallest (colloidal) particles.

A few specimens were made with two other glasses. One had a batch formulation of Al_2O_3, 12; BaF_2, 8; B_2O_3, 16; and SiO_2, 44, in mole percent.[8] It was composed of silane-treated particles of 44 to 480 μm and its refractive index n_D^{25} was 1.564. The other had a batch formulation of SiO_2, 78; B_2O_3, 6; BaF_2, 11; and Al_2O_3, 5, in mole percent. The powder particle sizes ranged from about 1 to 50 μm and the refractive index n_D^{25} was 1.50 with slight variations in some particles.

One or another of the foregoing four glasses was added in varying amounts to combinations of monomers (or monomers and polymers) containing suitable initiators to cause polymerization. The monomers and polymers used were:

1.) Ternary eutectic dimethacrylate. This monomer is composed of the eutectic composition of three crystalline dimethacrylates. They are bis(2-methacryloxyethyl)isophthalate, bis(2-methacryloxyethyl)terephthalate, and bis(2-methacryloxyethyl)phthalate.[11] This monomer has been used previously in an experimental anterior composite filling material and in a posterior temporary composite filling material.[9,12] It is a non-volatile liquid having a viscosity of about 2.4 poises at 27°C. The refractive index n_D^{25} of its polymer is 1.548.

2.) Stypol 46-4005 (Freeman Chem. Corp.). This monomer is of the type described as BIS-GMA[10] and is the type currently being used as one of the monomers in several commercial composite filling materials for anterior teeth. It is very viscous, non-volatile, and light yellow in color. The refractive index n_D^{25} of its polymer is 1.568.

3.) Methyl methacrylate (MMA) (Rohm and Haas) CO.

4.) PMMA (Fisher Scientific Co.)

5.) PMMA and poly(ethyl methacrylate) (PEMA) copolymer, Type DJ (Rohm and Haas Co.).

6.) In many instances, certain commercially available denture base powders and liquids were used. These will be identified as they appear.

Some specimens were opacified with titanium oxide (Fisher Scientific Co.) and pigmented with cadmium red (United Color and Pigment Co.).

Some of the composite specimens made in this study were subjected to a finishing procedure similar to that in common use for acrylic resin denture base. The procedure consisted of initial finishing with a wet rag wheel charged with wet pumice followed by a polishing agent (Shure Shine, Aurora Dental Specialties Co.) on a dry rag wheel. They were then compared with PMMA specimens finished in an identical manner.

Fifteen specimens were made to determine the relative percentage of glass needed to give adequate radiopacity for diagnostic purposes. Twelve of these specimens were formed by polymerizing mixture of PMMA, PMMA-PEMA copolymer, MMA, and from 29 to 57.5% by weight glass. One specimen was clear denture base resin (Acri-Luc, Acri-Lux Dental Manufacturing Co., Inc.), one specimen was pink denture base resin (Justi-Tone T-3, H. D. Justi Co., Division of Williams Gold Refining Co., Inc.) and one specimen was a pink denture base resin containing barium sulfate [Stellon (pink radiopaque), Amalgamated Dental Co., Ltd.]. The specimens (as most of those in this investigation) were made by compression molding the doughy mixtures in a gypsum mold 28 mm square and about 3 mm deep. The square specimens were ground to a thickness of 2.0 ± 0.1 mm, were cut in two, and had the corners rounded so that the test pieces would more nearly simulate portions of broken dentures than square pieces. They were then placed in various positions on a tissue equivalent phantom (Rando Phantom, Alderson Research Laboratories, Inc.).

Radiographs were made at 80 KV for 12.5 milliampere seconds (50 MA for 1/4 second) at a source-film distance of 72 inches. Medium speed films (14 x 17 in.) were developed for 5 minutes at 68°F. Filtration equaled a total of 2.5 mm of aluminum.

The refractive indexes of 33 commercially available denture base resins were determined using an oil immersion method.

Results and discussion

In order for denture base material to have wide acceptance, it must be non-toxic, have translucency and color that simulates gingival tissue, have adequate physical properties, and should be workable by methods that are in common use.

To obtain maximum translucency in a resin-glass composite, it is necessary that the refractive indexes of the matrix and filler be as nearly alike as possible. The refractive index n_D^{25} of the primary glass selected as the filler was 1.535. Therefore, it was necessary for the refractive index of the resin matrix to be near enough to this value so that when opacifiers such as coloring pigments were added, the composites would have translucency simulating oral soft tissues.

The refractive indexes of the 33 commercially available denture base resins were, with one exception, in a range of

1.491 to 1.496. This indicates that they were all composed essentially of PMMA (n_D^{25} ~1.492). The one exception (Unibase, Austenal Dental Division, Howmet Corp.) had an index n_D^{25} of 1.5635 and is a styrene-acrylonitrile copolymer. Although the refractive index of Unibase was nearly ideal for the purpose of this investigation the material was not studied further because it required techniques and equipment not commonly utilized. Many styrene containing copolymers also have refractive indexes n_D^{25} above 1.5. Although these types of materials represent interesting areas for possible future development, they were not studied in this investigation because of their rather unique handling and molding characteristics.

Composite specimens were made using two pink denture base resins (Justi-Tone T-3, H. D. Justi Co and Acralite 88, Acralite Co., Inc.) as the matrix and 40% by weight of the glass as the filler. Both resins had a refractive index n_D^{25} of about 1.494. The mixes reached a doughy consistency and could be packed using techniques like those used with conventional powder-liquid denture base systems. The addition of glass appeared to slightly reduce the flow of the doughy material. The optical translucency of the finished specimens was somewhat lower than identical specimens with no glass and the color was changed to an unlifelike gray-pink. Both the color and optical translucency would be unacceptable in a denture base resin. A similar specimen made with a clear denture base resin (Acri-Lux, Acri-Lux Dental Mfg. Co.) and containing 40% by weight glass was yellowish-gray in color and had greater translucency than the pink colored specimens with no glass. These results indicate that the opacifiers present in commercially available pink denture base resins result in greater opacity than that obtained by the addition of 40% glass to a clear resin alone. This gives some latitude for the use of additional opacifiers in attempts to arrive at the proper color for a denture base material containing the glass filler.

Specimens were made of mixes containing the ternary eutectic dimethacrylate monomer (n_D^{25} = 1.548 for polymer) with 25%, 50%, and 79% by weight glass. The mixes did not reach a doughy state and did not flow under pressure in the manner of a mix of PMMA-MMA. The resulting specimens were reasonably translucent, but contained many voids and air bubbles. Because the character of mixes containing this monomer does not seem well adapted to pressure molding techniques and because the specimens contained air bubbles and imperfections that were not easily avoided or removed, they were not investigated further.

Another series of specimens was made utilizing BIS-GMA and MMA without glass. These materials, being liquids, were heat-cured in test tubes, and the resulting specimens were transparent (Fig. 1). By adjusting the ratio of BIS-GMA to MMA, transparent specimens could be obtained with refractive indexes almost identical to that of the glass. For example, the polymer of a mix containing 60% BIS-GMA and 40% MMA by weight had a refractive index n_D^{25} of 1.538. Addition of glass to mixes such as this yielded specimens of excellent translucency.

PMMA powder was added to mixes containing the glass, BIS-GMA and MMA in order to achieve a doughy consistency. Some of the resulting specimens still exhibited excellent translucency. An example of one such mix contained 34.5% glass, 34.5% polymer (Acri-Lux, clear), 14.8% BIS-GMA and 16.2% MMA by weight. The specimen from this mix approached transparency (Fig. 2). However, these mixes did not have doughy characteristics but became somewhat rubber-like in texture. The rubber-like texture increased as the amount of BIS-GMA was increased. Mixtures containing 15% or more by weight of BIS-GMA were very difficult to pack and adhered severely to the polyethylene films used for trial packing. Sticking also occurred when cellophane and Teflon® films were used. Mixes made with less than 15% BIS-GMA could be pressure molded. The same poor handling characteristics remained but to a lesser extent and there was a loss of translucency as less BIS-GMA was used. Because of their rather poor packing and handling characteristics, mixes of this type were not investigated further. As with the styrene-containing polymers, these materials offer an interesting avenue for further development of a composite denture base having a high degree of light translucency.

Another method of obtaining greater light translucency is to use glass containing particles of larger size. This acts to reduce the area of glass-resin interface and thereby reduces the amount of light scatter. To illustrate this factor, a specimen was made using glass particles with a size range of 44 to 480 μm mixed with Acri-Lux clear polymer and Acri-Lux monomer. The glass had a refractive index n_D^{25} of 1.564. The specimen was extremely translucent (Fig. 3) but would not be acceptable as a denture base resin because it could not be finished to a smooth surface using methods in common use. One might expect such a material to have poorer strength properties than a similar specimen made with smaller particles.[13]

Attempts to gain greater translucency by using the glass powder from which the smallest particles had been removed were only partially successful in that the specimens had only slightly better translucency than those made with the primary glass powder. Apparently, the method for removing the particles was not entirely successful. It is these small particles (less than a few μm) that are most effective in scattering light.

Specimens were made using the experimental glass containing 11 mole percent of the BaF_2. The refractive index n_D^{25} of this glass was about 1.50. The specimens were made from mixes containing 41% glass, 40% PMMA-PEMA copolymer, and 19% MMA by weight. The optical translucency of these specimens was not improved over similar specimens containing the glass with 28 mole percent of BaF_2 but there was much less gray discoloration. Whether the absence of the gray color was due to fewer impurities is not known. In any case, these specimens lacked the same degree of radiopacity due to the reduced amount of BaF_2 in the glass filler. The possibility of obtaining a whiter material by using different glasses exists. Such materials would be easier to tint to the color of the gingival tissues.

The foregoing investigation of light translucency and handling characteristics reveals that several combinations of polymers and radiopaque glasses have characteristics that would make them possibilities for development into acceptable composite denture bases. However, specimens composed essentially of PMMA and glass seemed to offer the best combination of properties for immediate development. In order to determine if acceptable color and translucency could be achieved, several specimens were made from mixes containing PMMA, MMA and the glass to which was added cadmium red pigment with and without titanium oxide opacifier.

The composite specimens colored with cadmium red with no titanium oxide opacifier were reddish brown in color and totally unacceptable. Composite specimens colored with the cadmium red pigment and with an equal amount of titanium oxide had acceptable translucency and color. A moderate blue or gray tinge remained. A typical specimen yileding these results was made from a mix containing 38.5% PMMA, 38.5% unsedimentated glass, and 23.0% MMA to which was added 0.029% by weight each of the cadmium red and titanium oxide. It should not be concluded that this combination of pigment and opacifier, either in amount or type, represents the best available for the purpose intended. These results only point out that a composite material of this type can be developed with ranges in color and optical translucency that simulate oral tissues.

Finishing procedures were more time-consuming and difficult for the glass-containing specimens and removal of gross scratches required more effort. The finished surfaces did not reflect light as well as specimens containing no glass. Evidently, the pumice particles are not hard enough to give the exposed glass particles a planed surface. Hence, the glass interfered with the incident light and caused it to be scattered. The finished surfaces of the glass filled specimens felt smooth to the tongue and were barely distinguishable in this respect from the surfaces of unfilled specimens. They appeared to be sufficiently smooth and reflected enough light to be esthetically acceptable. Such surfaces might however, be susceptible to staining in the oral environment.

One of the radiographs made on the tissue equivalent phantom is seen in Figure 4. This and other radiographs were examined by two radiologists to determine the weight percent of glass required to yield adequate radiopacity for diagnostic purposes. It may be seen in Figure 4 that all of the 11 glass-containing specimens are visible to some degree even when superimposed over the mediastinal area. This area was selected because foreign bodies lodged there are relatively difficult to locate. It was agreed that even the specimen containing 29% glass would be of aid in locating a swallowed or aspirated denture but that the more glass present, the better it would be for diagnostic purposes.

The specimen made of pink PMMA in Figure 4 is invisible and demonstrates the problem of locating foreign bodies of this composition. Other radiographs showed that the specimen containing $BaSO_4$ was only slightly radiopaque and would be of little diagnostic value in locating a foreign body.

Summary and conclusions

A series of radiopaque resin-glass composite specimens was made for the purpose of evaluating them for use as a denture base material. The evaluation included molding and handling characteristics, light translucency, radiopacity, and overall suitability for use as denture base materials.

Several combinationsof monomer, polymer, and radiopaque glasses were used. The addition of a silane treated radiopaque glass having a refractive index n_D^{25} of 1.535 to clear PMMA denture base resin resulted in specimens of greater optical translucency than commercially available pink denture base resins. Such formulations could be pigmented and opacified to produce specimens that simulated oral soft tissues in color and translucency. These formulations appeared to have the best characteristics for immediate development.

Other monomer, polymer, and glass combinations were investigated. Specimens made from mixes containing BIS-GMA, PMMA, MMA and the glass gave the greatest translucency but handling and molding characteristics were less than ideal. This combination and others using styrene copolymers offer areas for further investigation.

Optical translucency was also improved by using glass particles of larger size. One such specimen (using glass particle sizes of 44 to 480 μm) was extremely translucent. Some evidence was obtained that removal of very small glass particles (less than a few microns) would also be an effective method for improving optical translucency.

A radiographic survey indicated that specimens containing 29 to 57% of the glass by weight all had sufficient radiopacity to be of aid in localization of swallowed or aspirated denture fragments made from such materials. Specimens containing the higher percentages of glass would be more easily located.

Finishing procedures on the composite specimens did not yield as smooth a surface and required more time than identical procedures on PMMA specimens. The finished surfaces of the composite specimens felt smooth to the tongue but might stain easily in the oral environment.

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Legends

FIGURE 1: A 5 mm thick specimen polymerized from a mix containing 60% BIS-GMA and 40% MMA by weight. The almost total transparency can be seen from the clarity of the typewritten letter beneath the specimen. The refractive index n_D^{25} of the copolymer is 1.538.

FIGURE 2: The specimen on the left (B) is a commercially available PMMA pink denture base resin. The specimen on the right (C) was from a mix containing 34.5% of the glass, 34.5% clear polymer (n_D^{25} = 1.492), 14.8% BIS-GMA, and 16.2% MMA by weight. Both specimens are about 2.75 mm thick and are against a narrow black tape on frosted glass illuminated from behind. Note the greater translucency of the glass-containing specimen.

FIGURE 3: The specimen on the left (D) is a commercially available pink denture base resin with no glass

(refractive index n_D^{25} = 1.492). The specimen in the middle (E) contains 40% glass (particle size 44 to 480 μm; refractive index n_D^{25} = 1.564) and 60% clear denture base resin (n_D^{25} = 1.492).

The specimen on the right (F) is composed of 40% glass (particle size 1 to 50 μm; refractive index n_D^{25} 1.535) and 60% PMMA. The illumination is the same as in Figure 2. Note the extreme translucency achieved in specimen E with the large particles even though the glass used has a refractive index higher than that of the glass used in specimen F.

FIGURE 4: Chest radiograph made on a tissue equivalent phantom on which 11 glass-containing specimens and one commercially available denture base resin were superimposed over the mediastinal area. The radiograph was exposed at 80KV for 12.5 MAS at a target film distance of 72 inches. Filtration equalled 2.5 mm of aluminum (AP view).

Specimen No. 1 is composed of a commercially available pink denture base resin. Specimen No. 2 contains 29% glass; No. 3, 33% glass; No. 4, 36% glass; No. 5, 39% glass; No. 6, 42% glass; No. 7, 44% glass, No. 8, 46% glass; No. 9, 49% glass; No. 10, 51% glass; No. 11, 53% glass, and No. 12, 54% glass. All of the glass-containing specimens are visible to some degree whereas the commercially available resin is invisible.

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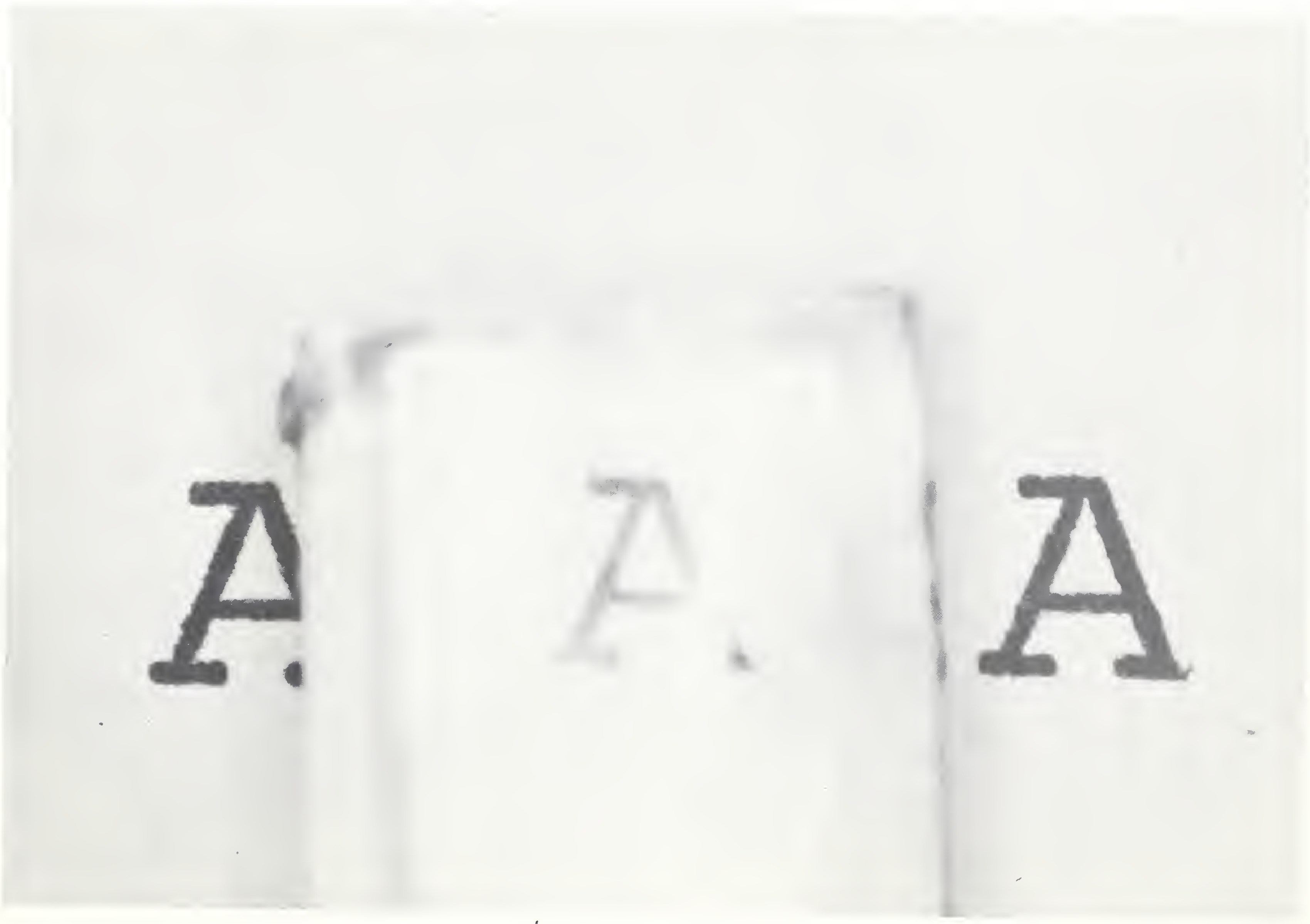

Fig 1

Fig 2

Fig 3

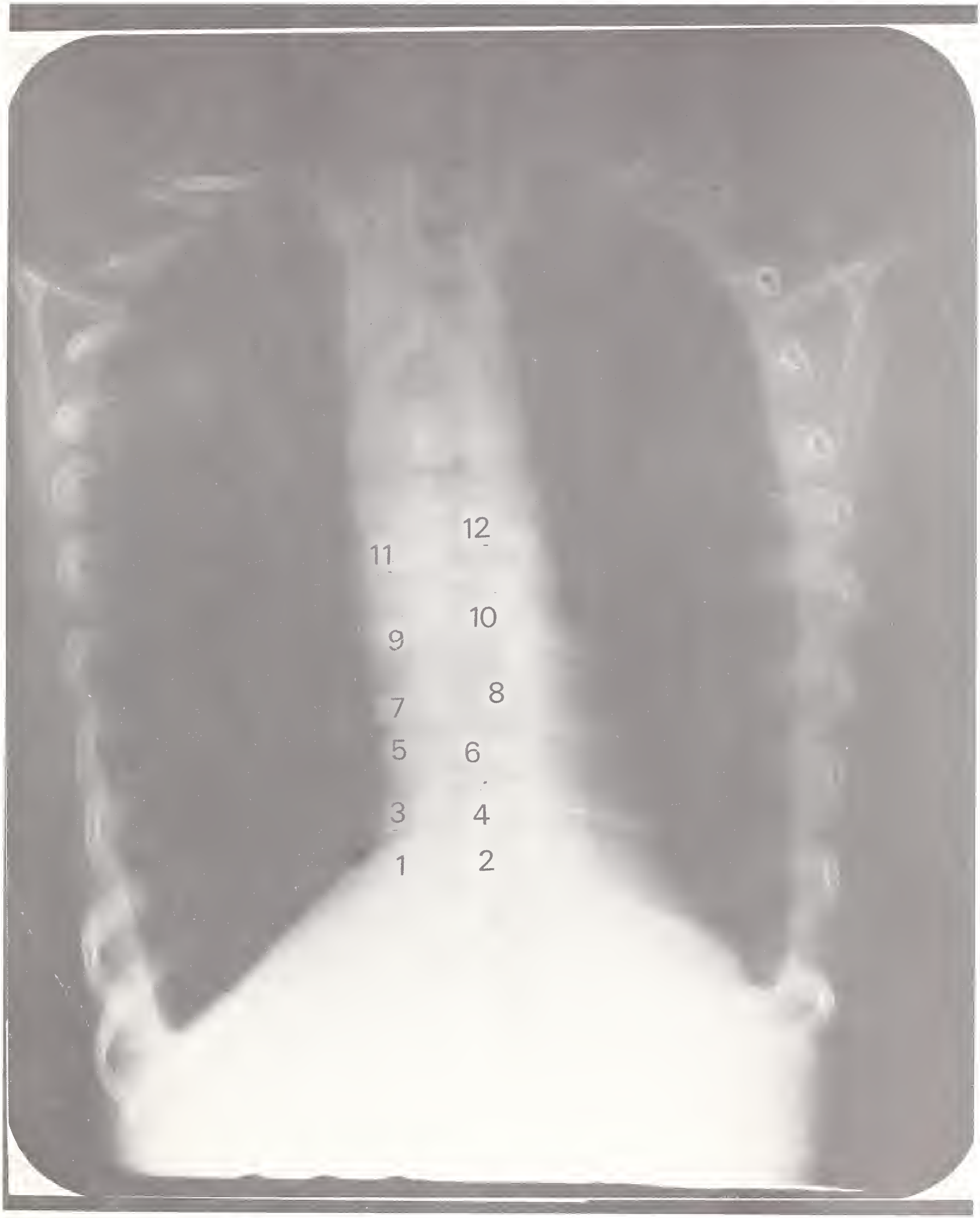

fig 4