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on

EBA CEMENTS

by

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EBA Cements

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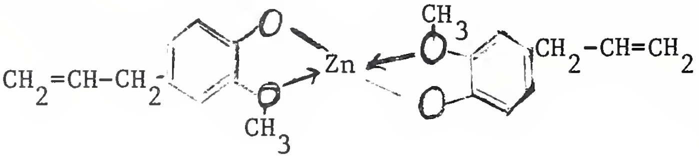
O-Ethoxybenzoic acid (EBA) containing cements are an outgrowth of studies to improve zinc oxide-eugenol (ZOE) cements which were first reported in the dental literature about one hundred years ago (1-3). Over the years ZOE cements have found a wide range of applications in dentistry: as temporary restoratives, sedative bases, cementing media, for crown and bridge work, in pulp capping, as soft tissue packs in oral surgery and periodontics, as root canal sealers in endodontics and with modifying agents as impression pastes. The ZOE cements possess much better compatibility than most dental materials with both the hard and soft tissues of the mouth (4-7). They have excellent sealing properties (8) and their sterilizing effectiveness (9) has been demonstrated. ZOE cement also acts as a palliative or anodyne and as a mild non-irritant antiseptic. Their low strength which may not be large enough to resist forces of mastication and their lack of resistance to wear and disintegration deter more extensive use in temporary restorations.

SETTING MECHANISM OF ZOE CEMENTS

A number of studies have shown that the set mass resulting from mixes containing the proper proportion of zinc oxide and eugenol consists of zinc oxide embedded in a matrix of zinc eugenolate chelate with any excess eugenol being sorbed by both zinc eugenolate and the unreacted zinc oxide (10-11). More detailed studies of the infrared spectra have confirmed the bisdioxachelate structure of zinc eugenolate (12).



The crystal structure of this compound has been investigated by Douglas (13) and Cartz (14). X-ray diffraction of commercial ZOE products or experimentally prepared formulations which also have a large excess of zinc oxide yield extremely small values for the relative intensity ratios of the principle peaks of zinc eugenolate to ZnO. This suggests that in these cements the zinc eugenolate reaction product is formed below the 2% level resolvable in standard preparations (15-16). High resolution microscopy also indicates that the zinc eugenolate product in commercial formulations is small and is confined to the reaction interface (17). These formulations also contain about 5% free eugenol after hardening (18).

The setting reaction is speeded up by the presence of an accelerator such as zinc acetate. Presence of water or a decrease in the pH of the reaction mixture also reduces setting time. Water reacts with zinc oxide to form the hydroxide which in turn reacts with eugenol (19).

(1) $ZnO + n\ H_2O \longrightarrow n\ Zn(OH)_2$

(2) $n\ Zn(OH)_2 + 2n\ \text{eugenol} \longrightarrow n\ Zn(\text{eugenol})_2 + 2nH_2O$

The formation of the hydroxide is slow, but acid speeds up the reaction.

(3) $n\ ZnO + 2n\ CH_3COOH \longrightarrow n\ Zn(CH_3COO)_2 + n\ H_2O$

$$(4)\quad \underline{n\ Zn(CH_3COO)_2 + 2n\ H_2O \rightleftharpoons n\ Zn(OH)_2 + 2n\ CH_3COOH}$$

$$n\ ZnO + n\ H_2O \longrightarrow n\ Zn(OH)_2$$

Since the zinc hydroxide reacts with eugenol reaction (4) goes to the right. Obviously, zinc acetate can be substituted for acetic acid, but to start the reaction a trace of water must be present. Commercial formulations generally contain zinc acetate dihydrate as accelerator which furnishes the water to initiate the reaction.

MODIFIED ZOE AND EBA CEMENTS

Low strength is unquestionably the main weakness of ZOE cements. A number of studies have been undertaken during the last decade to upgrade the properties of the cements. The following approaches have been taken:

1. Replacement of zinc oxide by other metal oxides.
2. Incorporation of fillers, reinforcing or modifying agents.
3. Substitution of eugenol by other chelating agents.

Only limited studies have been made to substitute other metal oxides for zinc oxide (11). Cupric eugenolate can be prepared by a procedure similar to that used in the synthesis of zinc eugenolate. A slight excess of a methanolic solution of cupric acetate monohydrate is reacted with eugenol at 60°C for one hour (16). Employing the same reaction conditions, that is, refluxing methanolic solutions of eugenol with mercuric-, lead-, nickelous or calcium acetate did not yield the respective metal eugenolates. Attempts to synthesize the cupric or nickel isoeugenolates also were unsuccessful.

Addition of rosin or hydrogenated rosin improves the working properties of the mixes. Hydrogenated rosin is commonly used since it is stable to oxidation and yields cements with good color stability. Incorporation of up to 20% polymer dissolved in eugenol to improve the physical properties was first suggested by Curtis (20). An experimental cement containing surface-treated zinc oxide (80%) and poly(methyl methacrylate) (20%) powder and a liquid consisting of 99% eugenol and 1% acetic acid had a compressive strength of 54.0 MN/m^2 (550 kg/cm^2, 7820 psi), a tensile strength of 4.1 MN/m^2 (42 kg/cm^2 600 psi) and a solubility and disintegration value of 0.008 g/cm^2 (21). A clinical evaluation of this cement as an intermediate restorative material at intervals of 60 days for a period of 12 months showed this formulation to be superior to three other experimental cements with regard to the maintenance of anatomical form and marginal integrity (22). Products incorporating poly(methyl methacrylate) in the powder have become commercially available both as luting agents and intermediate restoratives.

The knowledge gained from the characterization of the reaction products lead to extensive investigations with the ultimate aim to obtain improved cements by substitution of other complexing agents for eugenol. Eugenol isomers capable of forming chelates were synthesized (23) and the effect of the position of substituents on the behavior of the isomers as evidenced by their ionization constants and reactivity with zinc oxide was determined (24). In the reaction of eugenol isomers with zinc oxide, the 1,2,3-trisubstituted isomers do not react readily compared to the unsymmetrically 1,2,4- or 1,2,5-trisubstituted one, indicating that the chelation reaction is greatly influenced by steric hindrance of the bulky neighboring allyl groups. The chelation reaction may also depend to some degree on the ionization constants since the more acidic chavibetol reacts somewhat faster than eugenol.

Zinc oxide will react with many chelate-forming compounds to yield coherent products (25). Mixes containing o-ethoxybenzoic acid (EBA), salicylaldehyde, acetylacetone, o-ethoxyacetic acid or lactic acid form hard products within one hour at room temperature. Some of these products disintegrate in water.

Cements obtained from o-ethoxybenzoic acid (EBA) and metal oxides of group II of the periodic table or lead oxide have been studied in considerable detail (26). Products formed from zinc oxide and EBA-eugenol solutions in the absence of an accelerator harden more rapidly and have higher strength and lower solubility and disintegration values than those made with EBA alone (figures 1 and 2). Most useful properties are obtained with liquids containing between 50 to 70% EBA. However, these cements have a high water solubility. Substitution of 2-propoxy -5-methylbenzoic acid, a higher more hydrophobic homologue for EBA, yields cements with unexpectedly high water solubility and disintegration (26,27). On incorporation of rosin or hydrogenated rosin the water solubility is greatly reduced (26). Addition of a reinforcing agent such as monocalcium phosphate, heat-treated fused quartz or aluminum oxide gives products with compressive, shear and tensile strengths that are three to four times those of conventional ZOE formulations. Thus, these EBA containing products have mechanical properties similar to those of zinc phosphate cements.

The properties of cements, based on zinc oxide, hydrogenated rosin, EBA and eugenol have been studied in detail (28). The strength of the cements is nearly independent of the particle size of zinc oxide and fused quartz. The carbon dioxide and water content of the zinc oxide also have little effect on the physical properties of the hardened product (28-30). Alumina reinforced EBA cements have physical properties superior to those of cements reinforced with fused quartz (31). The preferred composition contained 64% zinc oxide, 30% tabular $A\ell_2O_3$ and 6% hydrogenated rosin. A slurry prepared from 1.7 gm of powder per 0.2 ml of liquid can be mixed easily and will harden in less than ten minutes. The resulting product has a compressive strength of 93 MN/m^2 (950 kg/cm^2, 13,500 psi) and a film thickness of 26 μm (Table 1). With one-surface inlays, these cements adhere at least as well as commercial zinc phosphate cements and give much higher tensile adhesion values than ZOE products. Similar formulations have become commercially available and have been well accepted as luting agents in crown and bridge cementation. On incorporation of more powder into the mix, excellent base materials can be obtained. Especially desirable is their high ten-minute compressive strength of 46.1 MN/m^2(470 kg/cm^2, 6,680 psi) which can easily withstand the forces encountered in condensing an amalgam.

The brittleness of these luting agents limits their use for temporary restorations of multiple surface carious lesions in areas subject to heavy masticatory forces (32). Stress bearing characteristics of EBA cements can be improved through the incorporation of powdered polymers of relatively low elastic moduli (30). The most suitable resins are methacrylate copolymers, although vinyl copolymers may also be potentially useful. Other resins, because of their resilient nature are difficult to obtain in powdered form. A cement made from powder containing 58.2% ZnO, 27.3% $A\ell_2O_3$, 5.4% rosin and 9.1% methyl methacrylate copolymer and liquid containing 62.5% EBA and 37.5% eugenol had one week tensile and compressive strength of 11.5 MN/m^2(117 kg/cm^2, 1660 psi) and 65.1 MN/m^2 (664 kg/cm^2, 9430 psi) respectively. Thus, the addition of the polymer greatly increases the tensile strength of the hardened cement. These markedly higher tensile strength values are probably more important than the somewhat lower compressive strength and the clinical results described later bear out this point.

Cements containing rosin have somewhat higher tensile strength, but are more soluble and set more slowly than those to which hydrogenated rosin has been added (30). Improvement in the physical properties of a formulation containing 58.2% ZnO, 27.3% $A\ell_2O_3$, 5.4% hydrogenated rosin and 9.1% methyl methacrylate copolymer in the powder and 62.5% EBA-37.5% eugenol in the liquid was not obtained on increasing the (1) hydrogenated rosin content, (2) percentage of eugenol, and (3) ratio of zinc oxide to aluminum oxide reinforcing agent. Addition of 0.5% aluminum sulfate decreases very slightly the solubility and disintegration of cements containing rosin or hydrogenated rosin. A vinyl chloride-vinyl acetate copolymer-containing cement had one week tensile and compressive strength of 9.8 MN/m^2(100 kg/cm^2, 1420 psi) and 91.5 MN/m^2(933 kg/cm^2, 1330 psi), respectively. Incorporation of an acrylonitrile-butadiene-styrene terpolymer, a polyacetal resin or various grades of commercial polycarbonate molding powders produced materials with physical properties somewhat lower than those containing acrylic copolymer. A summary of the physical properties of conventional and reinforced ZOE cements, alumina reinforced, plastic-modified EBA cements and zinc phosphate cements is given in Table 1.

A comparison of the first commercially available EBA crown and bridge cements has been made by Phillips and coworkers (33). Properties investigated were compressive and tensile strength, film thickness, solubility and disintegration in both water and acid and retentive characteristics as determined by the amount of tensile force required to remove one-surface inlays from prepared cavities following cementation with the various agents. Physical properties of an experimental alumina-reinforced EBA cement and commercial EBA cements of unknown composition have also been studied by Custer and Anderson (34). The properties of typical commercial EBA cements have been measured in a collaborative test program which had as its aim the development of a specification for ZOE and EBA type cements (35).

Mechanism of Setting of EBA Cements

The products formed on hardening of commercial EBA cements have not been completely characterized (16). Cements made up of zinc oxide and a liquid consisting of either EBA or 62.5% EBA-37.5% eugenol were pulverized. The powder was extracted by shaking with 50 ml of methanol for 6 hours. After centrifuging, the methanol layer was decanted and the remaining powder was dried at 110°C and weighed. From cements containing EBA, the original liquid was removed quantitatively (Table 2). Cements containing EBA and eugenol lost 60 to 70% of their liquid component on extraction. Probably all the EBA was removed by the methanol extraction. The results were confirmed by heating the dried unextracted solid residue in a crucible to remove any remaining organic matter. There was no loss in weight on heating the residue of the cement prepared with EBA liquid. The EBA-eugenol containing cement showed a 30 to 40% loss in weight which accounted for all the unextracted liquid. Thus, eugenol is much less readily extracted, and hence more firmly bound than EBA in the hardened cements.

To study the reaction product, zinc oxide (2 g, 0.0246 mole) and o-ethoxybenzoic acid (8 g, 0.048 mole) were stirred together and set aside. After two months at room temperature, the mixture consisted of a soft layer on top of a hard layer. The x-ray diffraction did not give any peaks. The product was partially soluble in hot water, insoluble in methanol, ethanol, chloroform or dimethylformamide.

The reaction products were added to warm acetone and filtered. On evaporation of the solvent an amorphous material separated from the filtrate. The solid residue, insoluble in warm acetone, could be dissolved by boiling in acetone for 10 minutes. A solid (m. p. 92-100°C) crystallized on cooling to 0°C. After drying in a vacuum, analysis for carbon and hydrogen indicated that the compound was zinc o-ethoxybenzoate (Anal: Calcd. for $C_{18}H_{18}O_6$ Zn: C, 54.63, H, 4.58. Found: C, 54.8; H, 4.6) Absence of an infrared absorption peak around 1750

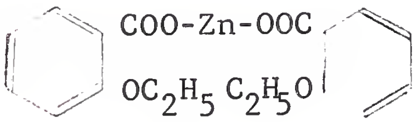
cm^{-1} indicated that no unreacted-COOH is present. The broad absorption band of o-ethoxybenzoic acid around 1230 cm^{-1} which can be attributed to the ethoxy group (36) is present in the zinc derivative as a sharp band at 1240 cm^{-1}. The spectrum of o-ethoxybenzoic acid has absorptions at 1745 cm^{-1} and also carbonyl absorptions at 1594 and 1609 cm^{-1}. For the primarily ionic bonded zinc o-ethoxybenzoate, the absorption peak of the -COO Zn/2 group falls in the same region at 1600 cm^{-1}. Since the uncoordinated $-COO^-$ group also absorbs in the same region (37), it was not possible to establish from the infrared spectrum whether the o-ethoxybenzoate possesses a chelate structure.

The same compound was obtained on heating 20 g (0.12 mole) of EBA, 5 g (0.061 mole) of zinc oxide and 20 ml of methanol on a steam bath until most of the solvent had evaporated. On cooling in a refrigerator, a white solid crystallized which, on recrystallization from chloroform, had a melting point of 90-103°C. The infrared absorption spectrum was identical with the spectrum of zinc o-ethoxybenzoate obtained by the procedure described above. (Anal: Calcd. for $C_{18}H_{18}O_6$ Zn: 54.63, H, 4.58. Found: C, 54.3; H, 4.6).

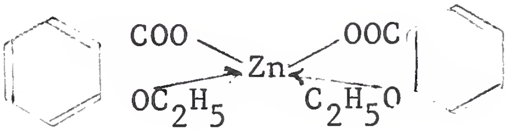
The zinc o-ethoxybenzoate could also be synthesized in 20% yield from 12.3 g (0.075 mole) EBA dissolved in 20 ml methanol and 8.8 g (0.04 mole) zinc acetate by heating for 6 hours on a steam bath, filtering and dissolving the residue in hot chloroform.

Slurries using powder-liquid ratios of 10:1, 5:1 and 1:1 of zinc oxide powder and EBA or 62.5% EBA- 37.5% eugenol liquid were prepared and allowed to harden at 37°C and 100% relative humidity. X-ray diffraction patterns showed only minor changes on varying the powder-liquid ratio with all patterns resembling closely those of zinc oxide.

On addition of EBA to zinc oxide, either a salt (I) or chelate complex (II) can form:



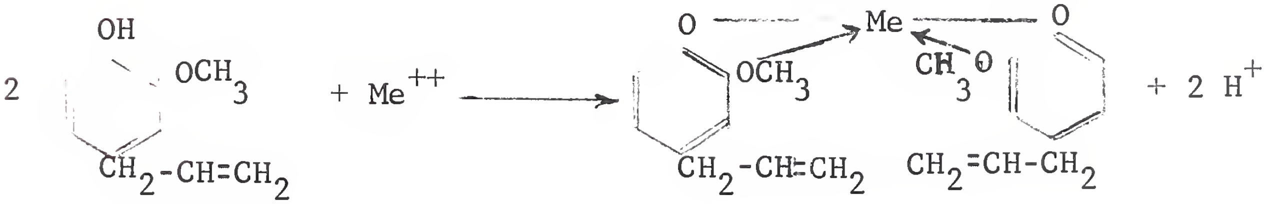
I



II

Possible formation of a chelate was studied (16) by titration of an aqueous solution of EBA with base in the presence of zinc ions and Job's spectrophotometric method of continuous variation (38).

The first procedure depends on the fact that most metal chelates may be considered as formed by the displacement of a weak acidic portion of the chelating agent by a metal ion (39). Thus, the addition of metal ion causes a drop in pH and the greater the tendency for metals to combine with a given chelating agent, the greater the drop in pH.



eugenol
weakly ionized.

This simple technique of checking for chelate or complex formation is not very sensitive for EBA since we deal with a moderately strong acid which is fairly strongly ionized. Hence, there is little decrease in pH if chelation occurs. Results of the titration of EBA with base in the presence and absence of Zn^{++} were inconclusive.

The composition of chelates can often be determined by a simple colorimetric technique introduced by Job (38). For the chelating reaction:

$$A + nB \rightleftharpoons A\ B_n$$

$$K = \frac{[A\ B_n]}{[A][B]^n}$$

where [A] is the concentration of the metallic ion and [B] that of the chelating agent. If [A] + [B] = constant, it can be shown that when concentration $[A\ B_n]$ is a maximum

$$[B]/[A] = n;$$

that is, for a constant total concentration of metal and chelating agent, the concentration of chelate with respect to unreacted metal or chelating agent is greatest when the metal and chelating agent are brought together in the same ratio in which they exist in the chelate. If the chelate absorbs light in the visible or ultraviolet region, a plot of optical density versus composition of the solution under the restriction imposed above will give a curve with a maximum at the composition corresponding to the formula of the chelate. If substances are present that absorb light in the same region as does the chelate, the difference in optical densities between the chelate and the estimated amounts of unchelated absorbing substances may be plotted as a function of concentration.

The absorption of aqueous EBA and eugenol solutions as well as of solution of these compounds containing zinc sulfate were measured in the ultraviolet (250-360 µm). EBA and eugenol solutions follow Beer's law. They show an absorption peak around 292 µm, whereas $ZnSO_4$ does not absorb at this wave length. Job's method of continuous variation was applied to EBA-$ZnSO_4$ solutions having a total concentration of 4×10^{-4} M. No maximum was observed by plotting optical density versus composition of the solution. This result does not necessarily indicate that no chelate formation takes place since some chelates have absorption spectra that do not differ significantly from those of the chelating agent. MacKenzie and coworkers (40) have shown that ionic chelates have nearly the same absorption spectra as their chelating agent, but that the absorption spectra for covalent bonded chelates contained strong absorption bands characteristic of the chelate, and hence of the metal-donor bond. Since EBA is a moderately strong acid, its anion should be a fairly strong conjugate base. Formation of an ionic complex with a divalent metal ion such as Zn^{++} is likely to occur, especially since oxygen donors favor ionic bonds.

Eugenol forms a five-membered chelate whereas EBA may give a six-membered ring. Measurement of the chelate stability constants K as well as the formation constants k_1 and k_2 for the reaction

$$Me^{++} + Chel^{-1} \rightleftharpoons MChel^{+}$$

$$MChel^{+} + Chel^{-1} \rightleftharpoons MChel_2$$

$$K = K_1 \times k_2 = \frac{[MChel]_2}{[Me^{++}][Chel^{-1}]_2}$$

would yield valuable information since these constants would show the relative stability of the two ring systems.

Clinical Studies

The main purpose of a temporary restoration is sedation and protection of the tooth from irritants and decay. The ZOE cement is essentially neutral and, therefore, offers unusual pulpal protection. The EBA-containing cements have the same mild tissue reaction of unmodified ZOE cements, which are much superior in this respect to zinc phosphate cements (41-43).

Unset cements caused some necrosis and a moderately severe inflammatory reaction when they were first inserted into rat muscle (42). Granulation tissue formed in the region and healing proceeded rapidly, producing a fibrous capsule to the implant. When set materials were used as implants, the EBA-containing cement was always less irritating than zinc oxide-eugenol cements. Bhaskar and coworkers (43) investigated the pulpal response of four types of restorative materials. Class V cavities were prepared in 78 teeth of three miniature swine. The animals were killed after 1, 2, and 3 weeks and the teeth were examined microscopically. A powder containing 57% ZnO, 28% aluminum oxide, 9.5% poly(methyl methacrylate) copolymer and 5.5% rosin and liquid made up from 66.7% EBA and 33.3% eugenol was used. The restorative material appeared to be biologically acceptable to the dental pulp. No irreversible pulp damage was observed. Odontoblastic disruption and inflammatory infiltrate were not severe. They were least pronounced in the ZOE restoration, very slightly more marked in a commercial, resin modified ZOE and the EBA formulation and most prominent in teeth restored with cyanoacrylate containing restorative material. The layer of reparative dentin formed in response to the filling materials was proportional to the degree of odontoblastic disruption and the inflammatory infiltrate. It was much more pronounced in the teeth that were restored with cyanoacrylate and EBA than in teeth filled with ZOE cements. Thus, in cases in which the therapeutic aim is to require a thick layer of reparative dentin, a cavity base with either the EBA or cyanoacrylate is preferable. It would be of interest to study if the reparative and secondary dentin formation produced by EBA cements is as rapid as that formed after the use of calcium hydroxide. Coleman and Kirk (42) filled cavities scheduled for extraction for orthodontic reasons with ZOE and EBA cements. The teeth were extracted after periods ranging from 24 hours to three weeks. The teeth were fixed in 10% formol saline, decalcified and examined histologically. Little or no pulpal reaction could be attributed to either the ZOE or the EBA materials. The odontoblast layer was usually intact. Although some vacuolation was present in this region, this was also seen in the control teeth where no cavities had been prepared.

There has long been a deep interest in an improved ZOE cement that would be suitable for permanent cementation of cast restorations. The modified ZOE or reinforced EBA cements have been employed successfully as crown and bridge cements and appear to be well suited for this purpose. The absence of irritation on the dentine-pulp complex and the resulting freedom from postcementation symptoms gives them a big advantage over zinc phosphate cements. Since their compressive strength is much higher than that of unmodified ZOE cements, their retentive properties are improved and approximate those of zinc phosphate cements (33,44,45). A clinical study using 186 full cast crown bridge retainers and 205 full cast crowns has been reported by Horn (46). The span of the bridges cemented with this material was limited to a maximum of two consecutive pontics of bicuspid width. Nineteen of the full cast crown bridge retainers were of the cantilever type. Resin veneers were protected from the excess EBA cement by coating them with silicone grease. No cavity liners or medicaments were applied. The crowns were not completely filled with cement, but a coating was applied to the internal surfaces and a small amount was allowed to flow into any crevices or depressions on the teeth prior to insertions. Dryness was not maintained after the restorations had been seated by applying pressure for two or three minutes. After cementation, abutment teeth were not painful, and the marginal relationships were not unduly distorted. In selected cases, tests with ice-cold water seemed to indicate excellent insulation. This effect may be caused by the ability of the cement to obtund pain.

A number of crown and bridge cements incorporating EBA have become commercially available in the United States and in Europe. Many products have film thickness of less than 25 μm and are recommended for the final cementation of metal crowns and bridges retained by metal crown, porcelain or plastic jackets, porcelain-over-metal restorations, and gold-veneered-with-resin restorations.

No clinical data are available regarding the retention of orthodontic bands cemented with EBA cements. Bands cemented with an experimental cement containing 90% ZnO and 10% hydrogenated rosin powder and 62.5% EBA and 37.5% eugenol required three times as much force to accomplish removal as bands cemented with ZOE, but the retention values were considerably lower than those obtained for phosphate or silicate cements (47).

Zinc phosphate cement has been the preferred material for use as an intermediary base beneath metallic restorations. Zinc phosphate is preferred over conventional ZOE and calcium hydroxide because of its superior strength, despite its inferior biological and slightly poorer thermal diffusion characteristics. When ZOE or calcium hydroxide bases are used, it is often recommended that they be overlaid with the stronger zinc phosphate cement (48-50).

The clinical significance of the compressive strength of a base material has not been defined. It is obvious, nevertheless, that when amalgam is condensed into the cavity preparation, the base must have sufficient strength to support the forces of condensation. If the base does not have sufficient strength, fracture or displacement of the base could permit the amalgam to contact the underlying tooth structure and thus negate the thermal protection afforded by the base.

Furthermore, in deep cavity preparation, the amalgam could be forced through microscopic exposures in the floor of the cavity and into the pulp (51-52). Chang, Swartz and Phillips (53), in experiments conducted under laboratory conditions, showed that with ZOE materials a minimum strength capable of supporting amalgam condensation ranges from 0.7 to 1.2 MN/m^2 (7 to 12 kg/cm^2, 100 to 170 psi).

Interest has increased in recent years in using zinc oxide-eugenol type cements as bases under amalgam and inlay restorations. These bases are non-irritating to the pulp and thus eliminate the need to protect the pulp with subbase materials when the zinc phosphate cements are used. The procedure is simplified, time is saved and the danger of pulp irritation is further controlled. The now available reinforced ZOE cements and especially the EBA cements, because of their increased early strength, are capable of withstanding the forces developed during condensation of amalgam and those forces which may subsequently be transmitted through the restoration.

EBA cements, employed as cement bases, usually utilize a higher powder-liquid ratio than when employed as luting agents. It is good practice to incorporate the maximum amount of powder into the liquid consistent with a usable consistency so that the powder will be in large excess in the hardened cement. EBA cements, because of their greater strength, seem to be well suited as a one-step base in deep cavities for gold, silicate cement and amalgam fillings (32). When this cement was placed in 32 vital but symptomatic teeth, symptoms subsided within two days. The cavity preparations were then completed and permanent restorations placed, leaving part of the EBA cement as a base. The teeth remained vital and nonsymptomatic.

An alumina reinforced EBA cement was placed as a base under a series of amalgam restorations that were packed with a calibrated spring plunger at a pressure of 140 kg/cm^2. When the teeth were sectioned after 48 hours, the base was still intact (Figure 3), whereas ZOE bases fractured at the pulpal-proximal line angle (31).

ZOE-type cements have been the preferred material for use over recently injured pulps caused by deep and extensive operating procedures. This is especially true in the teeth of children in whom secondary dentin has not yet formed a protecting barrier within the pulp chamber. The materials are radiopaque (54), seal a cavity better than other restorative materials (8, 55) and thus prevent organisms or moisture from the oral cavity gaining access to the cavity floor. This may be the reason for the higher percentage of negative cultures obtained when lining with ZOE instead of calcium hydroxide. Any residual organism probably remains in a latent form under sound restorations, because their environment has been altered and conditions for growth have become unfavorable. These organisms could become reactivated if saliva were to gain access to them through a leak in the restoration. Such leakage is much less likely if a ZOE or EBA lining is used. Thus, EBA cement, because of its excellent sealing characteristics (42), will assist in decreasing the number of organisms remaining in the dentin and, furthermore, will promote remineralization of decalcified dentine at the base of the cavity (43). These properties should make EBA cements the material of choice, especially in indirect pulp capping procedures since calcium hydroxide does not possess the excellent sealing characteristics, whereas ZOE or modified ZOE cement does not stimulate the formation of reparative dentin to any appreciable extent.

Human pulps which had been exposed in the course of normal operative procedures in five nonsymptomatic teeth were capped using an EBA containing cement and the cavities were filled (32). Within a week part of the material was removed and permanent restorations placed, leaving part of the previous cement filling as a base. None of the patients reported any symptomatology. None of the teeth showed any radiographic changes and all responded normally to vitality tests within the two to ten months observation period.

Studies of the possible use of EBA cements in root canal therapy and for gingaval dressing are not available. Requirements for an improved root canal sealer would include (1) a suitable consistency at the time of insertion into the canal, (2) good dimensional stability to avoid fissures resulting from shrinkage, (3) good adhesion, and (4) high degree of insolubility to body fluids (56). ZOE yields a fairly satisfactory hermetic seal, but is only slightly adherent to the cavity walls. Furthermore, according to Erausquin and Muruzabal, ZOE can be irritating to the periapical tissues (57), although the response is reduced by addition of acrylic polymer spherules (58).

In many patients it is desirable to treat dental restorative problems for extended periods of time with a long-term temporary or intermediate restorative material. Such occasion arises in teeth in highly carious mouths, particularly those of children where immediate excavation of all caries is indicated. This treatment arrests the caries and favorably alters the oral flora. Temporary restorations are then placed and the permanent restorations are inserted as scheduling permits. The Armed Forces also have unique dental requirements such as emergencies at remote sites or in combat zones that preclude the insertion of permanent restorations. Criteria for an acceptable "intermediate" restorative include (22): (1) a satisfactory seal between the cavity preparation and the material, (2) biologic compatibility with the pulp, (3) easy removal from the cavity preparation, (4) resistance to abrasion and attrition for an extended time, (5) ease of manipulation and placement, and (6) a longer service life than conventional ZOE temporary fillings.

Polymer reinforced ZOE cements because of their greatly improved physical properties (21), show a high degree of clinical acceptibility after a 12-month observation period (22). On the other hand, fused quartz (32) or titanium dioxide (22) reinforced EBA cements, despite their improved strength, proved unsuitable as temporary restoratives. Contrary to their low solubility and disintegration in water and dilute acids, the fused quartz reinforced EBA restoratives disintegrated rapidly under oral conditions (59). Thus, a low in vitro solubility value may be useful in comparing the relative solubility of products of similar composition, but is not necessarily an indication of the success of such restorations in the mouth. Comparisons have been made of the in vivo intraoral disintegration of cements using specially designed partial dentures so that cements are exposed to the oral environment (60). Results of these tests showed considerable patient variation in the rate and amount of cement lost. Abrasion played an important role in the loss of material with the greatest loss invariably occurring in those regions most subject to abrasion by the tongue. Thus, the in vivo disintegration appears to be an effect of the interaction of solubility and abrasion.

The resin modified alumina reinforced EBA cement, because of its demonstrated mechanical and palliative properties, especially its much higher tensile strength, appears to be very desirable for use as a long-duration temporary restorative.

In a limited clinical study (30), approximately 50 restorations, including complex restorations subject to heavy occlusal stresses, were placed using one formulation. Its powder component contained 58.2% ZnO, 27.3% Al_2O_3, 5.4% rosin and 9.1% methyl methacrylate copolymer.

A powder-liquid ratio of 1.2 gm powder per 0.2 ml of liquid was used. The material was usually mixed on a glass slab, but could also be prepared by mixing in a capsule employing a mechanical mixer. The unreacted eugenol was removed by blotting or by squeezing the mixed mass in an amalgam squeeze cloth. The material presented good manipulative properties and could be readily adapted to cavity walls and margins. Patients were recalled and observed periodically during the nine-month observation period. The restorative did not dissolve or disintegrate in the oral fluids. All restorations remained serviceable and showed only minimal signs of wear over the nine-month observation period. All teeth restored with this cement remained asymptomatic for the entire period of observation.

The formulation selected had a relatively high tensile strength, but the in vitro solubility and disintegration values were considerably higher (one week solubility and disintegration 0.94%) than those of other promising mixes. Since all restorations remained serviceable over the nine-month observation period, the in vivo solubility did not appear to be of any significance. Unreacted liquid in the clinical mixes was removed by blotting. It is conceivable that lower in vitro solubility and disintegration values would have been obtained if this procedure had been followed in the preparation of laboratory test specimens.

Direction of Future Work

The EBA cements, largely as a result of the extensive studies conducted during the last few years, have passed from their infancy to a state of incipient maturity. Further enhancement in physical and mechanical properties of EBA and other chelate-type cements for use as semipermeable "intermediate" restoratives would be desirable to make use of their excellent biological properties. However, progress in improving these materials may not be as rapid as one has become accustomed to during the last few years.

Basic investigations that would lead the way to the development of improved products should include pinpointing the exact mechanism of the setting of EBA cements. Determination of the chelate stability constants of potentially useful chelates as well as measurement of their hydrolytic stability would be most useful. Synthesis of prospective chelating agents and evaluating of the resulting cements would be desirable.

The existing fundamental knowledge makes it possible to conduct development of better EBA materials along many lines. Modest improvements may be obtainable by judicious selection of reinforcing agents such as treated or spherical glass powders or the partial replacement of zinc oxide by another reactive metal oxide, such as mercuric oxide. Upgrading of formulations by whisker reinforcement does not look promising. Incorporation of slightly soluble fluorides that leach from the EBA cements at a controlled rate should be studied with the aim of reducing the solubility of the components of tooth structure and thereby bestow anticariogenic properties to these cements. Further studies of novel chelating agents to partially or wholly replace EBA in cementitious compositions, especially those that yield a strong bond at the tooth-restorative interface, are a potentially fertile field for developing a greatly superior product. Even if such a breakthrough is realized, clinical application of such compositions would be entirely dependent on the results of histological, pathological and clinical studies in order to prove beyond a doubt that such a product has the desirable biological properties that have made ZOE and EBA cements so desirable as dental restorative materials.

Besides the enhancement of properties of EBA cements resulting from successful research efforts, it is anticipated that a major advance in the near future will be the availability of many new commercial products of this type, tailor-made to the wide spectrum of specific applications needed by the practicing dentist.

The product of the future will combine convenience with versatility. It will possess excellent manipulative properties, will mix with ease to a predetermined, carefully controlled powder-liquid ratio, will have a setting time that will be relatively unaffected by environmental parameters such as temperature and humidity, will have a low film thickness when required, and if desired, can be color-coded to indicate the stage of treatment of the tooth.

The findings obtained on pulp capping and on using EBA cements as sedative restorations and bases point, however, to avenues for further clinical research. Such studies should establish more clearly any potential advantages of EBA cements as bases under silicate cement or metallic fillings, as pulp capping or cementing media and as intermediate restoratives.

Summary

During the last few years considerable interest has been generated in improving zinc oxide-eugenol cements. A better understanding of the setting mechanism of these cements has become available which has led to the development of products with enhanced physical and mechanical properties usually containing o-ethoxybenzoic acid (EBA). These materials show the mild reactions to the tissues including the dental pulp similar to ZOE cements, but also stimulate the formation of

reparative dentin. Physical properties of the EBA-containing cements approach those of the biological and physiological less desirable zinc phosphate cements. The EBA cements have been well-accepted as luting agents for fixed restorations and as insulating bases. They appear to be the material of choice for indirect pulp capping. Resin modified EBA restoratives show good stress-bearing characteristics and should find applications as an "intermediate" restorative.

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TABLE 1

PHYSICAL PROPERTIES OF DENTAL CEMENTS*

	Powder-Liquid Quantities	Setting Time	Tensile Strength+		Compressive Strength+		Solubility and Disintegration
	gm/ml	min	MN/m^2	kg/cm^2	MN/m^2	kg/cm^2	%
Zinc oxide-eugenol (ZOE)	1.0-2.2/0.4	3-8	1.4-2.5	14-25	16.7-38.3	170-390	0.02-0.20
Reinforced ZOE	0.6-1.1/0.3	3-8	1.5-6.9	15-70	39.2-75.5	400-770	0.05-0.80
EBA (Al_2O_3 reinforced)	1.6-2.0/0.2	7-9	3.9-7.4	40-75	58.9-93.1	600-950	0.05-0.13
EBA (plastic modified)	1.1-1.3/0.2	7-8	6.6-9.8	66-99	50.0-78.5	510-800	0.13-0.94
Zinc phosphate cement	1.4/0.5	7-8	3.2-4.6	33-46	68.7-147.1	700-1500	0.10-0.20

* Some of the data given in this Table are taken from the results of the collaborative test program - Zinc oxide - Eugenol Dental Cements ISO/TC Committee 106/WG1 - Filling Materials

\+ One day

TABLE 2

Weight Loss of Cements on Solvent Extraction

Cement Containing Zinc Oxide and	Extraction with CH_3OH	Loss of Liquid on Heating CH_3OH Insoluble Residue	Extraction with $CHCl_3$
	%	%	%
Eugenol	10-12	80-90	~80
EBA	100	0	119[a]
EBA and eugenol	60-70	30-40	102[a]

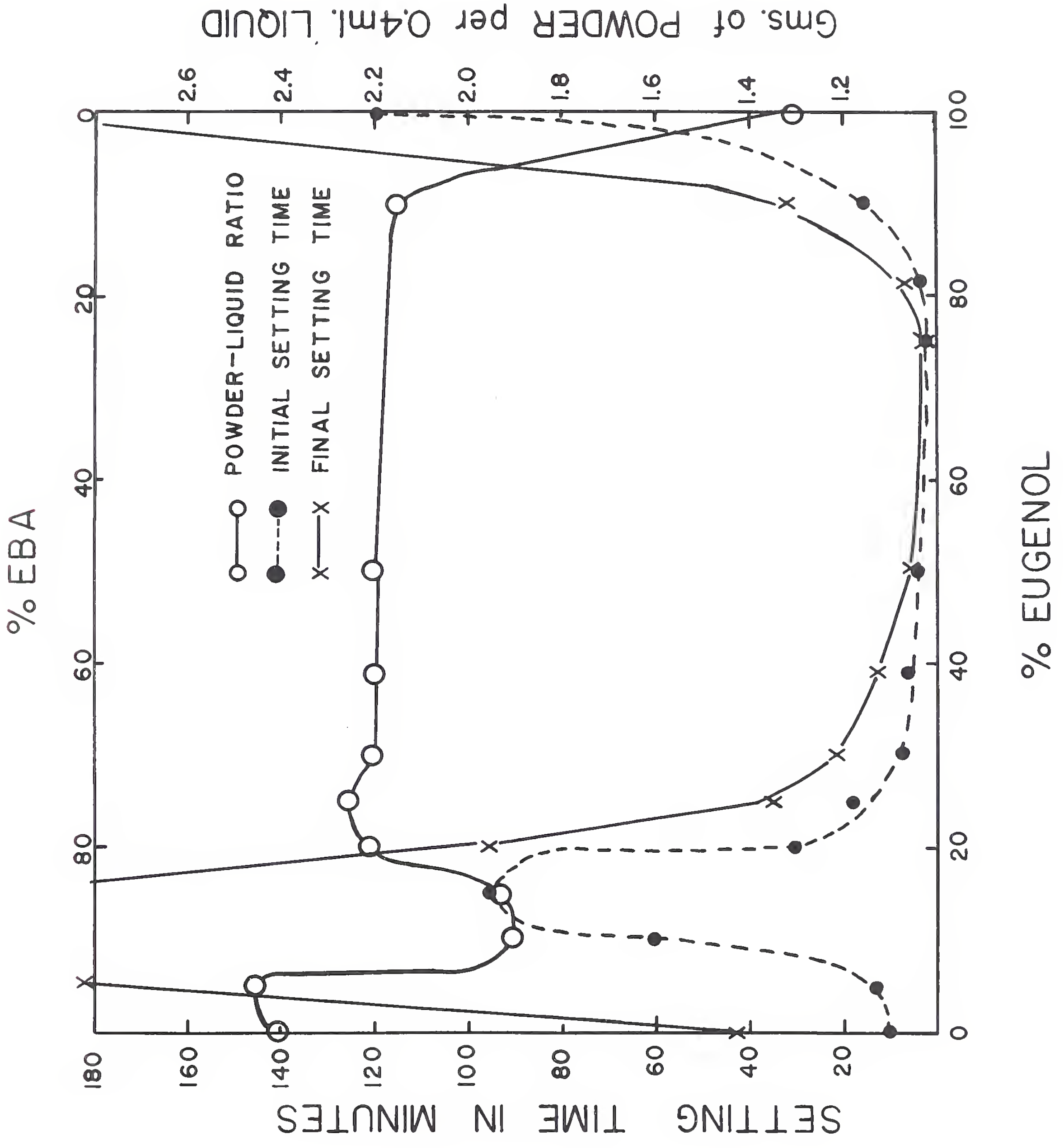
[a] including some solid extracted with $CHCl_3$

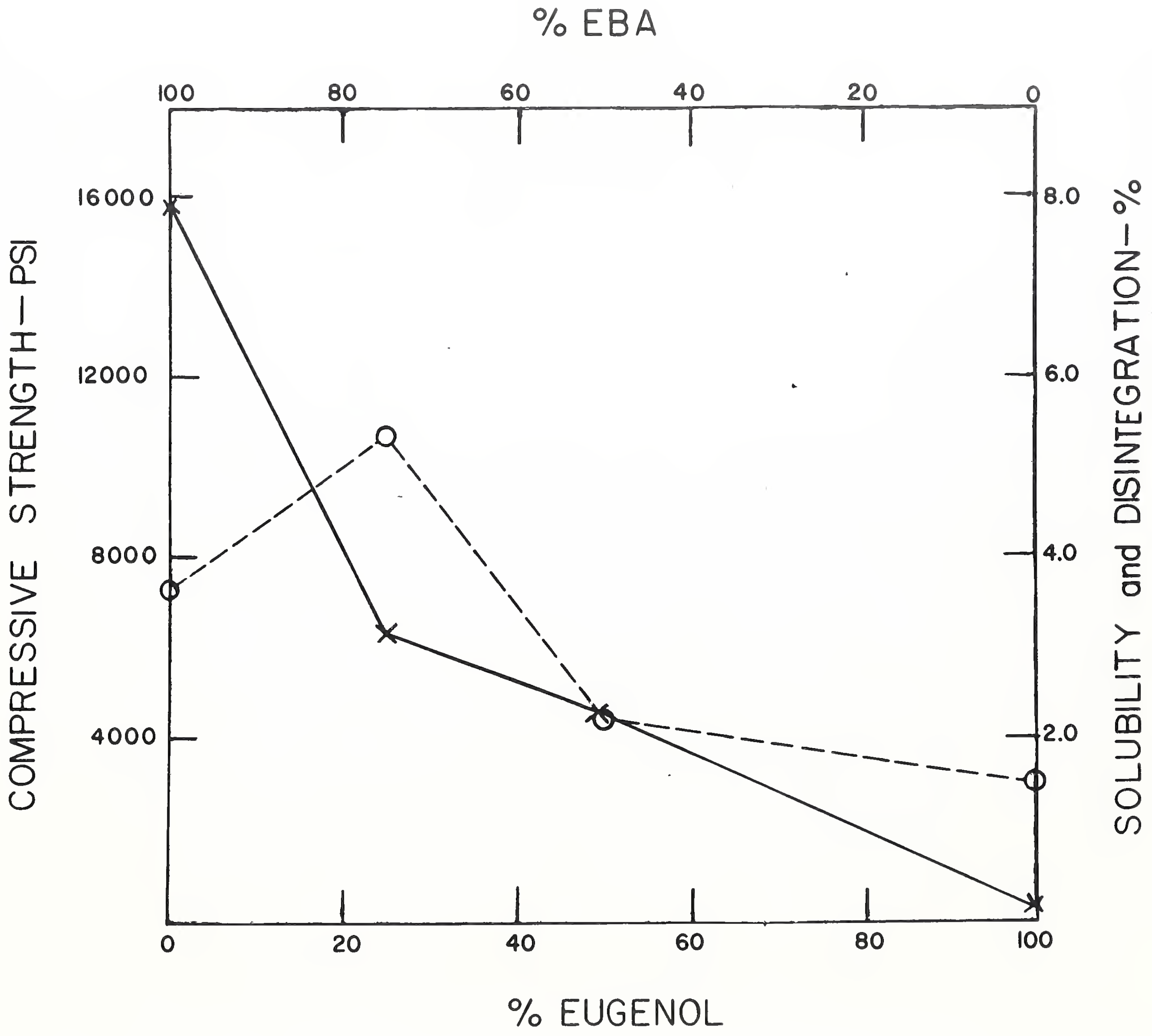
Figures

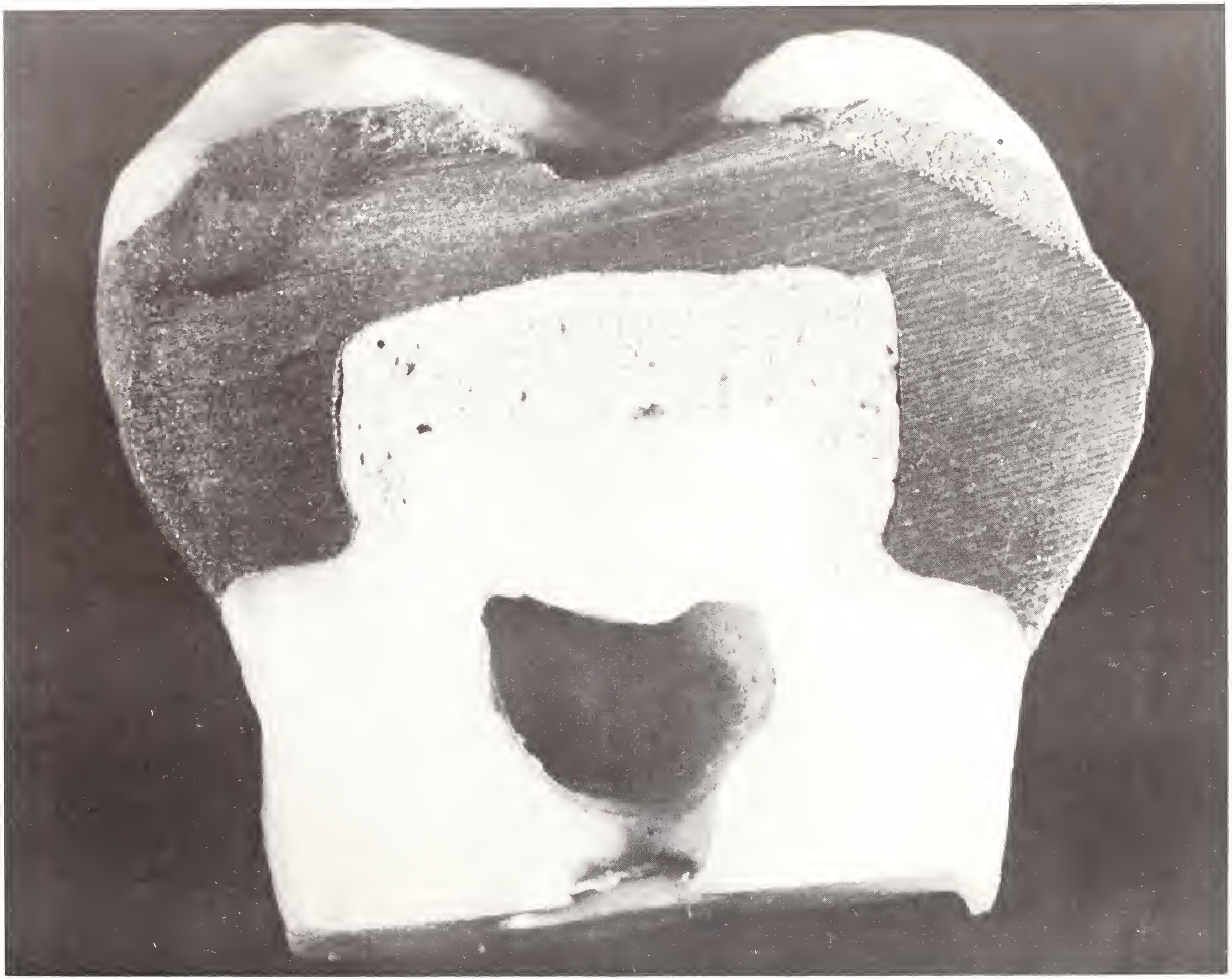
Figure 1. Effect of composition of the liquid on setting time and standard consistency powder-liquid ratio of ZnO-EBA-eugenol mixes (25).

Figure 2. Effect of composition of the liquid on compressive strength and solubility and disintegration of ZnO-EBA-eugenol cements. x-----x solubility and disintegration. o-----o compressive strength (25).

Figure 3. Section through an amalgam restoration condensed under 140 kg/cm^2 (13.8 MN/sq.m) packing pressure against an Al_2O_3 reinforced EBA base with a ten-minute compressive strength of 470 kg/sq.cm (46.2 MN/sq.m) (31).


% EBA
0
20
40
60
80
% EUGENOL
0
20
40
60
80
100
SETTING TIME IN MINUTES
20
40
60
80
100
120
140
160
180
Gms. of POWDER per 0.4ml. LIQUID
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
POWDER-LIQUID RATIO
INITIAL SETTING TIME
FINAL SETTING TIME


% EBA
100
80
60
40
20
0
COMPRESSIVE STRENGTH—PSI
16000
12000
8000
4000
SOLUBILITY and DISINTEGRATION—%
8.0
6.0
4.0
2.0
0
20
40
60
80
100
% EUGENOL



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