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An Improved Zinc Oxide-Eugenol
o-Ethoxybenzoic Acid Cement

by

Gerhard M. Brauer*
Lawrence Sangermano**

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

**Guest Worker, U. S. Army, Dental Research Section, National Bureau of Standards, Washington, D. C.

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AN IMPROVED ZINC OXIDE-EUGENOL-
o-ETHOXYBENZOIC ACID CEMENT

Abstract

Incorporation of rosin and/or metallic oxides such as mercury or lead oxide into the zinc powder of zinc oxide-o-ethoxybenzoic acid (EBA)-eugenol mixes greatly reduces the water solubility and disintegration of otherwise suitable cements. Cements having higher powder-liquid ratios, rapid setting times and improved compressive strengths have been obtained. The most desirable compositions employ powder-liquid ratios of 2.8 to 3.6 g per 0.4 ml of liquid, and harden within a few minutes to give cements having negligible solubility and disintegration and crushing strengths ranging from 8,000 to 11,700 psi. Subject to clinical evaluation these cements should prove useful in many dental applications.

1. INTRODUCTION

In a previous investigation [1] the reactions of various compounds containing groups capable of forming chelates with metals were studied. o-Ethoxybenzoic acid (EBA)-eugenol-zinc oxide mixtures were found to harden rapidly to cementitious products having greatly improved compressive strength and density compared to the conventional zinc oxide-eugenol cements used in restorative dentistry. However, the best value for the 24-hour solubility and disintegration test [3] for these products was 2.5% even on incorporation of a silicone. Later studies by Phillips and Love [2] showed that various formulations containing o-ethoxybenzoic acid-eugenol and zinc oxide had solubility and disintegration values as low as 1.2%. These investigators also reported that the inflammatory reaction of selected formulas to the connective tissue of the rat was mild and the tissue tolerance was superior compared with zinc phosphate cements.

This study deals with investigations to reduce the water solubility and disintegration of EBA-eugenol-zinc oxide cements without lowering their desirable properties. Previous investigations [4] showed that substitution of 2-propoxy-5-methylbenzoic acid (that is a higher homologue of EBA with an additional methyl group substituted in the side chain) for EBA did not lower the solubility and disintegration of the resulting cements.

Another approach was attempted, that is addition of metallic oxides, or fillers such as rosin to the zinc oxide powder. Earlier results [1] had shown that alkaline earth oxides as well as mercury or lead oxides gave faster setting mixes with EBA than those containing zinc oxide. Unfortunately, the high water solubility of cements containing alkaline earth oxides disqualifies them for use in the oral cavity. This study therefore, deals mainly with the results obtained with EBA-eugenol-zinc oxide mixes which contain small amounts of rosin and/or mercuric or lead oxide.

2. MATERIALS

All materials used were reagent grade products. The rosin was sieved through a No. 100 sieve.

Powders were mixed in a V shaped glass mixer which was rotated end over end for several hours.

3. EXPERIMENTAL

3.1 Consistency

Whenever possible a slurry of standard consistency was used. The standard consistency was determined as outlined in American Dental Association Specification No. 9 for Dental Silicate Cement [3]. Since the formulations employed showed a great increase in the powder-liquid ratio as compared to conventional zinc oxide-eugenol slurries it was often difficult to prepare rapidly a mix of standard consistency. Hence, a mix which appeared to be suitable for dental application but containing a lower powder-liquid ratio than a standard consistency mix was often used. Mixing times were also increased to a maximum of 2 minutes. Powder-liquid ratios of formulations are given in Table 1.

3.2 Setting Time

Setting times of mixes prepared at 23°C were determined at 37°C and 100% relative humidity using a Gilmore needle as described in American Dental Association No. 9 for Silicate Cement [3].

3.4 Compressive Strength

The procedure of American Dental Association Specification No. 9 [3] was used for measuring compressive strength.

Some difficulties were encountered in packing compressive strength specimens containing zinc acetate into the molds. The slurries are very adhesive and stick to the walls of the cavity of the mold. Furthermore, the slurries start to harden within 3 minutes from start of the mix and then become too viscous to flow freely into the mold. Hence, it was necessary to use an amalgam plugger to pack the slurries into the mold.

4. RESULTS

Results of tests conducted with EBA-eugenol-zinc oxide mixes are shown in Table 1. Addition of rosin, red mercuric oxide, barium oxide, zinc, lead or mercuric acetate speeds up markedly the setting reaction. With mercuric acetate mixes can be obtained which harden too fast to be useful clinically. On incorporating mercuric oxide or rosin in the mix the powder-liquid ratio is increased to 2.70 to 3.60 g per 0.4 ml liquid. (Powder-liquid ratio of zinc oxide-eugenol mixes is 1.4 g per 0.4 ml liquid). This higher powder-liquid ratio brings about a substantial increase in the density of the hardened cement. Addition of oleic acid or rosin improves the mixing characteristics of the slurries, but rosin appears to be superior as far as the physical properties of the hardened cement are concerned.

With the exception of barium oxide or lead acetate there is a significant reduction in the solubility and disintegration on adding the various oxides. Addition of lead oxide produces a somewhat greater reduction in the solubility and disintegration than mercuric oxide, but the latter compound gives products having superior compressive strengths. Especially satisfactory values are obtained by incorporating rosin in the mix which results in cements having less than 0.1% solubility and disintegration. Mixes containing rosin alone have maximum compressive strength of 10,300 psi (compared to 3,000 psi for commercial zinc oxide-eugenol cements). This value is only 1,400 psi below the optimum value of 11,700 psi obtained on addition of 5% mercuric oxide to the zinc oxide and employing a liquid composition containing 62.5% EBA and 37.5% eugenol. Higher compressive strength values are obtained on increasing the rosin concentration from 6% to 10%. Above a critical concentration of rosin in the mix the compressive strength is lowered considerably. Thus a cement containing 18.2% rosin has a compressive strength of only 4,400 psi. Addition of zinc acetate or mercuric acetate, although it may be desirable for speeding up the setting reaction, will result in reduced compressive strength.

Studies by Phillips and Love (2) have shown that EBA-eugenol zinc oxide cements are non-toxic. The addition of rosin should not appreciably change this behavior, but incorporation of mercury oxide or especially lead oxide may be undesirable. However, as can be seen from Table I addition of these oxides even in small amounts is not necessary to obtain desirable cements. Studies of the tissue tolerance of the various compositions are now under active investigation.

Undoubtedly improvement in the mixing properties as well as faster setting times can be obtained by slight modifications of these formulations. The advantageous properties of the cements reported here make it highly desirable to obtain detailed toxicological, and clinical data for these and similar formulations. If such studies should yield favorable results cements containing EBA-eugenol zinc oxide and rosin may prove to be desirable as temporary fillings, as cementing medium for crowns and bridges and as impression materials.

REFERENCES

1. Brauer, G. M., White, E. E. and Moshonas, M. G. The reaction of metal oxides with o-ethoxybenzoic acid and other chelating agents. J. D. Res. 37: 547 (1958).

2. Phillips, R. W. and Love, D. R. The effect of certain additive agents on the physical properties of zinc oxide-eugenol mixtures. J. D. Res. 40:294 (1961).

3. Specification No. 9 for dental silicate cement. American dental association specifications for dental materials, 1960. American Dental Association, Chicago, Ill.

4. Brauer, G. M. and Simon L., National Bureau of Standards Report No. 7142. The synthesis of 2-propoxy-5-methylbenzoic acid and its reaction with zinc oxide.

TABLE I

PROPERTIES OF EBA-EUGENOL-ZINC OXIDE MIXTURES

Composition*			Powder used per 0.4 ml Liquid	Setting Time	Solubility and Disintegration	Compressive Strength
Powder	Liquid					
	EBA	Eugenol				
	%	%	g	Min	%	PSI
100% ZnO**	-	100**	1.40	8	0.1	3,000
100% ZnO	70	30	2.20	21	2.7	-
97% ZnO, 3% HgO	70	30	2.80	14	2.02	11,100
95% ZnO, 5% HgO	70	30	2.80	16	2.45	11,400
90% ZnO, 10% HgO	70	30	2.80	17	2.14	10,200
95% ZnO, 5% HgO	62.5	37.5	2.80	10	1.08	11,700
95% ZnO, 5% HgO	58	42	2.90	6.5	0.70	9,200
95% ZnO, 5% HgO	55	45	2.90	9	0.67	9,900
95% ZnO, 5% HgO	50	50	2.90	6	-	8,300
86.4% ZnO, 4.5% HgO, 9.1% rosin	62.5	37.5	3.30	11	0.01	8,700
86.4% ZnO, 4.5% HgO, 9.1% rosin	55	45	3.20	10.5	0.03	8,800
89.6% ZnO, 0.36 $Zn(Ac)_2$,10% rosin	75	25	2.70	8	-	6,100
81.8% ZnO, 18.2% rosin	75	25	2.75	6.5	-	4,400
89.6% ZnO, 0.36% $Zn(Ac)_2$,10% rosin	70	30	2.90	7	-	8,200

TABLE I - Continued

PROPERTIES OF EBA-EUGENOL-ZINC OXIDE MIXTURES

Composition* Powder	Liquid EBA	Liquid Eugenol	Powder used per 0.4ml Liquid	Setting Time	Solubility and Disintegration	Compressive Strength
	%	%	g	Min	%	PSI
94% ZnO, 6% rosin	70	30	3.40	14	-	8,600
93.8% ZnO, 0.2% $Zn(Ac)_2$, 6% rosin	70	30	2.90	9	-	7,400
90% ZnO, 10% rosin	70	30	3.60	15	-	8,700
90% ZnO, 10% rosin	70	30	3.40	21	-	8,600
90% ZnO, 10% rosin	62.5	37.5	3.30	14	0.00	10,300
89.6% ZnO, 0.36% $Zn(Ac)_2$, 10% rosin	62.5	37.5	2.70	6	-	7,200
89.95% ZnO, 0.05% $Hg(Ac)_2$, 10% rosin	62.5	37.5	3.30	9	-	7,900
94.5% ZnO, 5% HgO, 0.5% $Hg(Ac)_2$	70	30	2.30	4	-	-
95% ZnO, 5% HgO	55.2	40+4.8***	2.90	-	-	-
97% ZnO, 3% PbO	70	30	2.70	9	3.12	8,200
97% ZnO, 3% PbO	62.5	37.5	2.50	5	0.76	7,800
98% ZnO, 2% PbO	62.5	37.5	1.70	6	2.15	7,700
96.5% ZnO, 3% PbO, 0.5% $Pb(Ac)_2$	62.5	37.5	2.50	6	0.90	7,400
95% ZnO, 5% BaO	70	30	2.30	11	7.58	4,000

* Percentage by weight for solids and by volume for liquids.
** Commercial product.
*** Oleic Acid.