

# **NATIONAL BUREAU OF STANDARDS REPORT**

10 533

Progress Report

on

**DENTAL CEMENTS, DIRECT FILLING RESINS, COMPOSITE  
AND ADHESIVE RESTORATIVE MATERIALS: A RESUME**



**U.S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS**



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### DENTAL CEMENTS, DIRECT FILLING RESINS, COMPOSITE AND ADHESIVE RESTORATIVE MATERIALS: A RESUME

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U.S. DEPARTMENT OF COMMERCE  
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Dental Cements, Direct Filling Resins,  
Composite and Adhesive Restorative Materials: A Resumé \*

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Dental Cements, Direct Filling Resins,  
Composite and Adhesive Restorative Materials: A Resume

Synopsis: This resume concerns: (1) experimental and commercial dental cements and restorative and adhesive materials usually containing nonmetallic inorganic components; (2) the biocompatibility of (1) with oral tissues; (3) proposed methods of bioevaluation; (4) the oral environment; (5) the nature of the hard tooth tissue; (6) cavity treatment; (7) agents for bonding the restorative material to the tooth; and (8) 112 references.

The cements include those based on: (C-1) zinc oxide-eugenol with additives such as zinc acetate, rosin, polymers and most important o-ethoxybenzoic acid (EBA); (C-2) metallic oxides-phosphoric acid; (C-3) acid phosphate salts-water; (C-4) aluminosilicate glass-phosphoric acid; (C-5) zinc oxide-polyacrylic acid; (C-6) methyl methacrylate-poly(methyl methacrylate) with or without inorganic fillers. Direct filling resins (C-6) without filler and composite restorative materials (C-6) with filler are based on acrylic resins or reaction

(ii)

products of acrylic (methacrylates) with other resins. Coupling agents include cyanoacrylates, epoxy-acrylic adducts and polyurethanes. The 10 tables give composition, values for pertinent physical properties or dental requirements. (C-2) dominates the cements but (C-1) with (EBA) and (C-5) which has some adhesion to hard tooth tissues and stainless steel may displace (C-2). (C-4) restorative materials are anticariogenic and widely used but are being supplanted by composite restorative materials.



## Cements

Cements developed for special purposes are extensively used in dentistry as filling materials, luting media, obtundent dressings, impression pastes and as a base for other restorative materials.

Current dental cements usually consist of a powder or paste that is mixed with a paste or liquid. The resultant mixture passes through a plastic manipulative state, which is probably colloidal, and has a continuing increase in viscosity until it finally solidifies.

Currently used cements include: (1) zinc oxide-eugenol and modifications thereof; (2) phosphoric acid liquid mixed with a variety of metal oxides or mixtures of them including zinc oxide, magnesium oxide, cupric oxide, cuprous oxide, manganese oxide, and/or with a complex, alkaline, aluminosilicate glass, or acid phosphate salts mixed with water; (3) resin cements based on acrylic monomers and polymers; and (4) a new cement with a modified zinc oxide powder and a polyacrylic acid liquid.

Zinc oxide-eugenol cement (ZOE). About a century ago one of the currently used cements consisting of powdered zinc

oxide mixed with eugenol was used in dentistry. The set cement is a complex solid consisting of particles of zinc oxide bound together by zinc eugenolate and of eugenol which is sorbed by both the zinc oxide and the zinc eugenolate.<sup>(1)</sup> The hardening time of an unmodified zinc oxide-eugenol cement is very long, usually several days, if moisture is absent.

Perhaps the first important additive was small amounts of zinc acetate which accelerated the reaction. Later, hydrogenated rosin was added to increase strength and decrease brittleness. Polystyrene and poly(methyl methacrylate) have a similar effect. . Because of low strength, poor abrasion resistance and disintegration in the mouth, a search was made for other metal oxides and chelating agents that would improve the values for the foregoing pertinent physical properties. One of these investigations recommended a solution of eugenol and o-ethoxybenzoic acid (EBA), which when mixed with powdered zinc oxide, had a short setting time and a marked increase in compressive strength and, unfortunately, in water solubility.<sup>(2)</sup> Powdered quartz<sup>(2)</sup> and alumina<sup>(3)</sup> additions further enhanced the quality.

A comprehensive review of zinc oxide-eugenol type cements with an extensive bibliography is available.<sup>(4)</sup>

There are now commercially available modified zinc oxide-eugenol cements with characteristics which some users believe are suitable for permanent cementation of restorations in the mouth, but until solid clinical evidence is available, caution is advised because of their water solubility. These cements have obtundent properties and have little or no irritating effect on the pulp. The biologic acceptance of zinc oxide-eugenol based cements is the best available and has become almost a standard for comparing the effects of other cements.

Table 1 shows the composition and proportions of powder and liquid with values for a few pertinent physical properties of certain zinc oxide and eugenol-based cements. The table cannot be used for direct comparisons of the effect of additives because of the many variables not only in the substances used in compounding the cements but also in the test procedures, especially the proportions of powder and liquid. The table does give some idea of the range of highest values for compressive strength encountered in



Table 1

## Zinc Oxide-Eugenol Based Cements: Composition and Properties

Composition in weight percent		Powder-liquid proportions	Time of setting	Solubility and disintegration after 7 days	Compressive strength at 7 days *
Powder	Liquid				
(5)	(5)				
Zinc oxide 99.8 Zinc acetate 0.2	Eugenol 100	Grams of powder in 0.4 ml of liquid 2.2	Minutes 5.5	% by weight 0.1	kgf/cm <sup>2</sup> 140
Zinc oxide 70.25 Hydrogenated rosin 29.40 Zinc acetate 0.35	Eugenol 85 Olive oil 15	8.5	9.0	0.02	390
Zinc oxide 68.8 Silica 30.6 Zinc acetate 0.6	O-ethoxybenzoic acid 75 Eugenol 25	3.25	8.0	3.2	820
Zinc oxide 89.7 Silica 10.0 Zinc acetate 0.3	O-ethoxybenzoic acid 47.5 Eugenol 47.5 Poly(methyl-methacrylate) 5.0	Variable	4	2.68	510
Zinc oxide 64 Alumina 30 Hydrogenated rosin 6	O-ethoxybenzoic acid 62.5 Eugenol 37.5	4.2	8.5	0.03	1060
Six available commercial cements		Variable	7-20	---	24 hour 6-220

\* 1 kgf/cm<sup>2</sup> = 14.223 psi

existing and experimental cements having a zinc oxide-eugenol base. Most of the values were obtained by test methods, or variations thereof, given in American Dental Association Specification No. 8 for Dental Zinc Phosphate Cement. (9)

Current research is centered on developing high-strength, low-solubility cements with good bioacceptance not only for temporary filling materials, but more importantly, for cementing media.

Zinc Phosphate Cements. Dental cements based upon a phosphoric acid liquid have been used in dentistry for at least a century and a half. The most important one is zinc phosphate cement in which powdered sintered zinc oxide and magnesium oxide (usually 9:1 ratio) is mixed with a phosphoric acid solution buffered by aluminum or zinc salts and sometimes by both. These cements are often improperly referred to as oxyphosphate of zinc cements but they contain no oxy-salts.

The set cement consists of unreacted cores of powder particles bound together with a matrix of the phosphates of

zinc, magnesium and aluminum. Prior to this hardened state the mixed but not completely set cement is in a plastic doughy state which some investigators believe is colloidal.

Crowell<sup>(10)</sup> showed that  $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$  was the principal crystalline phase in the set cement and that the desirable plasticity of mixed but unset cement was caused by  $\text{ZnHPO}_4 \cdot 3\text{H}_2\text{O}$  being formed in the cement liquid during mixing.

The requirements of the first revision (1933-1967)<sup>(11)</sup> and the current revision (1968)<sup>(9)</sup> of A.D.A. Specification No. 8 for Dental Zinc Phosphate Cement and properties of dental zinc phosphate cements<sup>(12)</sup> on the List of Certified Dental Materials as established by the American Dental Association<sup>(13)</sup> and some later values are given in Table 2.

Although there have not been any significant improvements in zinc phosphate cements since early in this century, nothing has been able to displace their use because nothing better has been developed for a sufficient time to determine the long-time clinical behavior. It may be that the improved



zinc oxide-eugenol or the new zinc oxide-polyacrylic acid type cements will displace zinc phosphate cements but it takes time to displace old materials unless there are gross and dramatic improvements in clinical performance in the new ones.

In Japan water-settable zinc phosphate cements were developed in which the powder contained not only zinc oxide but also phosphate salts, some of which were acidic. The liquid was water.<sup>(17)</sup> The powder of one consisted of zinc oxide, monozinc phosphate and tertiary zinc phosphate<sup>(18)</sup> while others contained monocalcium and monomanganese phosphates.<sup>(16,19)</sup>

The properties of these "water-settable" zinc phosphates have been determined by several investigators. Data from two<sup>(15,16)</sup> are given in Table 2.

The water-settable phosphate cements cannot compete with the customary zinc phosphate cements because the acid phosphate salts are too hygroscopic resulting in poor keeping qualities.



Table 2  
Zinc Phosphate Cements: Composition and Properties  
Zinc Phosphate Cements

(9) Requirements of revised ADA Specification No. 8 for Dental Zinc Phosphate Cements (1968- )*	Arsenic Content	Consistency of Mix	Time of setting		Maximum film thickness		Compressive strength (minimum - 24 hours)†	Solubility and disintegration (maximum - 24 hours)
	Maximum percentage by weight 0.0002	Grams of powder in 0.5 ml of liquid to produce a disk 30 ± 1 mm in diameter	Min.	Max.				
			minutes	minutes	Type 1 μm	Type 2 μm	kgf/cm²	% by weight
			5	9	25	40	700	0.2
(11) Requirements of former ADA Specification No. 8 for Dental Zinc Phosphate Cement (1938-1967)	0.0002	Same	4	10	40		(Minimum - 7 days) 840	(Maximum - 7 days) 0.30
(12,13) Range of values for zinc phosphate cements on List of Certified Dental Materials (1958)	<0.0002	1.3 ± 0.3  (1.2 ± 0.1)**	7 ± 1  (8 ± 1)**		30 ± 10		1180 ± 280	0.1 ± 0.1
					(25)**	(28±2)**	(840 ± 50)**	(0.1 ± 0.0)**
(14) Composition Percentage by weight			Disk was 34 ± 1 mm in diameter		17		950	0.14
Powder		Liquid						
ZnO	89.5	PO₄	57.9	9				
MgO	9.4	Al	2.8					
BaCrO₄	0.8	Mg	0.3					
			1.00					

Water-settable zinc phosphate cement

(15) New Calmix (Sankin Chemical Industry Co., Ltd. (Tokyo, Japan)		1.6	8½	75	670	0.4
Powder (16) Monomanganese phosphate (coated with zinc hydroxide) Zinc oxide	Liquid					
	Water	---	5½	31	850	0.36
Monomanganese phosphate dehydrated 240°C for 50 minutes Zinc oxide	Water	---	6½	27½	1250	0.34
Monomanganese phosphate dehydrated 250°C for 50 minutes Tertiary zinc phosphate	Water	---	6½	28	1100	0.08

\* The same as Federation Dentaire Internationale (FDI) Specification No. 6 for Dental Zinc Phosphate Cement. Internat. Dent. J. 13:138 March 1963 and International Organization for Standardization (ISO) Draft ISO Recommendation No. 1566. Dental Zinc Phosphate Cement.

\*\* Range of unreported values for six zinc phosphate cements currently in use. Data from American Dental Association Council on Dental Materials and Devices, Chicago, Ill.

† 1 kgf/cm<sup>2</sup> = 14.223 psi.



Copper Phosphate Cements. The copper phosphate cements are being used less and less because they irritate the pulp tissue more than the zinc phosphate and zinc oxide-eugenol cements. In addition, the black copper cement is many times more soluble in water than is zinc phosphate cement.

Data from the most extensive investigation<sup>(20)</sup> of the properties of these cements are given in Table 3. The values were derived by the methods described in the A.D.A. Specification No. 8 for Dental Zinc Phosphate Cement--First Revision (1938).<sup>(21)</sup>

Zinc Polyacrylate Cements. An entirely new cement<sup>(23)</sup> is being found useful. It is appropriately called zinc polyacrylate cement but has been called zinc carboxylate cement. It is made by adding zinc oxide to an aqueous solution of polyacrylic acid using the conventional hand mixing method. One of the special features of the experimental cement is its ability to adhere to tooth enamel and dentin<sup>(23)</sup> (Table 4) and to stainless steel.<sup>(25)</sup>

The cement is patented through the National Research and Development Corporation in the United Kingdom.<sup>(23)</sup> Two commercial products are available (March 1970)--Durelon,

Table 3

## Copper Phosphate Cements: Composition and Properties (24)

Composition of powder percent by weight	Grams of powder in 0.5 ml of liquid to produce a disk 30 ± 1 mm in diameter*	Time of setting minutes	Film Thickness μm	Compressive strength at 7 days †† kgf/cm <sup>2</sup>	Solubility and Disintegration at 7 days % by weight
(20) Ames Copper Cement  CuO 91.5 Co <sub>3</sub> O <sub>4</sub> 8.4 ---	2.2†	5	50	1550	2.7
(20) Fleck's Red Copper Cement  Cu <sub>2</sub> O 23.9 ZnO 66.7 ---	1.5	5 - 5½	25 - 30	1040	0.5
(6) Ames Copper Cement	Grams of powder in 0.4 ml of liquid to produce a disk 25 ± 1 mm in diameter** 5.5	5.5	---	630	3.7
(6) Fleck's Red Copper Cement	3.5	3.5	---	1480	0.05

\* Cementing consistency--ADA Specification No. 8 for Dental Zinc Phosphate Cement (21)

\*\* Filling consistency--ADA Specification No. 9 for Dental Silicate Cement (22)

† Recommended by manufacturer

†† 1 kgf/cm<sup>2</sup> = 14.223 psi

Table 4  
Zinc Polyacrylate Cements  
(Liquid-aqueous solution of polycarboxylate acid. Powder essentially zinc oxide)

Material	Powder/Liquid Ratio	Adhesive strength		Compressive strength *	Tensile strength (diametral)*	Water uptake	Dimensional change (linear)	Solubility
		Enamel*	Dentin*					
Experimental (23)	2:1	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	% by weight	%	% by weight
Lining 1		(A)	(A)	1200	140			
Lining 2		150	50	910	105			
Cementing				670	64			
Experimental (26)	2:1	85						
		78-87						
		57						
		45						
Cementing	3:1	79						
Poly-C (24)	(by weight)	(D)		(M)	(G) (L)	(D)	(D) (J)	
Lining	1:50	(B) (C)		460	56-79	3.0 (R)	+ 0.8	
Lining	1:43	0 to 22		537 (N) (O)	(H)			0.8 (V)
Cementing	1:92			372 (P)	32-34	2.3 (D) (S)	+ 0.5 (D) (J)	0.4 (V)
Cementing	1:38			452 (P)				
Durelon	1:4 to 1:6	11 to 98 (B) (C)(D) 0 to 61 (E)		(K)	(F)	(D) (Q)	(D) (J)	
				143 - 499	46-64	5.2 - 7.2	+ 4.2	
Durelon** (24)						1.3 - 1.4 (D) (U)		0.6 (V)
DeTrey's (24)	2:5 to 3:48		(B)		(I)	(T)		(V)
Zinc Phosphate Cement		0 (D)	702-1075	54-62	0.9		0.3	

\* 1 kgf/cm<sup>2</sup> = 14.223 psi

\*\* Samples obtained from manufacturer's improved batches.

- (A) Values converted from lb/in<sup>2</sup> to kgf/cm<sup>2</sup> and rounded off.
- (B) If the assembly fell apart in handling a zero value is given.
- (C) Teeth stored in 70% alcohol for some months before being used.
- (D) Powder/liquid ratio not given.
- (E) Teeth were freshly extracted (1-3 days).
- (F) Powder/liquid ratio 1.5:1
- (G) Powder/liquid ratio 1.6:1.
- (H) Powder/liquid ratio 1.9:1.
- (I) Powder/liquid ratio 3:1 - Specimens 3 to 64 hours old.
- (J) Calculated from author's data. Specimens were 3 weeks in water.
- (K) When Durelon was immersed in water for 28 days, the compressive strength decreased from 450 to 162 kgf/cm<sup>2</sup>.
- (L) Specimens 20 hours old.
- (M) Specimens 4 hours old.
- (N) Specimen 64 hours old.
- (O) When cement specimens were stored in water for 28 days compressive strength was 380 kgf/cm<sup>2</sup>. Powder/liquid ratio was not given.
- (P) When cement specimens were stored in water for 28 days, compressive strength was 470 kgf/cm<sup>2</sup>. Powder/liquid ratio not given.
- (Q) Specimens immersed in water from 180 to 288 hours. At 2000 hours the value was about 12 per cent and equilibrium had not been established.
- (R) Specimens immersed in water for 117 hours. At 2000 hours the value was about 6.5% with equilibrium having been established after about 250 hours of immersion.
- (S) Specimens immersed in water for 166 hours. At 2000 hours the value was about 4.5% with apparent equilibrium having been established after about 250 hours of immersion.
- (T) Specimens immersed in water for 800 hours with apparent equilibrium having been established after about 400 hours of immersion.
- (U) Specimens immersed in water for 163-164 hours. At 400 hours the value was about 2%. Equilibrium was not established. Projection of the curve of water uptake with time would give values for about 2.5% at 600 hours and about 3.8% at 1000 hours.
- (V) Solubility at 600 hours in water.

made by Espe, GmbH, Seefeld/Oberbay, Germany (USA distributor, Premier Dental Products, Philadelphia, Pa. 19107) and deTrey's Poly-C, made by Amalgamated Dental Co., Ltd., of the United Kingdom (USA distributor, Cladius Ash, Inc., 655-73rd Street, Niagara Falls, N. Y. 14304). In the advertisements for deTrey's Poly-C no mention is made of adhesion to the hard tooth tissues or to stainless steel. However, the Durelon advertisement states "long-lasting adhesion to tooth structure". Two investigators<sup>(24)</sup> determined the degree of adhesion and gave values for other properties of the two foregoing trade brands of zinc polyacrylate cements and of a zinc phosphate cement (deTrey's). They gave values of adhesion from 0 to as high as 98 kgf/cm<sup>2</sup> (0-1390 psi). The scatter of values in most types of adhesion tests is very great and these are no exception. Then, too, different types of tests for adhesion may give radically different values.

Naturally, if one had a material which was adhesive to both tooth enamel and to stainless steel one would immediately think of attaching orthodontic devices directly to the tooth

without the customary banding. Two authors in a series of investigations<sup>(25,27)</sup> have explored this technic. In the first article<sup>(25)</sup> circular stainless steel orthodontic buttons were cemented to polished enamel surfaces using polycarboxylate cement, silico-phosphate cement, zinc phosphate cement and copper phosphate cement and subjected to tension after storage for 48 hours in water at 37°C. The tensile strength bond values were 74 kgf/cm<sup>2</sup> (1050 psi), 27 kgf/cm<sup>2</sup> (380 psi), 4.6 kgf/cm<sup>2</sup> (65 psi) and 23 kgf/cm<sup>2</sup> (330 psi), respectively. Further investigation<sup>(26)</sup> showed that the tensile bond strength of several experimental polyacrylate cements were several times the magnitude of those of other dental cementing media. Most of the failures of the zinc polyacrylate cements occurred within the cement and not at the cement-enamel interface.

After investigating<sup>(27)</sup> the reaction of the bond to shear stress, to peel strength tests, to static and dynamic fatigue tests, to thermal cycling, to surface roughness variation and to contaminations likely to occur in the mouth, the authors believed that limited clinical trials are warranted in which the orthodontic appliance parts are attached directly to the surfaces of the teeth.



Smith, the inventor of the zinc polyacrylate cements,<sup>(23)</sup> is continuing his experimentation (at the University of Toronto)<sup>(28)</sup> by mixing other oxides with zinc oxide, with and without sintering, and by using liquids containing polyacrylic acid of molecular weights from 5000 to 300,000. Some of the combinations with powder-liquid ratios from 1.5 to 2.5 gave compressive strength from 631 to 914 kgf/cm<sup>2</sup> (9,000-13,000 psi) and tensile strengths from 56 to 106 kgf/cm<sup>2</sup> (800-1,500 psi). The solubility in water was less than 0.03%. This low water solubility value may have been derived by using the test for solubility and disintegration in A.D.A. Specification No. 8 for Dental Zinc Phosphate Cement.<sup>(9)</sup> The solubility in water using other test methods is apparently much higher<sup>(24)</sup> (Table 4). In fact, the high water sorption, which caused dramatic decreases in strength and stiffness and increases in dimensions,<sup>(24)</sup> is a very important factor when considering the use of polyacrylate cements in the mouth. The compressive strength is also rate and temperature dependent<sup>(29)</sup> which may in part account for some discrepancies in values of physical properties reported by various investigators. Therefore, it is not possible to compare directly the data given in Table 4 and elsewhere in the literature.



There are not at this time sufficient laboratory data and extended clinical experience to warrant the wholesale substitutions of zinc polyacrylate cements for zinc phosphate cements in dentistry, but certainly limited clinical use is and should be in progress primarily because of the adhesion between zinc polyacrylate cement and enamel.

How the adhesion occurs is not known. Smith<sup>(23)</sup> believes that polyacrylic acid reacts with calcium on the surface of the enamel and that polyacrylic acid may form complexes with proteins. No evidence is presented to show that a chelation does occur.

The zinc polyacrylate cements are an exciting development and the development of other carboxylate cements is in progress.

Silicate Cement. Silicate cements have been used in dentistry for about a century primarily as a restorative material for use where esthetics and caries prevention are of utmost importance.

When a pulverized complex alumino-silicate glass containing magnesium, fluorine, calcium, sodium and

phosphorous is mixed with an aqueous solution of orthophosphoric acid buffered by aluminum or zinc salts or both, a hard strong mass results that simulates the color and optical properties of the tooth.

The chief fault of these cements as a restorative material is their solubility in the mouth. The average life of a silicate cement restoration is about 3 to 4 years. Silicate cement restorations disintegrate in a decay-like manner. That part of a silicate cement restoration which is in a relatively self-cleansing area will remain virtually undissolved while that part which lies in an area where food and other debris collect will be selectively dissolved. Even then, there will be comparatively little recurrent decay about silicate cement restorations probably because of their high fluoride content and because this fluoride content decreases the solubility of the enamel in acids. (30)

Specification requirements, composition and values of pertinent physical properties of some silicate cements as obtained according to A.D.A. specification procedures are given in Table 5. One sees that improvements have been made in these cements over the last few

Table 5

## Dental Silicate Cements: Composition and Properties

(9) Requirements of revised ADA Specification No. 9 for Dental Silicate Cement (1962- )	Arsenic Content	Consistency of mix	Time of setting at 37°C		Opacity at 24 hours		Solubility and disintegration	Compressive strength at 24 hours*
Maximum per- centage by weight 0.0002	Grams of powder in 0.40 ml of liquid to produce a disk of cement 25 ± 1 mm diameter	Min.	Max. Minutes	Co. %	Max. Co. %	Maximum Percentage by weight 1.0	Minimum kgf/cm <sup>2</sup> 1700	
(1950-1962)	0.0002	Same	3	8	0.35	0.55	1620	
Range of values (12) (13) for silicate cements on List of Certified Dental Materials (1958)	<0.0002	1.4 ± 0.15	5 ± 1	all within 0.35- 0.55	0.35- 0.55	1.0 ± 0.3	1770 ± 140	
Range of values (31) for silicate cements on List of Certified Dental Materials (1965)	<0.0002	1.5 ± 0.07	5 ± 1	all within 0.35- 0.55	0.35- 0.55	0.5 ± 0.1	1950 ± 160	
<b>C o m p o s i t i o n (22)</b>								
Powder % by wgt	Liquid % by wgt.							
SiO <sub>2</sub> - 39.9	PO <sub>4</sub> - 47.4							
Al <sub>2</sub> O <sub>3</sub> - 27.7	Al - 2.3							
Ca - 5.9	Zn - 5.6							
F - 15.4								
Na - 6.6								
P <sub>2</sub> O <sub>5</sub> - 4.0								
Ignition loss (110°C)	0.8							
SiO <sub>2</sub> - 39.7	PO <sub>4</sub> - 48.6							
Al <sub>2</sub> O <sub>3</sub> - 35.8	Zn - 8.9							
Ca - 3.2								
F - 11.0								
Na - 6.5								
P <sub>2</sub> O <sub>5</sub> - 3.9								
Ignition loss (110°C)	0.0							

\* 1 kgf/cm<sup>2</sup> = 14.223 psi



decades as reflected by decrease in the maximum solubility values permitted in the American Dental Association specification from 2.0% (1938-1950), to 1.4% (1950-1962) to 1.0% (1962- ), and an increase in the minimum values permitted for compression strength from 1260 kgf/cm<sup>2</sup> (18,000 psi) (1938-1950) to 1620 kgf/cm<sup>2</sup> (23,000 psi) (1950-1962) to 1700 kgf/cm<sup>2</sup> (24,200 psi) (current). The testing time was decreased from one week to 24 hours in the 1950 revision. This caused the 24 hour values for solubility to decrease on the average 0.25% from the one week values and the value for compressive strength was on the average 100 kgf/cm<sup>2</sup> (1420 psi) less at 24 hours than at one week.

The values obtained on retesting the silicate cements on the List of Certified Dental Materials (as established by the American Dental Association) in 1958<sup>(12)</sup> and in 1965,<sup>(31)</sup> also given in Table 5, reflect the decrease in solubility and increase in strength of those silicate cements between 1958 and 1965.

Pulver<sup>(32)</sup> took the analysis<sup>(22)</sup> of a commercial silicate cement powder and liquid (given at the bottom

of Table 5) and calculated the approximate formula:--  
Batch Composition of Cement Powder.--per cent by weight  
as  $\text{SiO}_2$ -39.9;  $\text{Al}_2\text{O}_3$ -30.2;  $\text{CaF}_2$ -4.0;  $\text{Na}_3\text{AlF}_6$ -19.2 and  
 $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ -6.7. The liquid composition was by  
weight per cent  $\text{H}_3\text{PO}_4$ -41.3;  $\text{Zn}_3(\text{PO}_4)_2$ -17.8 and  $\text{H}_2\text{O}$ -40.9.  
Pulver<sup>(32)</sup> concluded that an aqueous solution of citric  
acid would be a more appropriate test medium for  
solubility than distilled water.

Wilson and his associates explored in exhaustive  
and scholarly investigations<sup>(33-44)</sup> the nature of  
silicate cements with special emphasis on modifying  
them so that they would endure the rigors of the mouth  
environment better than the available ones. He inter-  
preted from his results that there is not much probability  
of significantly improving silicate cement. There are  
just too many circumscribing parameters that relate to  
the specific use of silicate cement in dental health  
service.

Zinc silico-phosphate cements. The zinc silico-phosphate  
cements, as the name implies, are a kind of hybrid  
between zinc phosphate cements and silicate cements, but

their properties are closer to the silicate cements. The zinc silico-phosphate cements are probably the most durable in the mouth of any of the dental cements based on phosphoric acid and since they contain large quantities of fluoride, they are also probably anticariogenic.

Some of the cements are made by incorporating large quantities of zinc oxide in the silicate cement glass and at least one has a powder that is a mechanical mixture of silicate and zinc phosphate cement powders in an approximate ratio of 9 to 1. Compositions<sup>(22)</sup> of each type, respectively, by weight per cent, follow:

Powder:  $\text{SiO}_2$  - 14.6;  $\text{Al}_2\text{O}_3$  -15.6; Ca-3.2; F-5.9; Na-2.9;  $\text{P}_2\text{O}_5$  -2.1; ZnO-53.2; MgO-2.3;  $\text{H}_2\text{O}$ -0.1 and ignition loss at  $120^\circ\text{C}$ -0.1.

Liquid:  $\text{PO}_4$ -55.7; Al-2.4; Zn-3.1 and Mg-0.7.

Powder:  $\text{SiO}_2$ -36.5;  $\text{Al}_2\text{O}_3$ -26.3; Ca-5.9; F-12.0; Na-4.6;  $\text{P}_2\text{O}_5$ -3.2; ZnO-9.4; MgO-0.5; and ignition loss at  $900^\circ\text{C}$ -6.9.

Liquid:  $\text{PO}_4$ -48.1; Al-1.9 and Zn-4.4.

The requirements of A. D. A. Specification No. 21 for Dental Zinc Silico-phosphate Cement<sup>(45)</sup> and the test values<sup>(31)</sup> for current American and foreign cements are given in Table 6.





Table 6

## Properties of Dental Zinc Silico-Phosphate Cements

(45)	Type	Consistency of mix (Diameter of Disk)	Time of Setting at 37°C		Compressive strength at 24 hours**		Film Thickness	Solubility and Disintegration at 24 hours	Opacity 24 hours		Arsenic Content
			Min.	Max.	Min.	Max.			Min.	Max.	
Requirements of ADA Specification No. 21 for Dental Zinc Silico-Phosphate Cement	I Cementing	25 ± 1	5	9	1400		50	wt.% 1.5	Co, % 0.35	0.90	Wt.% 0.0002
	II Filling	25 ± 1	3	8	1700		--	1.0	--	--	0.0002
	III Dual		5 3	9 8	1400 1700		50 --	1.5 1.0	0.35 --	0.90 --	0.0002 0.0002
(31)	I Cementing (2 cements)	Grams of powder in 0.4 ml of liquid 1.0 ± 0.05	12 ± 6		1160 ± 330*		38 ± 2	1.2 ± 0.4	Complied		No trace
	II Filling (4 cements)	1.5 ± 0.12	7 ± 3		1470 ± 270*		--	0.6 ± 0.4	Complied		No trace
	III Dual (5 cements)	1.2 ± 0.14 1.5 ± 0.31	10 ± 1 5 ± 1		1280 ± 260* 1580 ± 220*		44 ± 2 --	0.9 ± 0.0 0.5 ± 0.1	Complied		No trace

\* Range

\*\* 1 kgf/cm<sup>2</sup> = 14.223 psi.

Resin Cements. Composite cements with a plastic binder such as poly(methyl methacrylate) and inorganic fillers such as calcium or barium carbonate, quartz, mica, alumina or calcium tungstate were used to a small extent for almost 20 years. The mineral filler contents ranged from 5 to 67 weight per cent.<sup>(46)</sup> Because of their relative insolubility, it was believed that the resin cements would displace zinc phosphate cements as a luting medium. However, this has not occurred principally because:

(1) they possess a short working interval between completion of the mixing and seating of the appliance. A crust forms on the mix quickly as the monomer evaporates; (2) it is difficult to remove set cement that accumulates in the spaces between the teeth when an appliance is being seated; (3) water seeps at the resin cement-tooth interface; and (4) they cause a more severe reaction on the pulp than that caused by zinc phosphate cements.

When prepared at a standard consistency the resin cements had setting times from 4 to 12 minutes, polymerization shrinkage from about 3 to 8 per cent by volume, expansion (caused by water absorption) from

about 0.6 to 1.8 per cent by volume, aqueous solubility from 0.1 to 0.4 per cent weight loss, optical opacities from 0.45 to 1.00  $C_{0.70}$  values, film thickness from 10 to 120  $\mu\text{m}$ , a radiopacity of 0.8 to 2.9 film density on a 2 mm thick specimen, and compressive strength from 527 to 879  $\text{kgf/cm}^2$  (7,500 - 12,500 psi).<sup>(46)</sup>

The resin composite cements are adhesive to tooth enamel if the tooth is kept dry. Otherwise, water penetrates along the resin cement-enamel interface and rapid separation of the cement from the enamel occurs.<sup>(46)</sup>

#### Direct Filling Resins, Composite and Adhesive Materials.

During World War II in Germany the auto- or self-polymerization of dental acrylic resins was induced by adding a tertiary amine (0.5 to 3%) to methyl methacrylate and 0.5% benzoyl peroxide to the powdered poly(methyl-methacrylate) with which it was mixed.<sup>(47)</sup> Soon there appeared on the world dental market similar direct filling resins and many thought there was here at last a replacement for the decades-old silicate cement. But this idea was short lived because the direct resin restorations discolored, leaked, caused severe pulp response, and

allowed a high incidence of recurrent decay. For these reasons they were abandoned by a great many practitioners. Improvement made by the substitution of N, N-dimethyl-p-toluidine for the previously-used tertiary amines gave less discolored reaction products and the use of p-toluene sulfinic acid as an initiator to decompose the organic peroxide gave even better results. Later, ultraviolet absorbers were added to the formulations so that most present-day direct filling resins and composites have reasonably good color stability in the mouth.

After these relatively simple self-curing direct resin filling materials came the modern composites which are partially displacing silicate cement. The composites are based upon a three component system as illustrated in Table 7 but adhesive cavity primers are largely in the research and testing state.

The addition of the reinforcing fillers with an appropriate coupling agent to bond the inorganic filler to the polymer matrix improved the direct filling resins. The volumetric shrinkage on polymerization was halved, the compressive strength was doubled, and the modulus of elasticity was increased about six fold (Table 8).

Table 7

## Modern composite restorative materials

Component	Contents*
Liquid	Monomers Stabilizers Accelerator UV absorber
Powder	Inorganic filler, treated with a silane coupling agent Benzoyl peroxide
Cavity primer	Coupling agent for improving the bond between filling material and hard tooth tissue

\* These basic ingredients are supplied commercially in various forms, such as paste-liquid, paste-paste or powder-liquid, formulated as two or more components that are mixed prior to use.

Table 8

Properties of composite dental restorative materials as compared with direct filling resins, human enamel and dentin

Material	Volumetric shrinkage on polymerization	Compressive strength *	Tensile strength*	Modulus of elasticity*	Indentation resistance (54)	
					Depth	Recovery
(48) Silica-reinforced polymer as developed by Bowen	% 2.8	kgf/cm <sup>2</sup> 1600	kgf/cm <sup>2</sup> 280	kgf/cm <sup>2</sup> x 10 <sup>-6</sup> 0.1125	μm 55	per cent 77
(48) Direct filling resin	6.2	750	280	0.0183	(54) 95-115	60-80 (54)
(49-51, 53) Human dentin	--	2100-3940	530	0.0844-0.1968	46 (48)	85 (48)
(50-53) Human enamel	--	980-3940	105	0.0914-0.8577	33 (48)	86 (48)

\* 1 kgf/cm<sup>2</sup> = 14.223 psi.

In addition, the coefficient of thermal expansion was reduced from about  $120 \times 10^{-6}/^{\circ}\text{C}$ , to from 40 to  $18 \times 10^{-6}/^{\circ}\text{C}$   $[30-40^{\circ}\text{C} (86-104^{\circ}\text{F})]$  while that of the tooth crown (enamel and dentin) is about 10 or  $11 \times 10^{-6}/^{\circ}\text{C}$ . Other properties of the hard tooth tissues are also presented in Table 8.

To the best of the author's knowledge all of currently successful filling resins are acrylic resins or are adducts of acrylic, principally methacrylates, with other resins. The reason for this is that the acrylic resins, principally methacrylates, most nearly meet the circumscribing dental requirements as listed in Table 9. It is not feasible to indicate these requirements in the order of their importance. For example, a resin may be perfect in all respects except that it is black--and therefore, totally unacceptable for restoring a front tooth in which esthetic requirements are paramount.

Many resins have been developed and tested but have not reached commercial production. Among these are:

(1) Polystyrene which was injected into tooth cavities.

The restorations failed because of poor marginal integrity. (55)





Table 9

Dental Requirements of Plastic Filling Materials

1. Polymerizable in the mouth environment.
  - 1.1 Suitable mixing, working and setting times.
  - 1.2 Ease of placing and finishing.
  - 1.3 Minimal residual monomer.
2. Optical characteristics that permit a formulation that simulates the tooth.
  - 2.1 Color match with the tooth.
  - 2.2 Opacity similar to that of the tooth.
  - 2.3 Matching index of refraction.
  - 2.4 Resistance to staining in the mouth by foods, tobacco smoke, cosmetics and bacterial products.
  - 2.5 Color stability in the mouth.
3. Biocompatibility and preventive capacity.
  - 3.1 Not seriously irritating to the pulp and to the gingiva.
  - 3.2 Low systemic toxicity.
  - 3.3 General passivity.
  - 3.4 Anticariogenic properties.
4. Dimensional stability.
  - 4.1 Low polymerization shrinkage.
  - 4.2 Low dimensional change on absorbing water.
  - 4.3 A coefficient of thermal expansion as close to that of the tooth as possible ( $10 \times 10^{-6}/^{\circ}\text{C}$ ).
  - 4.4 Minimum change on release of stress on absorption of water.
5. Adequate mechanical properties.
  - 5.1 Strength.
  - 5.2 Elastic modulus.
  - 5.3 Elastic limit.
  - 5.4 Indentation resistance and recovery.
6. Adequate physical properties.
  - 6.1 Abrasion resistance to food, dentifrices and teeth.
  - 6.2 Softening point higher than temperatures encountered in the mouth.
7. Adhesive to tooth tissues.
8. Insolubility.
9. Low water absorption
10. Adequate shelf life.
11. Radiopacity.

(2) Polyamide, which was also injected into tooth cavities but was discontinued because the restorations failed cosmetically.<sup>(55)</sup> (3) An aziridino polyester composite that was introduced commercially in 1959 under the trade name of "Cadurit" had relatively poor physical properties.<sup>(56)</sup> After a three year clinical trial it showed poor color stability and surface loss.<sup>(57,58)</sup> This material had inferior physical properties compared to those of poly(methyl methacrylate) as determined in the laboratory and had inferior clinical behavior--a reasonably good correlation. Cadurit is an example of a filling material being placed upon the market seemingly without adequate laboratory or clinical testing. (4) A polycarbonate that was softened and injected into tooth cavities.<sup>(58)</sup> It maintained reasonable marginal accuracy and was color stable. The material never reached commercial production although one large company in Germany made an injection apparatus for its use. The material would be, in the author's opinion, unable to compete commercially with current dental restorative

materials because of the technic involved. (5) Epoxy resins were thought to have possibilities as a direct filling resin. At least one company attempted to fabricate an epoxy material but it could not be used clinically because moisture interfered with its polymerization and the dentin surface could never be made moisture-free.<sup>(59)</sup> (6) Cyanoacrylates, none of which have proved successful as a direct filling resin but a n-butyl- $\alpha$ -cyanoacrylate composite has some possibilities as a dental cementing medium.<sup>(60)</sup> Another cyanoacrylate, methyl- $\alpha$ -cyanoacrylate, as a component for a composite used as a fissure sealant in caries prophylaxis had limited success<sup>(61)</sup> but has now been abandoned for a new sealant composite<sup>(62)</sup> containing the reaction product of bisphenol A and glycidyl methacrylate<sup>(48)</sup> and is polymerized by UV light.<sup>(62)</sup> The technic is simple and in one year of clinical testing only one fissure became uncovered. All treated teeth were free from decay after one year, but matched control teeth had caries in 42% of the pits and fissures.<sup>(62)</sup>

The outstanding development in the preparation of a successful composite restorative material to date has been the work of R. L. Bowen, a research associate from the American Dental Association at the National Bureau of Standards. (48,63-67) In his material, the resin matrix is the addition-reaction product of bisphenol A and glycidyl methacrylate (BIS-GMA). Viscosity of the resultant product was lessened when methacrylate monomers, stabilizer, and accelerator were added. These constituted the liquid component. The powder consisted of vinyl silane-coated fused silica and benzoyl peroxide. Another silane now seems more appropriate. (67) BIS-GMA, while not completely color stable, is used in almost all of the commercially available composite restorative materials made in the U.S.A. The trade names of some of these and some physical property values from two recent reports (68,69) are given in Table 10. The methods used in references 68 and 69 were not usually identical which may account for some of the differences among the data.

One group of workers (69) also reported the water sorption of the four materials listed in Table 10 as about

Table 10

## Physical Properties of Some† Commercial Composite Dental Restorative Materials

Brand Name#	Manufacturer	Setting Time	Volumetric Polymerization contraction	Coefficient of thermal expansion†	Indentation Resistance		Strength			Modulus Elastic*	Reference
					Depth	Recovery	Compressive*	Tensile*	Shear		
Addent 35 (R)	Minnesota Mining and Manufacturing Co. St. Paul, Minnesota	Min.	%	x 10 <sup>6</sup> /°C	µm	%	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup>	kgf/cm <sup>2</sup> x 10 <sup>-6</sup> **	(68)
		4.5	1.3	33	65	69.8	1434	330	471	0.0935	
Addent 12 (R)			2.0	45			1462			0.0914	(69)
		4.5	1.2	27	77	69.7	2039	415	696	0.1139	(68)
Dakor (R)	Caulk Division of Dentsply International Inc., York, Penna.		3.1	43			2137			0.1125	(69)
		1.5	1.5	41	97	62.3	1223	141	302	0.0548	(68)
Adaptic (R)	Johnson and Johnson, New Brunswick, N.J.		3.5	50			1115	244		0.0703	(69)
			1.5	22						0.1195	(69)

† Similar materials having similar values are Blendant, manufactured by Kerr-Sybron Corporation, Detroit, Michigan; DFR, manufactured by Surgident Ltd., Los Angeles, California and Posite, manufactured by American Consolidated Manufacturing Co., Inc. Philadelphia, Penna.

# Color stability was reported as "change" in (68) and (69) in all the brands, except (68) reported "no change" in Dakor.

\* 30 days in water at 37°C.

\*\* The values were inadvertently reported as 10<sup>3</sup> lb/in<sup>2</sup> in (68) and as psi x 10<sup>5</sup> in (69).

† Temperature range in (68) was 24-88°C; in (69) possibly 0-52°C. The linear values given in (69) were converted to volumetric values by multiplying by 3.

// 1 kgf/cm<sup>2</sup> = 14.223 psi.



1.5% weight gain for Addent 35, 1.0% for Addent 12, 0.75% for Adaptic. The Dakor specimens during the sorption test declined 3% in weight. The solubility was about 3% for Dakor, about 1% for Addent 12, 0.5% for Addent 35, 0.25% for Adaptic. The author is not aware of any clinical investigations that might reflect the foregoing laboratory findings or those reported in Table 10. Comparisons are also difficult since there is no American Dental Association specification for the resin composite restorative materials, but standard test methods have been adopted for specimen preparation, indentation resistance and recovery, opacity and Knoop indentation hardness.<sup>(70)</sup> Other proposed tests are being prepared for abrasion and abradability, adhesion, dimensional change on hardening, on absorption of water and on change in temperature, extractible plasticizer, time of setting, sorption and solubility. All of the foregoing are being woven into a future specification of the American Dental Association for composite dental restorative materials.

A new development involving three crystalline dimethacrylate monomers<sup>(71)</sup> with melting points slightly above room temperature, which liquefy in ternary eutectic proportions, seems suitable for composite formulations. The three monomers synthesized by Bowen are: bis(2-methacryloxyethyl)isophthalate, (MEI); bis(2-methacryloxyethyl)terephthalate, (MET) and bis(2-methacryloxyethyl)-phthalate (MEP). They are condensation products of 2-hydroxyethyl methacrylate (HEMA) and the corresponding acid chlorides of the phthalic acid position isomers.<sup>(71)</sup> The approximate ternary eutectic proportions, 47% (MEI), 38% (MEP), and 15% (MET) melt at about 16°C. Since the monomers are crystalline, they are relatively easy to purify and since the ternary eutectic is a nonvolatile liquid of a suitable viscosity at room temperatures and has a very low toxicity, it was used in the formulation of a resin composite which is now undergoing clinical trials. The Epoxylite Corporation, P. O. Box 3397, South El Monte, California 91733 has synthesized these methacrylate monomers in custom batches.



Reinforcing fillers, (bonded to the resin matrix by a coupling agent) that have been advocated or used in resin composite restorative materials include fused silica, quartz, beta-eucryptite ( $\text{CaAl}_2\text{SiO}_5$ ), glass beads and rods, "tricalcium phosphate"<sup>(72)</sup> and certain porcelain and ceramic materials. The latter, also called micro-crystalline glasses, have attractive properties such as high translucency, favorable refractive indexes and thermal expansion coefficients approximating zero.

Adhesives. None of the dental restorative materials are adhesive to untreated human enamel and dentin, which they abut, with the possible exception of a methacrylate resin in which an alkylboron compound, such as tri-n-butylboron, is used as a hardening agent.<sup>(73)</sup> An experimental material of this type has been tested clinically with evidence of adherence to the dentin, but not in every case, so the usual retentive undercuts in preparations for plastic restorations cannot be omitted.<sup>(74)</sup>

In designing a restorative material that will adhere to enamel and dentin under mouth conditions or in designing a cavity primer which would serve as a coupling agent

between enamel and dentin and restorative materials, it is necessary to have extensive knowledge about calcified tooth tissues. These tissues are really natural composites as they consist of associated organic and inorganic portions in a structural entity with remarkable qualities. The organic portion of dentin is about 20% by weight, almost all of it being collagen, with fractional percentages of carbohydrate and lipids. In enamel, the organic content is less than 0.5 per cent. The major inorganic content of enamel and dentin is hydroxyapatite. Other ions such as sodium, potassium, chloride, fluoride, carbonate and citrate are present but their exact relationship with hydroxyapatite is not completely understood.

The cut surfaces of the cavity preparation are moist and are covered by debris from the machining involved. Various treatments have been used to prepare this surface for the reception of an adhesive. Acids, alkalis, enzymes and sequestrants have been used to "clean" the cavity surface by removal of the loose or partially attached debris as well as to remove selectively some of the organic or the inorganic portion of the dentin and enamel. These pretreatments usually

enhance the adhesion as measured by mechanical tests of various types. Adhesion test methods need to be standardized so comparable values in the literature will have some relevance to each other. The enhancement of the adhesion by the pretreatment of the surfaces of the tooth is probably in part not only due to removal of the debris but also due to selective dissolving of some of the components of enamel and dentin thus presenting a much greater surface area as well as a much more reactive one. In addition, the removal of material will not always be in parallel directions and thus there will be undercuts available into which the low-surface-tension monomers can flow. Hence, on polymerization, there will be considerable mechanical retention as well as retention from any chemical bonding that may occur. (75)

A cavity primer, if it is a successful coupling agent, that bonds the hard tooth tissues to the restorative material, must have chemical groups that will react with the tooth surface and the hardening resin and that will compete with the always-present water at the interface between the cavity surface and the composite restorative

material. The bond must be strong enough to withstand the stresses induced by polymerization, by subsequent water absorption and by the differential in thermal expansion of the tooth and the restorative material. The stresses induced by polymerization of direct filling resins ranged from about 28 kgf/cm<sup>2</sup> (400 psi) to 134 kgf/cm<sup>2</sup> (1900 psi) depending upon the geometry of the cavity.<sup>(76)</sup> The values for stresses induced or relieved by water absorption or by differential thermal expansion of the interface materials have not been found in the literature by the author.

There is a possibility that the stresses induced by bonding at the interface may be undesirable. Consequently a resilient type of acrylic or epoxide cavity primer has been investigated.<sup>(77)</sup> To the best of the author's knowledge, cavity primers of these types<sup>(77)</sup> have not appeared on the dental market.

Another development that has promise but has not yet reached commercial development is an adduct of N-phenyl glycine and glycidyl methacrylate.<sup>(78)</sup> Tensile bond strength values using this adduct between a dental

restorative composite material and enamel, dentin and fluorapatite (treated with a 10% aqueous solution of the sodium salt of ethylenediaminetetraacetic acid) were 55 kgf/cm<sup>2</sup> (780 psi), 26.7 kgf/cm<sup>2</sup> (380 psi) and 41 kgf/cm<sup>2</sup> (580 psi), respectively. It is now under experimental clinical trial.

Workers at the Gillette Research Institute first suggested<sup>(79)</sup> and have done considerable research on cavity primers based on polyurethanes.<sup>(80)</sup> In these reports,<sup>(79,80)</sup> several polyurethane-type compositions were used to couple dentin to a variety of restorative materials--amalgam, cement, direct filling resins and composites. A typical adhesive was prepared from equal parts by weight of tolylene diisocyanate (TDI) and a polypropylene glycol. Sometimes 0.01 per cent of tripropylamine was used as a catalyst. Other isocyanates and a number of polyglycols were used. Several adhered well to dentin and to a variety of restorative materials, were water resistant and performed well in thermal shock, tensile and compressive adhesion tests.<sup>(79)</sup> Later, reinforcing fillers such as titanium dioxide were used

to dilute the brown color of the polyurethanes as well as to increase the adhesive strength, as did etching with 50 per cent solutions of formic or citric acids. The preferred polyurethanes were compounded principally from refined castor oil and polymethylene polyphenyl isocyanate (PAPI) which, with the  $\text{TiO}_2$  filler and etching and debridement treatments of bovine enamel surfaces, gave butt joint strengths of about  $91 \text{ kgf/cm}^2$  (1300 psi). (80)

Other work, carried out by the Epoxylite Corporation, gave a preferred formulation of a cavity primer entitled NIH-302S-1 and consisting of:

<u>Part A</u>	<u>Parts by weight</u>
MDI (diphenylmethane-4, 4'-diisocyanate)	100
<u>Part B</u>	
Polybutadiene diol	5.0
Dibutyl tin laurate	0.575
Chloroform	94.425

Equal parts of A and B were mixed and applied to bovine enamel (pretreated by etching for five minutes



with a 50% solution of citric acid) with a cotton applicator and allowed to dry for five minutes. A tensile bond strength of about 92 kgf/cm<sup>2</sup> (1500 psi) was obtained on specimens of bovine enamel-primer-composite restorative material, the latter containing 82 per cent of inert filler. (81)

There has been some in vitro testing of polyurethanes as cavity primers. A polyurethane varnish was used as a cavity primer for 40 amalgam restorations which were then submerged in a fluorescent dye solution and cycled 0-37°-70°C. The microleakage was minimal. (82) Other formulations, using reacted products of various isocyanates and prepolymers with isocyanate end groups and with an excess of 2-hydroxyethyl methacrylate or the addition product of bisphenol A and glycidyl methacrylate, did not bond to tooth structure after one week in water and softened and darkened during storage in water. (83)

Inorganic polymers. Other than glasses and glass-like ceramics, no inorganic polymers seem to have dental application as restorative materials as revealed by an extensive and excellent review. (84)

Radiopaqueness. All materials used as operative or prosthetic restorative materials should be radiopaque so that they may be located radiographically if accidentally ingested or aspirated. To achieve radiopacity without destroying the life-like appearance of restorative materials was not accomplished until clear, colorless glasses were developed with an index of refraction near that of the suitable available synthetic resins and having elements with relatively high atomic numbers to give the desired radiopacity. At the same time it was necessary that these glasses be suitable as reinforcing fillers for dental restorative composite materials.<sup>(85)</sup> These glasses were prepared by melting together compounds yielding silica, boric oxide, alumina, barium oxide and barium fluoride. Barium made the glasses radiopaque, fluoride lowered the refractive indexes and alumina tended to stabilize the glasses.<sup>(85)</sup>

Biocompatibility. Dental restorative materials are usually placed against crown dentin, the calcified tissue between the thin enamel cover of the crown of the tooth and the pulp chamber in the center, which is normally



filled with soft tissues, blood and lymph vessels and nerves. The dentin is not solid but is filled with small canals containing extensions of dentin forming cells (odontoblasts) which line the pulp chamber. When the dentin is cut in cavity preparation these fibrils are also cut and some injury occurs to the odontoblasts. If an irritant or toxic substance is placed against the dentin, further injury or even death of the odontoblasts may take place. Therefore, the restorative material which is placed against the dentin should not irritate the pulp unduly. Most materials cause some injury but this injury is usually resolved and the odontoblasts recover and lay down additional dentin as they retreat. This dentin, sometimes called secondary dentin, is considered by some investigators but not by others as an effective barrier against further injury.

The transient and prolonged effects of most of the dental restorative materials in this review have been reported by a host of investigators using rat, dog, monkey and human teeth. Similar effects were observed on all of the foregoing. A rough rating of severity from

the least to the most severe gives the following approximate order: (1) zinc oxide-eugenol based cements;<sup>(86,87)</sup> (2) zinc polyacrylate cements;<sup>(23),(88)</sup> (3) zinc phosphate cement;<sup>(89)</sup> (4) zinc silico-phosphate cement; (5) restorative composites;<sup>(90)</sup> (6) silicate cements;<sup>(91)</sup> (7) direct filling resins;<sup>(92)</sup> resin cements;<sup>(93)</sup> and (8) black copper cements.<sup>(94)</sup> The earlier references have been given. Much confirmatory work has since been done and most of the work confirms that zinc oxide-eugenol cement is the blandest with almost no irritation and that black copper cements produce the most severe reaction. The foregoing order of arrangement is very relative and should not be taken too literally but in all of the materials cited except zinc oxide-eugenol based cements, and perhaps the zinc polyacrylate cements, an intermediary lining should be present between the restorative material and the dentin to protect the pulp.<sup>(95)</sup>

Bioevaluation. As new materials are being developed so rapidly, it is imperative that adequate bioassays be made. In the case of dental restorative materials this bioevaluation procedure has not been completely worked out

but the following have been suggested: <sup>(96)</sup> (1) an acute systemic toxicity test of the type known as LD<sub>50</sub> in which the dose of the material ingested, in grams per kilogram of body weight of the rat, will cause a 50 per cent mortality in 14 days; (2) a mucous membrane irritation test on non-rodent animals in which the material in question is held for 2 weeks in contact with the mucous membrane. The degree of irritation is judged by gross appearance as observed visually and by color photographs and by biopsy of tissues in and out of contact with the material; (3) a test for pulp irritation in which at least 30 teeth from middle aged patients are restored with the material and 30 similar untreated control teeth are available. Serial extraction of the teeth are made at 24 hours, 10 to 30 days and after 60 days, respectively. After preparation for histologic examination, serial sections are examined using twelve criteria and the restored and controlled teeth compared. Also, guide lines are being set up for the clinical comparison of restorative materials.

Mouth conditions. The mouth is a rigorous environment so only relatively passive materials such as noble metal alloys, chromium-based alloys, porcelain and organic polymers can resist the attack of foods and microbial metabolic products.

Recurrent decay and anticariogenic properties: Recurrent decay at the tooth-filling margin or at the cavity surface-filling interface frequently occurs and especially in persons with poor dental hygiene. Therefore, an ideal restorative material should have anticariogenic properties. Silicate cement is almost unique among the dental restorative materials in this respect because there is almost no recurrent decay around silicate cement restorations. One study showed that the direct filling resins had about 10 per cent recurrent caries after three years and no decay occurred around silicate cement restorations used as controls. (97) It is believed that the anticariogenic properties of silicate cement stem from its release of fluoride to the enamel which decreases the enamel solubility. (30)

Allergy. Allergic responses have been cited for all of the restorative materials employed in dentistry but the

number of responses is only a very small part of one per cent. This will hold true for countless substances with which humans come in contact.

Source references. Extensive information is presented for zinc oxide-eugenol cements, <sup>(4)</sup> EBA cements, <sup>(93)</sup> zinc phosphate cements, <sup>(14)</sup> copper phosphate cement, <sup>(20)</sup> zinc polyacrylate cements, <sup>(23-29)</sup> silicate cement, <sup>(22,33-44)</sup> zinc silico-phosphate cements, <sup>(22,31,45)</sup> resin cements, <sup>(46)</sup> composite restorative materials, <sup>(57,62,67,68)</sup> dental adhesives, <sup>(62,78,80)</sup> inorganic polymers, <sup>(84)</sup> and pulp reactions to restorative materials. <sup>(95)</sup> In addition, the following general sources are recommended: 99-112.

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