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DEVELOPMENT OF A SILICA-RESIN DIRECT FILLING MATERIAL

by

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

DEVELOPMENT OF A SILICA-RESIN
DIRECT FILLING MATERIAL*

Abstract

The reaction product of bisphenol A and glycidyl methacrylate, thinned with a reactive diluent and activated with dimethyl-para-toluidene, hardened at 37°C within 10 minutes when mixed with fused silica powder containing benzoyl peroxide. A compressive strength of 23,000 PSI was obtained using about 70 per cent silica particles which had been treated with a vinyl silane finish and which were fine enough to pass a U. S. Standard sieve No. 325. The solubility and disintegration was 0.04 per cent. The water sorption was 0.6 mg per cubic cm or 1.7 per cent by weight. The average coefficient of thermal expansion for three specimens was 24×10^{-6} per degree C between 30 and 40 degrees C. Other tentative physical properties are given.

1. INTRODUCTION

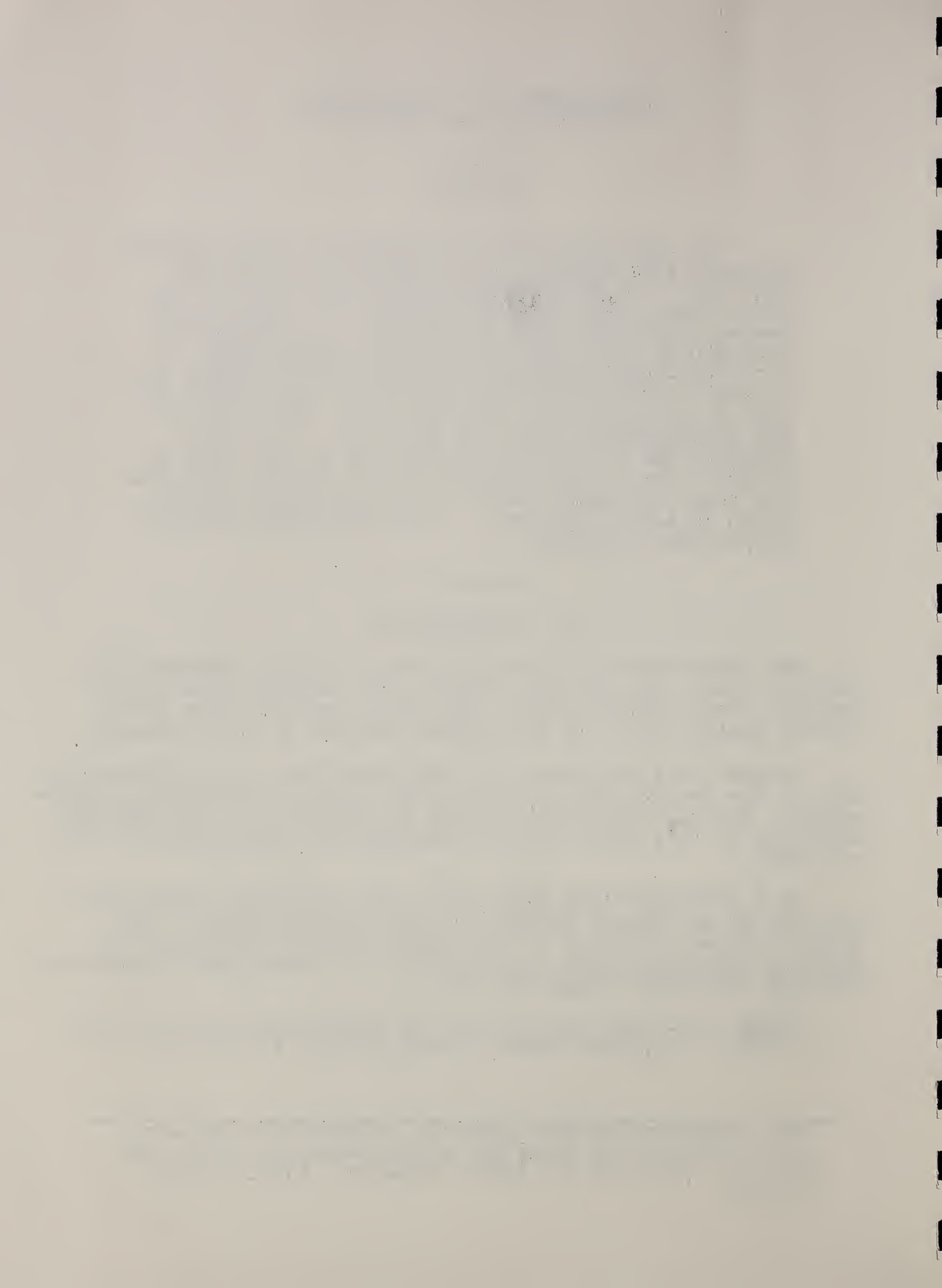
The development of a suitable direct filling material for anterior teeth that is less soluble than silicate cement [1] and more stable dimensionally than methyl methacrylate direct filling resins [2, 3] is the primary purpose of this research.

Progress has been made but such a material is not now available to the dentist for clinical trial or is it necessarily forthcoming. Further tests must be made to determine if the material described in this report will be suitable for experimental clinical trial.

In a previous study [4], one of the commercial epoxy resins was used as an organic binder for fused silica powder. The epoxy resin was selected as the organic binder because of its adhesive characteristics, insolubility, low shrinkage on hardening and other desirable properties [5].

Fused silica was selected as the reinforcing filler because it is clear, colorless, inert, strong and has a very low

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coefficient of thermal expansion. It is less likely to be abrasive than aluminum oxide or crystalline quartz since its hardness is only about 4.9 on the Mohs scale [6].

However, for a direct filling material, the available commercial hardening agents commonly used with epoxy resins would not be suitable due to either their toxicity or the long setting time at 37°C.

It had been observed that orthophosphoric acid gave rapid hardening of an epoxy resin [7] at room temperature. Considerable experimentation was done using this acid in various concentrations, but the hardening was strongly influenced by moisture and temperature. Prepared surfaces of extracted teeth appeared to inhibit the polymerization locally, possibly by neutralizing the acid. It was thought that polymerization should be effected by some means other than the ionic addition of the oxirane (epoxy) groups and by a means less likely to be seriously affected by the presence of moisture.

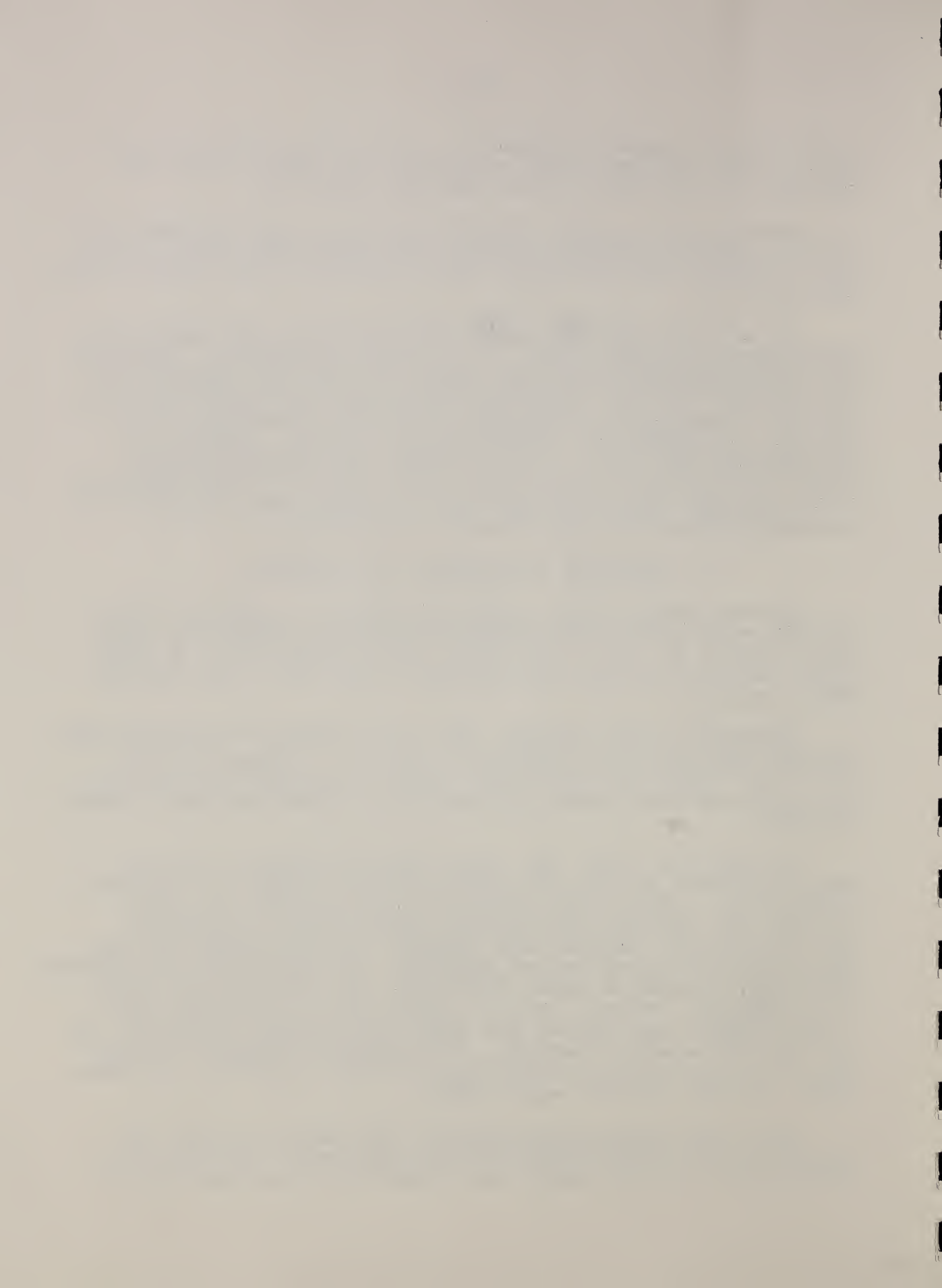
2. MATERIALS AND METHODS OF SYNTHESIS

It was decided that a compound (Figure 1) might be synthesized which would structurally resemble a commercial epoxy resin (Figure 2) [5, 7] but which would polymerize by a mechanism similar to methyl methacrylate, that is, a free radical chain reaction.

Synthesis of the liquid. The first attempt to prepare this compound made use of a commercial epoxy [7] (Figure 2) with which was reacted an equivalent weight of glacial methacrylic acid using moderate heat, polymerization inhibitors and a basic catalyst.

An improved method was found using bisphenol A with an excess (between one and two equivalents by weight) of glycidyl methacrylate. These were reacted in the presence of 0.5 to 1.0 per cent dimethyl p-toluidene which served as catalyst for the addition reaction and remained to serve later as activator for the polymerization catalyst. The synthesis was carried out under nitrogen at about 60°C until the reaction was shown to be complete (usually in 9-14 hours) by the following test. A small sample was removed and mixed with benzoyl peroxide. If the reaction was not complete, the unreacted bisphenol groups inhibited free radical polymerization [8]; otherwise, the small sample hardened within ten minutes.

When the reaction was complete, the sirupy product was stabilized with 0.006 per cent of hydroquinone. In some cases, hydrochloric acid was added equivalent to the oxirane groups



of the excess glycidyl methacrylate. This was to prevent the gradual reaction of the excess oxirane groups with the hydroquinone. As necessary, the sirup was reduced in viscosity with suitable reactive diluents such as methyl methacrylate and tetraethylene glycol dimethacrylate monomers. It was then ready for use with the prepared fused silica powder.

The powder. This powder was prepared by sifting clear colorless fused silica powder into 1.0% aqueous solution of tris- (2-methoxy ethoxy) vinyl silane [9] that was catalyzed with sufficient sodium hydroxide to give a pH of 9.3 to 9.8. One half per cent of the silane per weight of the fused silica was used. This slurry was dried at 125°C and cooled. After this treatment, the silica powder was water repellent or organophilic; when untreated it was very hydrophilic or easily wetted with water. After 1.25 per cent by weight of benzoyl peroxide was dispersed in it, this powder was ready to mix with the liquid.

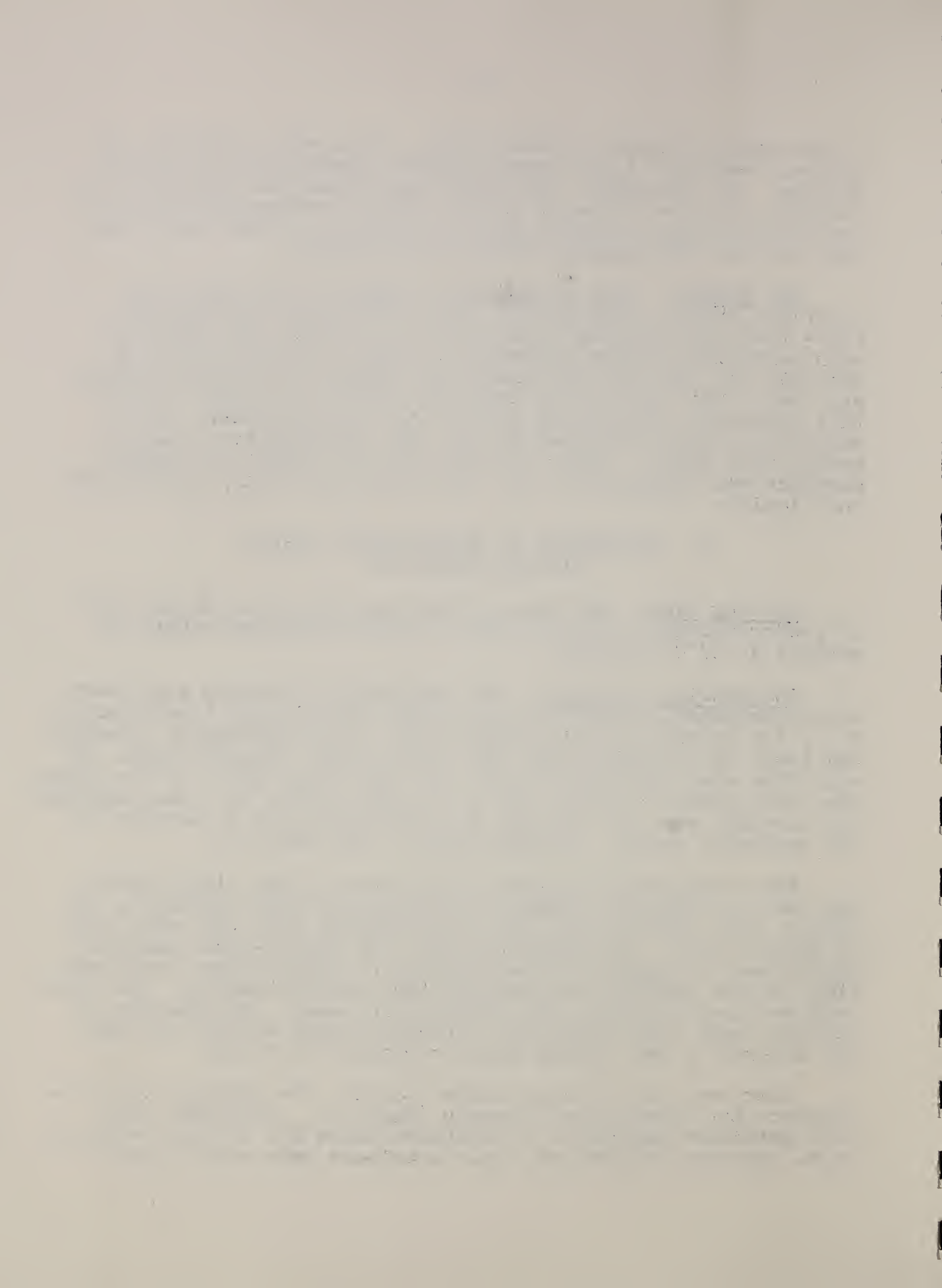
3. PROPERTIES OF EXPERIMENTAL DIRECT FILLING MATERIALS

Setting time. Mixtures containing from 70 to 80 per cent of powder and 30 to 20 per cent of liquid hardened within 10 minutes at 37°C (98.6°F).

Compressive strength. The compressive strength was determined according to the American Dental Association Specification No. 9 for Dental Silicate Cement [10]. The compressive strength was found to be higher when the vinyl silane treated powder was used than when untreated powder was used, especially if the specimens were stored in water for 7 days (See Table 1). The compressive strength was not the same for different lots or batches of the synthetic resin. (Compare Table 1 and Table 2).

The hydrolyzed silicone, in the case of the vinyl silane, can combine with the surface of the fused silica particles, exposing vinyl groups which can co-polymerize with the resin when it hardens [11]. Illustrating this, the silica-resin material was allowed to harden on the surfaces of glass slides that were vinyl silane treated and controls that were untreated. The specimens and controls were then immersed in water. The patches of material came loose from the untreated slides within two days, but adhered to the treated glass surfaces for a year.

With the vinyl silane treated silica, the particle size influenced the compressive strength (Table 2). Specimens made with particles passing U. S. Standard Sieve No. 100 but retained on No. 325 gave 15,000 psi while specimens made with "finer"



particles (Those passing U. S. Standard Sieve No. 325) gave 23,000 psi. Specimens prepared from a mixture of the particles showed an intermediate strength -- 18,500 psi*. All of these specimens had been immersed for 24 hours in distilled water at 37°C.

Solubility and disintegration. Solubility and disintegration was tested according to the American Dental Association Specification No. 9 for Dental Silicate Cement except that the weighing bottles were weighed after drying at 99°C and 110°C to detect organic leach products that might be driven off at the usual 149°C. The solubility and disintegration was 0.04 per cent by weight.

Water sorption. The water sorption was tested according to American Dental Association Specification No. 12 for Denture Base Resin [10]. The water sorption was 0.6 mg per square centimeter of surface area or 1.7 per cent by weight in 24 hours.

Coefficient of thermal expansion. The coefficient of thermal expansion was measured by means of an interferometer on three specimens containing 70 per cent vinyl silane treated fused quartz. The average was 24×10^{-6} per degree C between 30°C and 40°C.

Color stability. Color stability was tested by 24 hour exposure of half of each specimen to the light source described in the American Dental Association Specification No. 12 for Denture Base Resin [10], and by comparison of this with the other half that had been shielded with aluminum foil tape.

The color change was apparent but was less than that produced in comparable mixes made with a self-curing methyl methacrylate sirup (a monomer-polymer solution containing dimethyl p-toluidene) and the treated silica. In both cases the color change was believed to be due to the dimethyl p-toluidene activator [12].

The use of 1 per cent of a commercial ultraviolet absorber [13] by weight of the synthetic resin, prevented the color change produced by the lamp, without affecting the hardening time.

Opacity. The visual opacity when tested according to American Dental Association Specification No. 9 for Dental Silicate Cement was slightly above 35 per cent ($C_{0.70}$).

* This does not correspond to Table 1 because of slight differences in the synthetic resin.

The x-ray opacity could be raised to approximate that of tooth structure by using 20-30 per cent of clear colorless flint glass which contained about 35.5 per cent of lead oxide. This did not perceptibly affect the color or visual opacity on freshly prepared specimens.

4. SUMMARY

An experimental direct filling material is described which consists of about 70 per cent of powdered fused silica and about 30 per cent of a new crosslinked organic polymer. The organic binding agent resembles, in chemical structure, the commercial epoxy resins and contains methacrylate groups for free radical polymerization. The fused silica particles are surface treated with vinyl silane that can form stable chemical bonds to both the resin and to the silica. Any reinforcing filler, pigment or other inclusion, in a resin bonded material, should be treated with a suitable keying agent or finish that is capable of forming stable chemical bonds to both the resin and the included material. The solubility of silicate cements, the limitations inherent in the present methyl methacrylate direct filling resins and the promising results obtained in this study provide ample motivation for further pursuit along the present lines.

5. REFERENCES

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Table 1. Compressive strength of experimental direct filling materials

Specimens stored in water at 37°C for	Treatment of the fused silica powder ^a						With vinyl silane ²		
	Without vinyl silane ¹			With vinyl silane ¹			# Specimens	Average	S.D.*
	# Specimens	Average PSI	S.D.*	# Specimens	Average PSI	S.D.*			
1 hour	5	13,000	560	5	17,000	620	9	20,000	1,120
24 hours	5	11,000	620	4	16,000	550	6	22,000	1,210
7 days	4	7,500	230	5	12,000	550			
	"Kadon" (L. D. Caulk, Company)								
24 hours	5	10,500	200						

a Fused silica powder all passing a No. 40 U. S. Standard sieve.

* Standard deviation given by formula $\sqrt{\frac{\sum (\bar{x} - x_1)^2}{n-1}}$

1 Mixes from which specimens were made consisted of powder 67% and liquid synthetic resin (A-143-5) 33%.

2 Mixes from which specimens were made consisted of powder 80% and liquid syntehctic resin (A-152-41) 20%.

Table 2. Effect of particle size of vinyl silane treated used silica on compressive strength of experimental direct filling materials.*

Particle size of silica powder	Number of specimens	Average psi	S. D.**
All passing No. 100 sieve***	5	18,500	1,070
Passing No. 100 sieve but retained on No. 325 sieve***	5	15,000	900
All passing No. 325 sieve***	5	23,000	370

* All specimens stored 24 hours in water at 37°C; mixes from which specimens were made consisted of 68% powder and 32% liquid synthetic resin (A-160-48-).

** Standard deviation given by formula
$$\frac{(x - x_1)^2}{n - 1}$$

*** U. S. Standard Sieve Series.

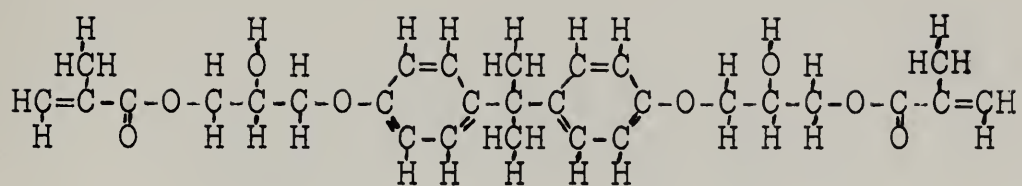


Figure 1. A compound resembling a commercial epoxy resin [5] but containing methacrylate groups for free radical polymerization.

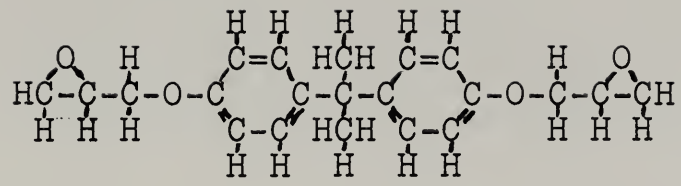


Figure 2. A simplified structure of a commercial epoxy resin [5, 7].

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