NOTES

Plasma Polymerization for Self-Curing PMMA Bone Cement

In this study two experimental methods were used to improve the tensile strength of self-curing PMMA bone cement: plasma-induced and plasma-state polymerization. A procedure was also developed for room temperature self-curing of PMMA resin. Experimental samples of cement were tested for tensile strength. The tensile test results indicate that additions of PMMA powder reduce the strength of self-curing PMMA bone cement. Plasma-induced PMMA can increase the molecular weight of an MMA and PMMA matrix; however, the matrix tensile strength does not increase as much as would be expected from its greater molecular weight. The lower values were most probably due to an extremely high viscosity matrix. The most significant finding is that plasma-treated zirconium oxide powder can improve the tensile strength of self-curing PMMA bone cement.

INTRODUCTION

Plasma-induced or plasma-initiated polymerization was first reported by Osada and his co-workers in 1978.[1] This type of polymerization process has a reaction mechanism quite similar to that of the conventional free radical polymerization, except for its initiation.[2,3] Conventional free radical polymerization is always initiated by thermally decomposed peroxides from which monoradicals are generated. On the other hand, plasma-induced polymerization is initiated from a multiradical compound produced by the plasma.[3] These differences in reaction initiation cause the molecular weight of a polymer formed by plasma-induced polymerization to be much higher than for polymer formed by conventional free radical procedure. Plasma-induced polymerization processes are applied in the research reported here to improve the strength of bone cement used for hip implants.

In our experimental work, a very high molecular weight polymer, plasma-induced PMMA, coexists with unreacted MMA monomer in a modified bone cement mixture. Namely, the ampoule of commercial bone cement is replaced by a modified MMA-PMMA mixture as illustrated in Figure 1B. Mixture molecular weight affects the tensile strength of bone cement formulations. The ultimate tensile strength and molecular weight of a polymer can be correlated by the relationship,

$$\text{Tensile Strength} = A - (B/M_w) \qquad (1)$$

where A and B are positive empirical constants, and M_w is the polymer molecular weight. This relationship, first reported by Flory[4] in 1945, indicates that a polymer's tensile strength increases nonlinearly with an increase in molecular weight.

Commercial bone cement consists of an ampoule containing liquid MMA monomer and a promoter (N,N-dimethyl-p-toluidine) and a package of powder containing PMMA, initiator (benzoyl peroxide), and a radiopaque material (barium sulfate or zirconium oxide). For use, bone cement is prepared by hand stirring the ampoule material into the powder at room temperature (see Fig. 1A). Ingredients polymerize in a few minutes to form a composite solid that will fix the implant in the bone. Studies of the mechanical properties of the commercial bone cement have been reported by others.[5-8]

In addition to the plasma-induced polymerization studies to improve the tensile strength of self-curing PMMA, plasma-state polymerization investigations were done. Plasma-state polymerization results in a polymer produced by forming covalent bonds between atoms, rather than between monomers.[9] By means of plasma-state polymerization an ultrathin polymer film can be deposited on a substrate surface. This film always adheres well to the substrate due to covalent bonding.[9] A plasma-state polymerization advantage is that it modifies the substrate surface properties without changing substrate bulk properties.[10] Since commercial self-curing PMMA bone cement usually contains a radiopaque material, cement is readily traceable by x-ray. However, since radiopaque powders are insoluble inorganic additives, they can reduce the tensile strength of bone cement due to poor surface adhesion between these powders and PMMA resin.[5] In our investigation various monomers were tested as surface modifiers for one radiopaque powder, zirconium oxide, by plasma-state polymerization (see Fig. 1C).

EXPERIMENTAL

The experimental techniques are described that were used to prepare both plasma-induced polymerization and plasma-state polymerization samples for tensile strength
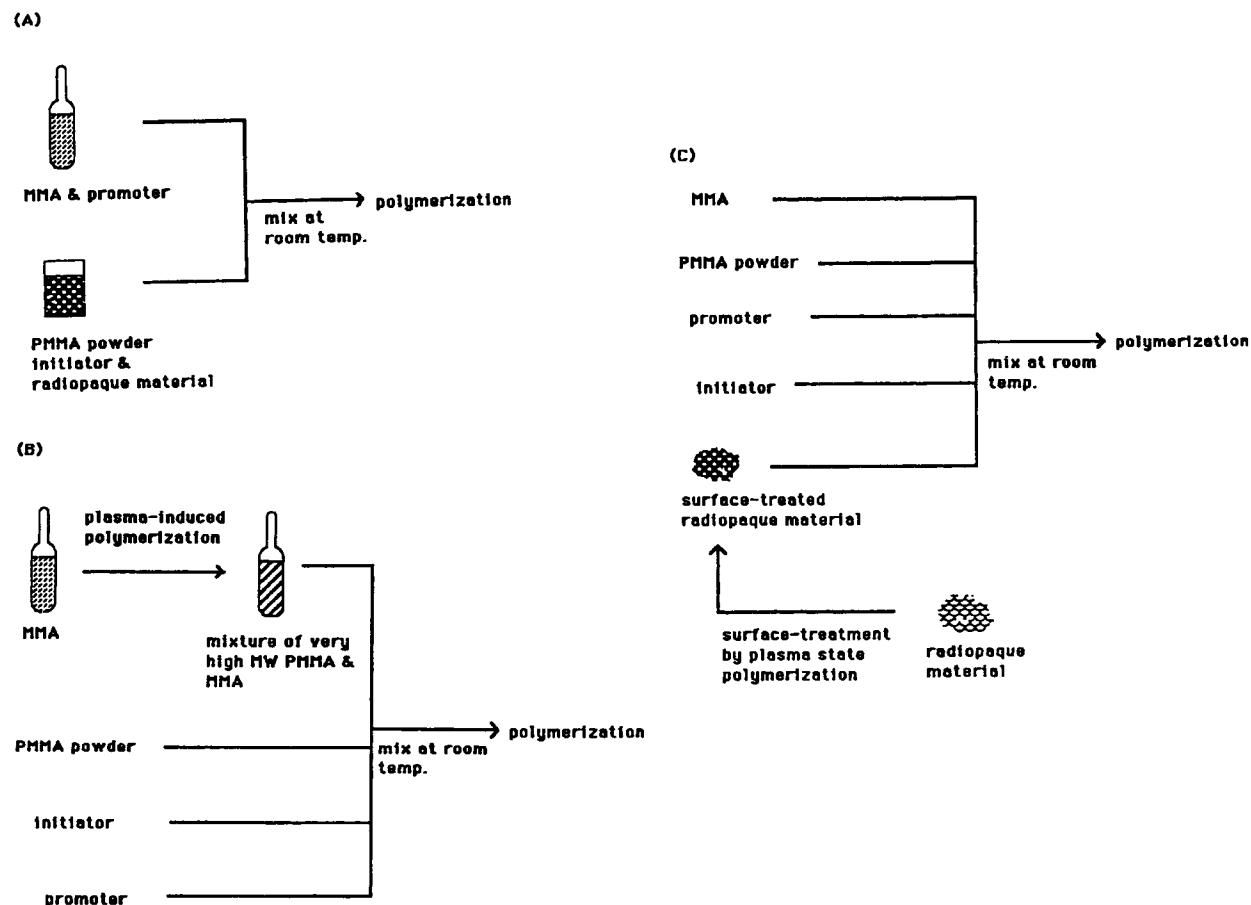
(A)

MMA & promoter

PMMA powder
initiator &
radiopaque material

mix at
room temp.

→ polymerization

(B)

MMA

plasma-induced
polymerization
→

mixture of very
high MW PMMA &
MMA

PMMA powder

initiator

promoter

mix at room
temp.

→ polymerization

(C)

MMA

PMMA powder

promoter

initiator

surface-treated
radiopaque material

mix at room
temp.

→ polymerization

↑

surface-treatment
by plasma state
polymerization

radiopaque
material

Figure 1   Bone cement mixing techniques. (A) currently used commercial, (B) plasma-induced, (C) plasma-state polymerization.

tests and evaluations. The experiments are preliminary investigations. Experimental procedures were not designed to optimize plasma polymerization conditions.

Plasma-Induced Polymerization

Plasma-induced polymerization samples were prepared as follows. First, 15 mL MMA monomer was vacuum-distilled at 38°C to remove the inhibitor, hydroquinone. The distilled MMA was pipetted into a 25 mL ampoule, then mounted on a manifold as shown in Figure 2. The distance between electrodes was 2 inches and each band width was approximately one-half inch. The ampoule was immersed in a liquid nitrogen bath which caused MMA to become solid. After the ampoule was evacuated to 10 mTorr, the valve between the ampoule and manifold was closed, and a 13.6 MHz radiofrequency generator was used to initiate polymerization. When the ampoule was removed from the bath, a blue glow discharge was observed above the solid monomer due to some vaporization.[1-3] This glow self-quenched within 1 min. After this plasma initiation, the ampoule was sealed by means of a propane torch. The

ampoule was then removed from the manifold and shaken in order to dissolve any active monomer species that might remain on the wall into the MMA. The ampoule was then placed in a 25°C water bath needed to maintain the polymerization at constant temperature.

Conversion and Molecular Weight Measurement

The degree to which the plasma-induced polymerization technique converted MMA into PMMA was monitored continuously with an oblique-line refractometer.[11,12] At a certain postpolymerization time the ampoule was broken. The plasma-induced PMMA–MMA mixture was dissolved in toluene, and slowly pipetted into methanol to precipitate the PMMA. The intrinsic viscosity, $[\eta]$, of the precipitated polymer was measured with a Cannon–Fenske viscometer, and methyl ethyl ketone was used as the solvent. The viscosity-average molecular weight, M_w, of PMMA was obtained by the following equation:[13]
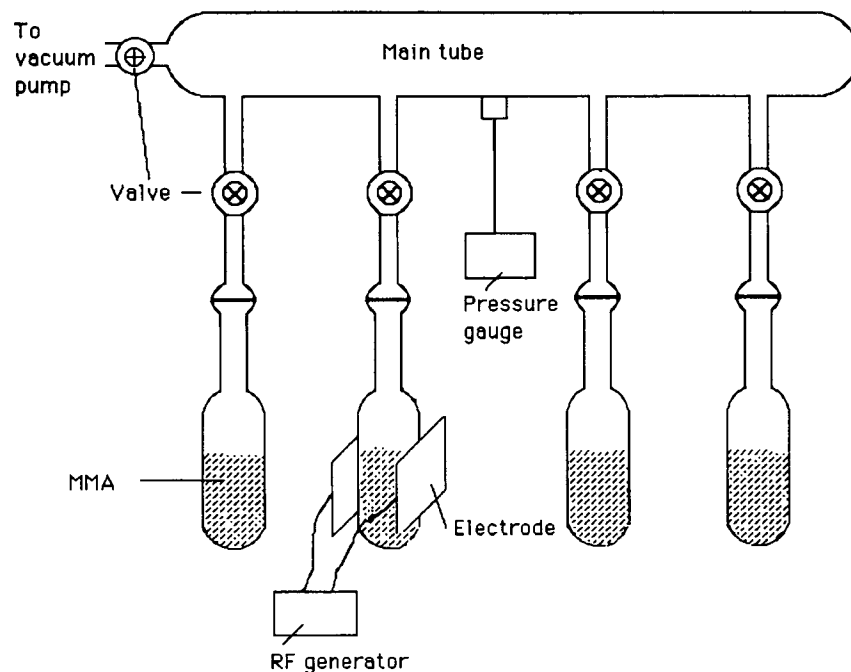
$$[\eta] = 7.1 \times 10^{-5} M_w^{0.72} \qquad (2)$$

Figure 2 Schematic of reactor for plasma-induced polymerization.

Specimen Preparation

The amounts of initiator (benzoyl peroxide) and promoter (N,N-dimethyl-p-toluidine) were 2% and 1% by weight, respectively, of the weight of MMA or of plasma-induced PMMA and MMA mixture. After these amounts were added, the MMA polymerized at room temperature within 40–60 min. Two different ratios of PMMA powder (Aldrich Chemical Company) to MMA, and to plasma-initiated PMMA and MMA mixture were investigated: (PMMA powder: MMA) or (PMMA powder: plasma-induced PMMA and MMA mixture) = 1 : 1, and = 2.2 : 1. These mixtures were stirred completely by hand and then poured into a mold.

Plasma-State Polymerization Apparatus

The plasma-state treatment apparatus (see Fig. 3) consisted of monomer input control valves, a 2-L round-bottom glass reactor vessel, a pressure gauge, a vacuum pump, a pair of electrodes connected to the 13.6 MHz radiofrequency power supply, a plotter linked to the pressure gauge to measure the monomer flow rate, and a motor to rotate the reactor vessel.[9] Once the untreated powder was placed in the glass reactor, the valve between the vacuum pump and the reactor was closed. After the vacuum pump was turned on, this valve was gradually opened to prevent the powder from being driven out with effluent gas. Since the powders are fine, they tended to entrap air, and system

evacuation to 10 mTorr took several hours per sample. The monomer gas was then fed into the system by opening the valve between the monomer source and the reactor, thereby controlling the monomer flow rate. The monomer flow rate was measured after the system pressure reached a steady state. When the valve between the reactor and the vacuum pump was closed, the pressure of the reactor increased steadily due to the continuous input of monomer gas into the reactor. Pressure increments were recorded by a plotter and also observed by means of a pressure gauge. After measuring flow rate of monomer, the valve between the reactor and vacuum pump was opened. Then, radio frequency power supply was turned on. A glow discharge was observed in the whole reactor. At this stage, the powder started to be plasma-treated. Three different monomers were tested; namely, ethyl silane, methyl methacrylate, and methane.

Plasma-State Treatment of Zirconium Oxide Powder

The plasma-state polymerization system operating treatment conditions are listed in Table I. The ratio of PMMA powder to MMA monomer to zirconium oxide was 83 : 41 : 9; this formulation is the same as used in commercial bone cement. The amounts of initiator (benzoyl peroxide) and promoter (N,N-dimethyl-p-toluidine) were 2% and 1% based on the weight of MMA, respectively. Once all of the components were mixed completely by hand, the specimen was cast-molded.
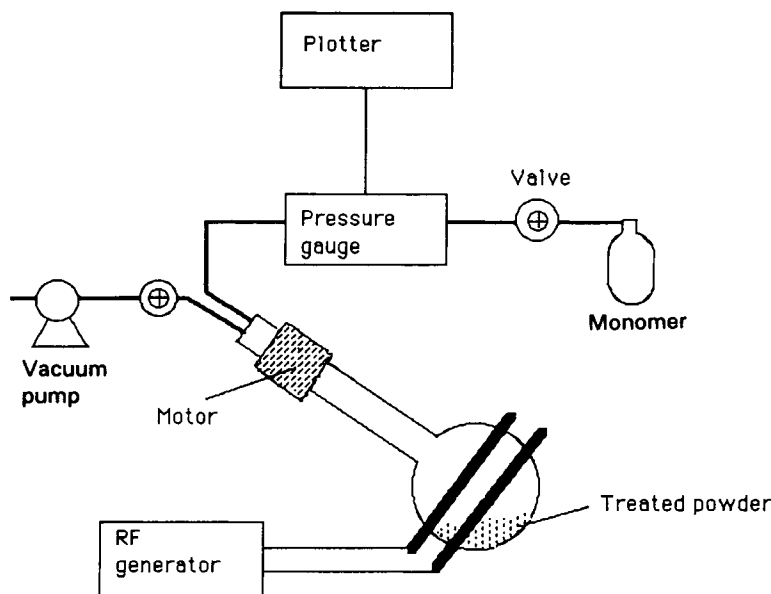
Figure 3   Schematic of reactor for plasma-state polymerization.

Tensile Strength Testing

Tensile strength measurements for each specimen followed ASTM D-638M guidelines. These measurements were made using a material testing machine (Tinius Olsen Testing Machine Company) at a head speed of 0.05 in./min. An analysis of the strength test results is presented in the next section.

RESULTS AND DISCUSSION

The major results of plasma-induced and plasma-state polymerization studies are described after discussion of the amount of initiator and promoter needed for polymerization at room temperature.

Room-Temperature-Curing PMMA

Based on the weight of MMA in the commercial bone cement, the initiator (benzoyl peroxide) and the promoter (N,N-dimethyl-p-toluidine) are approximately 1.6% and 2.8% by weight, respectively. However, our MMA did not polymerize using the same recipe. Haas et al.[14] claimed to use a similar ratio of N,N-dimethyl-p-toluidine and benzoyl peroxide to MMA as listed in product literature for bone cement. However, Rose et al.,[15] and Brauer et al.[16] strongly suggested that the amount of N,N-dimethyl-p-toluidine should be between 0.55 and 1.0%. At this lower promoter level the curing reaction would be more efficient. Our studies used 1.0% N,N-dimethyl-p-toluidine and 2% benzoyl peroxide.

Table I   Plasma State Polymerization Conditions for Zirconium Oxide

Monomer	Power (W)	Reactor Press (m Torr.)	Treatment Time (min./50 g Powder)
Ethyl silane	20	100	45
MMA	20	150	30
Methane	20	150	30
Ethyl silane	20	200	45
then air	20	200	15

Table II   The Kinetic Results of Plasma-Induced MMA Polymerization

Plasma-Induced Polymerization

Postpolymerization Time (Days)	Conversion (%)	Molecular Weight of PMMA ($\times 10^6$ g/mol.)
0.5	3	4
1	8	6
2	12	7
3	17	8

The particle size of PMMA in Simplex bone cement is quite different from that in our cement mixture. From scanning electron micrographs, the average diameter of the PMMA particle in the Simplex cement was found to be approximately 50 μm; ours were twice as large (i.e., 100 μm). Rose et al. reported that the polymerization of self-curing PMMA was affected by its particle size. Brauer et al.[16] also pointed out that ambient oxygen might be involved in the reaction between N,N-dimethyl-p-toluidine and benzoyl peroxide. Thus, evidence exists to correlate PMMA particle size with oxygen content, which suggests PMMA particle size significantly influences the availability of oxygen causing different polymerization rates for self-curing PMMA.

High-Molecular-Weight PMMA from Plasma-Induced Polymerization

Polymerization begins when the active species, formed by plasma treatment of the MMA vapor, is mixed with the liquid MMA monomer.[1-3] This reaction can be thought of as a "living" polymerization in that the degree of conversion and the molecular weight of PMMA increase with time. Experimental data presented in Table II show the molecular weight reached 6×10^6 g/mole and the conversion is 8% at 1-day post-polymerization. Since the viscosity of this PMMA–MMA mixture is high, it cannot be directly mixed with PMMA powder. The PMMA–MMA mixture is diluted with MMA at a weight ratio of 1 to 1. The diluted mixture is a homogeneous solution that has reasonable flow characteristics, although it contains 4% of very high molecular weight PMMA.

Tensile strength results of various samples are presented in Table III. The tensile strength of the *PMMA powder + MMA (weight ratio = 1 : 1) is the highest, and is about 7% greater than that of the commercial Simplex bone cement. The tensile strength of cast PMMA and injection-molded PMMA are 60 and 70 MPa, respec-

tively,[17] both of which are much higher than the other strengths listed in Table III. This indicates that the tensile strength can be increased if the content of PMMA powder in the self-curing resin is decreased. Radiopaque material used commercially, barium sulfate, has also been found to reduce the tensile strength of self-curing bone cement.[4] However, as seen in Table III, the tensile strength of commercial bone cement (containing radiopaque material) is still higher than that of the (PMMA powder + MMA) sample which does not include a radiopaque material, but has the same ratio of PMMA powder as found in the commercial cement. This effect could be caused by different amounts of initiator and promoter, or different particle sizes of PMMA powder.

The experimental results listed in Table III do not agree with the expectation that tensile strength increases with an increase in molecular weight [see eq. (1)]. The PMMA powder + PIP and the *PMMA powder + PIP samples which have higher molecular weights (due to the existence of very high molecular weight PMMA) should have higher tensile strengths than those of the PMMA powder + MMA and the *PMMA powder + MMA samples. The tensile strength of the PMMA powder + MMA sample is slightly higher than that of PMMA powder + PIP which contains high molecular weight PMMA. Further, the tensile strength of the *PMMA powder + MMA samples is much higher than that of *PMMA powder + PIP.

- McCormick et al.[18] found that tensile strength became independent of molecular weight as molecular weight exceeded a critical value. The viscosity average molecular weight of the commercial bone cement is about 1×10^5 g/mole.[14] If this value exceeds the critical value, improvements are not possible to the tensile strength by using a plasma-induced PMMA and MMA mixture to increase the molecular weight of resin. Based on this assumption, the tensile strengths of PMMA powder + PIP and *PMMA powder + PIP will be the same as that of PMMA powder + MMA and *PMMA powder + MMA, respectively. However, the experimental results show that the

Table III   Tensile Strength of Bone Cement With or Without Plasma-Induced PMMA Under Different Powder/MMA Ratio

Samples	Ultimate Tensile Strength (MPa)			
	Max.	Min.	Mean	Variances
Commercial Bone Cement (Surgical Simplex P)	43.92	41.11	42.23	1.21
PMMA powder + MMA (Powder : MMA = 2.2 : 1)	42.94	38.32	40.39	1.11
*PMMA powder + MMA (Powder : MMA = 1 : 1)	46.25	44.00	45.37	0.46
PMMA + PIP[a] (Powder : PIP = 2.2 : 1)	40.70	38.37	39.40	0.97
*PMMA powder + PIP[a] (Powder : PIP = 1 : 1)	39.44	38.66	39.05	0.28
Casting molding PMMA[17]			60.00	
Injecting molding PMMA[17]			70.00	

[a] PIP means the diluted plasma-initiated PMMA and MMA mixture, where plasma-induced PMMA and MMA mixture is diluted by equal weight of MMA.

Table IV Tensile Strength of Bone Cement with Different Plasma-Treated Zirconium Oxide

Samples	Ultimate Tensile Strength (MPa)			
	Max.	Min.	Mean	Variance
Without zirconium oxides (radioparent)				
Powder + MMA[a]	42.94	38.32	40.39	1.11
With zirconium oxides (radiopaque)				
Powder + MMA + zirconium oxide[b]				
Without treatment	32.29	30.37	31.63	0.89
Ethyl silane coating[c]	33.98	30.91	32.44	1.25
MMA coating[c]	38.19	36.37	37.27	0.81
Methane coating[c]	37.02	35.04	35.60	0.82
Ethyl silane coating[c] then air plasma	41.11	39.46	40.11	0.50

[a] The weight ratio PMMA powder to MMA is 2.2 : 1.
[b] The weight ratio, PMMA powder : MMA : zirconium oxides = 83 : 41 : 1.
[c] The samples contain zirconium oxide powder, which was treated.

tensile strengths of the samples with PIP are reduced. Vincent[19] reported that the presence of air bubbles, insoluble additives, and unreacted monomer could reduce resin tensile strength. Plasma-induced PMMA–MMA solution diluted with MMA is more viscous than MMA. This viscous solution could reduce the wettability of an additive powder, allow higher numbers of entrapped air bubbles, and reduce monomer mobility, thereby reducing the tensile strengths of the PIP samples.

Plasma-Treated Zirconium Oxide

Tensile strengths of the different plasma-treated zirconium oxide are shown in Table IV. Zirconium oxide treated with ethyl silane and oxygen has higher tensile strengths than zirconium oxide treated with MMA, methane, or ethyl silane. The tensile strength of the PMMA powder + MMA sample is reduced approximately 25%, when untreated zirconium oxide is added. This result is similar to the base of the commercial bone cement, where the tensile strength of the commercial radiopaque bone cement is lower than that of the commercial radiotransparent.[5] This reduction of tensile strength could be caused by the poor adhesion of zirconium oxide and matrix, which is lower than the cohesion of matrix.

Zirconium oxide is an inorganic compound, but its surface becomes organic as it is coated with plasma-polymer. During this process, the polymer (formed from plasma-state polymerization) deposits on the surface of zirconium oxide. Results in Table IV show that samples treated by different monomers have slightly higher tensile strength than untreated ones. This indicates that zirconium oxide with a plasma polymeric surface is more compatible with the PMMA matrix than untreated zirconium oxide. Data in Table IV indicate that different monomers contribute to different extents of adhesion between zirconium oxide and cement matrix.

The hydrophilic or hydrophobic properties of ethyl silane-treated zirconium oxide (with or without air plasma) were observed by placing samples on the water. Theoretically, hydrophobic samples will float, but the hydrophilic ones will quickly sink. Using this simple test, air plasma-treated samples of zirconium oxide are found to be hydrophilic, while the zirconium oxide sample without air plasma is hydrophobic.[20]

CONCLUSIONS

Plasma-induced MMA polymerization increases the molecular weight of the cement matrix, but the viscosity increases to a level that makes the flow process relatively impractical. The evaluation of plasma-treated materials by tensile strength test may not be the best method to investigate surface effects; however, the plasma-treated zirconium oxide powder seems to improve the overall performance of bone cement.

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