

Modifying the Setting Rate of an Addition-Type Silicone Impression Material

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Two methods for controlling the working time of an addition-type silicone impression material are presented. The progress of the polymerization reaction of this modified system was studied using viscosity and a new "compression set" technique. The physical properties are presented and compared to those typical of condensation silicones, and a method of clinical use is suggested.

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Introduction.

Silicone impression materials polymerized by the addition mechanism (Eqn. 1) offer improved properties over the condensation type (Eqn. 2), since no by-product is incurred. The properties of several rubber impression materials have been measured and compared by Craig.¹ The addition-type silicone was found to possess good elastic properties (recovery from deformation and low flow), very small dimensional change on setting, and a moderately short working and setting time.

The working time of impression materials is one important property the clinician has little control over if the manufacturer's directions are followed. A new commercial silicone*, based on addition polymerization, was selected to show two approaches that may be used to alter the setting rate of this class of polymers. The first approach modifies the addition polymerization reaction, while the second method takes advantage of a viscosity difference between the

base and catalyst components of the particular system.

Several investigators²⁻⁵ have studied the setting process of impression materials utilizing various methods of viscosity measurement, as will be done here. The most recent A.D.A. Specification No. 19⁶ describes a new "Compression-set" working time test which will be further developed here to show the variation in the setting behavior of impression materials. The Specification defines setting time as a transitional period when plastic properties permitting molding are lost, and elastic properties allowing removal over undercut areas are acquired. At present no specific test for measuring setting time is listed in the Specification.

Materials and methods.

The polymerization reaction within the system chosen occurs by reduction of a double bond using a chloroplatinic acid catalyst. This reaction is believed to occur by an acid-base mechanism rather than a free radical polymerization⁷. Using a similar approach as that of Kookootsedes and Plueddemann⁸, molecules containing triple-bonds may be added to the system, which have a retarding effect upon the polymerization rate. Phenylpropionic acid*, a triple-bond containing molecule showing minimal irritant properties, was chosen for this purpose.

Varying amounts of phenylpropionic acid (P.P.A.) were added to a 20 g (1/1 base to catalyst) mix, and the viscosity was followed using a heliopathic viscometer, fitted with special t bar-type spindles[†], coupled to a

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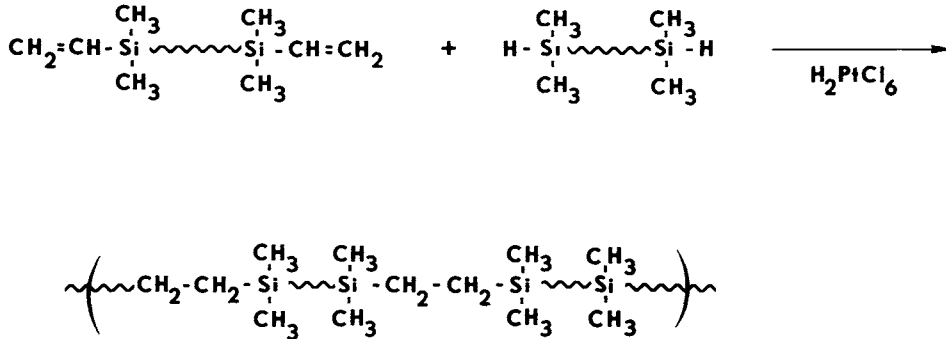
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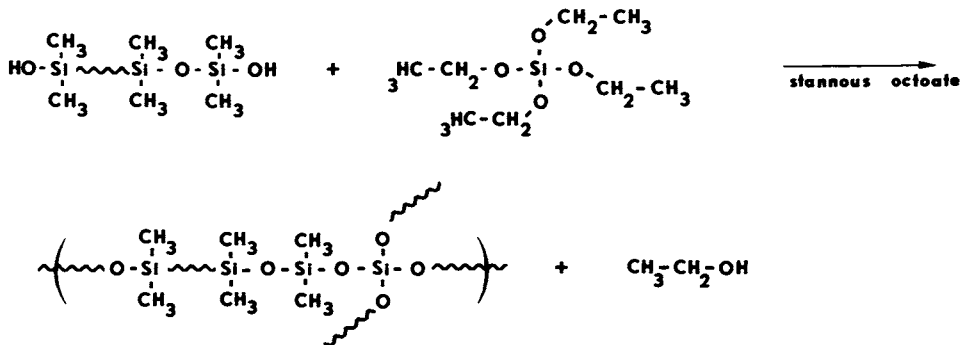
*President - regular body, Uni-Disco, Inc., P.O. Box 28014, Detroit, MI 48228. Currently distributed by Union Broach Corp., 36-40 37th Street, Long Island City, NY 11101.

*Aldrich Chemical Co., Milwaukee, WI 53233.

†Spindle cross length of 5 mm; Heliopathic Viscometer Model C, Brookfield Engineering Laboratories, Stoughton, MA 02072.



Equation 1. Addition-type silicone polymerization reaction.



Equation 2. Condensation-type silicone polymerization reaction.

pneumatic X-Y recorder.† The samples were contained in cups 3 cm in diameter and 3 cm deep, and the viscosity was measured at 37 C to follow the progress of the setting reaction. Since the required amount of P.P.A. for a 20 g mix was rather small and difficult to handle, dilution of the P.P.A. in dibutyl phthalate (D.B.P.) was done. A 0.2866 g phenylpropionic acid/10.0 ml dibutyl phthalate solution was found adequate for dispensing the required amount of phenylpropionic acid. Viscosity versus time for varying numbers of drops of this solution was followed to show the effect of the plasticizer (dibutyl phthalate).

The viscosity measurement showed a maximum viscosity for this system that can be measured prior to setting of the impression material, and as a result the viscosity curves terminated at about 12.5×10^5 centipoise. For this reason and to further de-

velop the new A.D.A. Specification No. 19 working time test method⁶, the time of data gathering was extended to a time after which the material sets. This new method may then show differences in setting rate and ultimate setting time for different materials.

Investigation showed that varying ratios of catalyst to base, for this system, would also alter the polymerization rate. The viscosity versus time and the above described "compression set" technique were studied for 0.25/1, 1/1, 2/1, 3/1, and 6/1 catalyst to base ratios.

The physical properties of these modified silicone systems were measured using the A.D.A. Specification No. 19 test method. Measurement of these properties at various times was done to determine the appropriate handling procedure for clinical use.

Cultures of human fibroblast cells were exposed to polymerized samples of these systems to initially determine the effect of phenylpropionic acid, a known skin irritant.

†Esterline Angus, X-Y 530-Recorder, Indianapolis, IN 46224

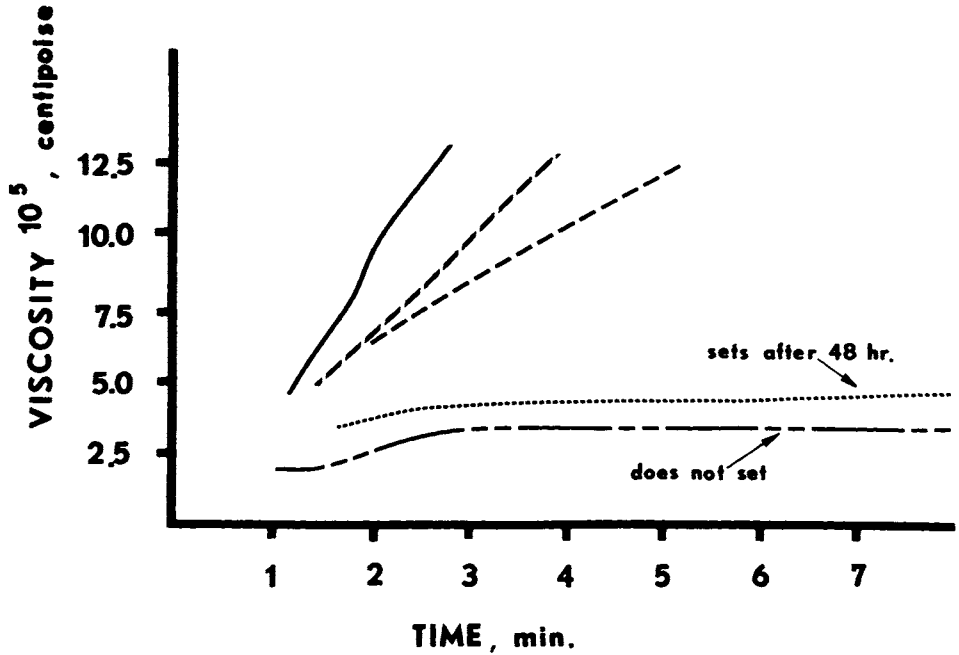


Fig. 1.—Effective range of phenylpropionic acid (PPA) in President regular body (R.B.) — 20 g mix. — no additives; 0.0055 g PPA; ---- 0.0113 g PPA; - - - 0.0518 g PPA; - - - - 0.1973 g PPA. Tests conducted at 37 C.

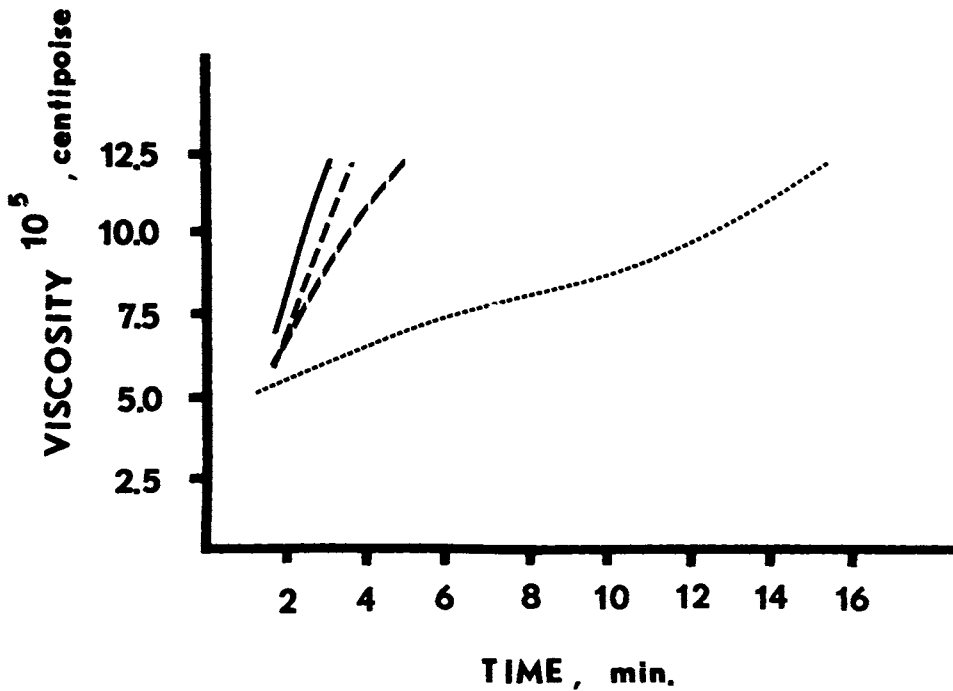


Fig. 2.—Effect of phenylpropionic acid (PPA) on setting rate of President R.B. at 37 C. — no additives; ---- 0.0055 g PPA/20 g mix; 10 drops 0.2866 g PPA/10 ml dibutyl phthalate; - - - - 15 drops 0.2866 g PPA/10 ml dibutyl phthalate.

TABLE 1
 PROPERTIES OF SILICONES DETERMINED ACCORDING TO A.D.A. SPECIFICATION 19*

	Consistency	% Per. Def.	% Strain	% Flow	% Dim. Change
Silicone Class 2	32 ± 6	< 2.0	2 to 20	< 0.2	< 0.60
Material					
President R.B.	32	0.07	2.6	0.03	0.05
President 2/1 - Catalyst/Base	30	0.15	2.8	0.03	0.04
President w/ PPA in DBP	31	0.30	3.8	v. small	0.09

*These values represent ultimate properties obtained through modifications in the test procedure allowing for differences in setting rate. The modifications are similar to those shown in Table 2.

Results.

Figure 1 shows the very small amount of phenylpropionic acid (P.P.A.) required to produce a polymerization rate slightly slower than the unmodified silicone system. Addition of an excessive amount of P.P.A. will prevent the material from setting. Figure 2 shows the "diluting" effect of adding the dibutyl phthalate (D.B.P.) solution to the system. the addition of 0.0055 g P.P.A./20 g mix is equivalent to the amount of P.P.A. contained in 15 drops of 0.2866 g P.P.A./10 ml D.B.P.

The variation in setting rate as indicated by the change in viscosity achieved by different catalyst to base mixing ratios is shown in Figure 3. The 3/1 base to catalyst ratio offers a slightly reduced setting time. Increasing the catalyst to base ratio, however, increases the time before setting.

The "compression set" data are presented in Figure 4, as the modification of the new A.D.A. Specification No. 19 working time test method. The unmodified system is seen to have a working time, the point at which the curve crosses the 0.2 mm horizontal

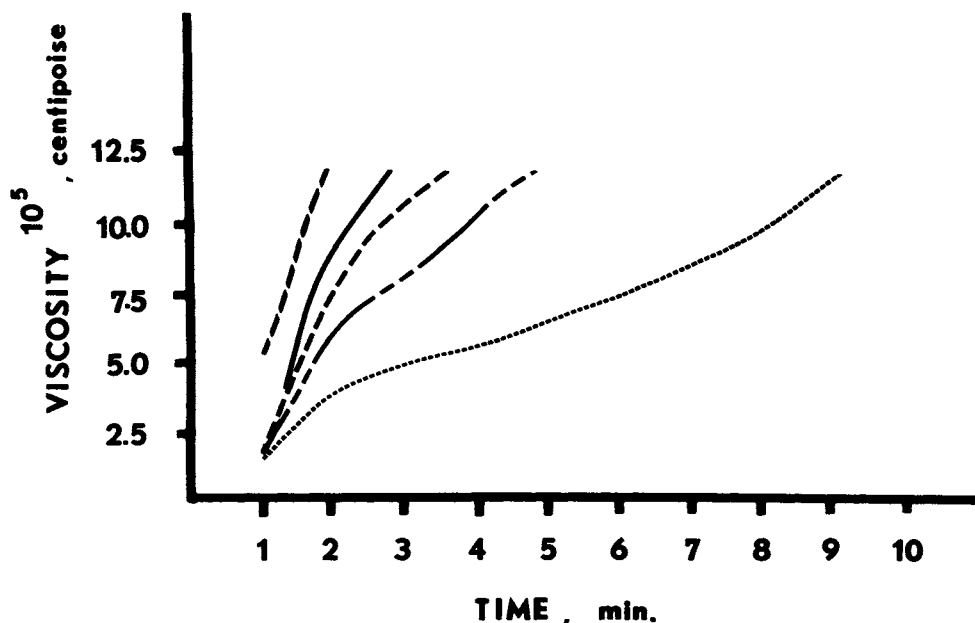


Fig. 3.—Effect of base (B) to catalyst (C) ratio on setting process at 37 C. // // // // 3/1 - B/C; ————— 1/1 - B/C; - - - - - 2/1 - C/B; - - - - - 3/1 - C/B; - · - · - 6/1 - C/B, President R.B.

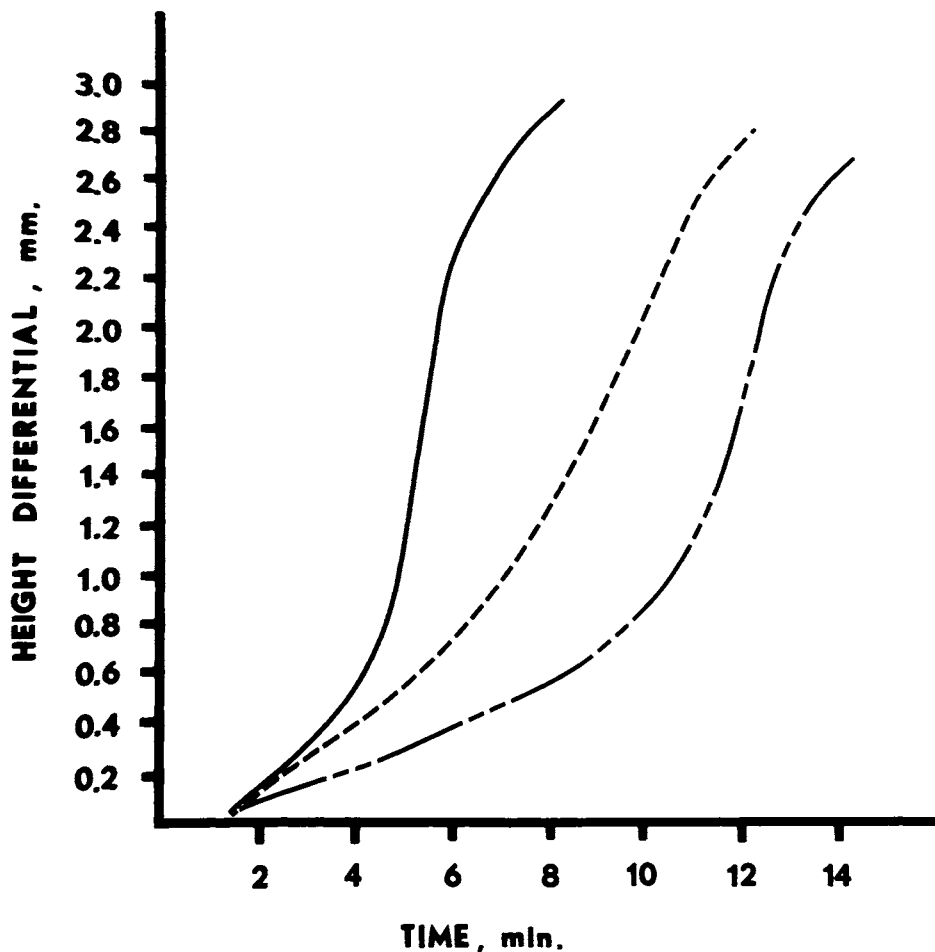


Fig. 4.—“Compression Set” data (A.D.A. Spec. 19) for President regular. —————no modifications; ----- 10 drops 0.2866 g phenylpropionic acid/10 ml dibutyl phthalate/20 g mix; - - - 3/1 - C/B mixing ratio.

line, of 2.5 minutes. The chosen P.P.A./D.B.P. concentration is also observed to have a working time of approximately 2.5 minutes. A catalyst to base ratio of 3/1 shows a working time of 3.5 minutes from this test.

Table 1 gives the A.D.A. Specification No. 19 test results for the unmodified system (regular body), the 2/1 catalyst to base mixing ratio, and 10 drops of 0.2866 g P.P.A./10 ml D.B.P. added to a 20 g mix of 1/1 base to catalyst. In Table 2 the P.P.A. containing material is the same concentration as given above.

Finally, Table 2 shows possible clinical use for each of the systems presented in Table 1, based upon the times at which the

physical properties are optimum versus the minimum amount of time required in the patient's mouth. These times were obtained using the A.D.A. Specification test.

TABLE 2
HANDLING OF MODIFIED PRESIDENT SYSTEM

President Regular	into mouth at 2 min. — remain for 3 minutes
President 2/1 — Catalyst/Base	into mouth at 6 min. — remain for 5 minutes
President Regular w/Phenylpropionic Acid	into mouth at 6 min. — remain for 7 minutes

Improved stone poured against impressions containing P.P.A. and D.B.P., in the concentrations used, reproduced detail satisfactorily and was not different from concentrations measured in unmodified addition silicone impressions. Culture studies showed no appreciable damage to fibroblast cells for the concentration of P.P.A. used within these experiments.

Discussion.

The purpose of the experiments was to offer expanded utility of a particular addition-type silicone system which provides satisfactory properties. The methods discussed show a means for customizing the polymerization rate of addition-type silicone systems to the particular needs of the practitioner. The working times developed were selected as possible improvements over the commercial system. Shorter or longer working times can be devised from the methods presented. The expected uses of these changes are within the areas in which the clinician may require primarily an extended working time such as in a syringe-tray technique. Use of this method may also provide assistance in a teaching environment where unfamiliarity with manipulation requires increased working time.

The unexpected slower rate of increase in viscosity observed with increasing catalyst concentration, Figure 3, is believed to be caused by the much lower viscosity of the catalyst paste compared to that of the base paste. The difference in the initial slope between the P.P.A./D.B.P. and 3/1 catalyst to base curves shown in Figure 4 indicates why the 2/1 catalyst to base system offers superior setting characteristics over the P.P.A./D.B.P. system.

The extension of the new working time test method allows comparison between the setting characteristics of different impression materials.

Further toxicity studies beyond the cell culture tests are recommended on phenyl-propionic acid prior to clinical use of this system.

Conclusions.

Two methods for customizing the polymerization rate of an addition-type silicone impression material are given. Each of these methods, within the concentrations shown, offers extended working and setting times with little effect upon desirable physical properties. Increased polymerization rates are also possible, but were not developed. Extension of the new A.D.A. Specification No. 19 working time test method to include the entire setting process offers an easy, low-cost method of comparing the setting characteristics of various impression materials.

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