1978

# The Effect of Variation of the Water/Powder Ratio on the Physical Properties of Improved Dental Stone

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## Recommended Citation

Sertich, Louis R., "The Effect of Variation of the Water/Powder Ratio on the Physical Properties of Improved Dental Stone" (1978). *Master's Theses*. 2976.
https://ecommons.luc.edu/luc_theses/2976

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# THE EFFECT OF VARIATION OF THE WATER/POWDER RATIO ON THE PHYSICAL PROPERTIES OF IMPROVED DENTAL STONE

BY

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A Thesis Submitted to the Faculty of the Graduate
School of Loyola University of Chicago in Partial
Fulfillment of the Requirements for the Degree of
Master of Science

April
1978

# ACKNOWLEDGEMENTS

I wish to thank Doctor James L. Sandrik for his unfailing enthusiasm, encouragement, and guidance.

I am extremely grateful to Doctor William P. Schoen for offering his continual advice and encouragement.

I gratefully acknolwedge the interest and advice of Doctor Brahma Sharma who gave freely of his time and knowledge.

I wish to thank Mrs. Marie Feng for her attention and encouragement.

I also wish to thank Doctor Louis Blanchet for his enthusiastic support and encouragement.

# VITA

Louis R. Sertich was born on March 14, 1955, in East Chicago, Indiana.

He graduated from Crown Point High School, Crown Point Indiana, in 1973, and attended the University of Notre Dame where he received his Bachelor of the Arts degree in Economics in August of 1976.

He began his graduate studies in the Department of Oral Biology of Loyola University in September of 1976. This thesis was performed in the Department of Dental Materials, under the direction of its staff.

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# CHAPTER I

## INTRODUCTION

In order to fabricate many restorations and devices outside the mouth, a model or die must first be made. There are several desirable properties that die materials must exhibit to be acceptable. The material must first be accurate, i.e. have the ability to reproduce all the fine detail recorded by the impression. It must also be able to reproduce fine margins.

The die material must not only have the ability to reproduce detail accurately, but it must also have excellent dimensional accuracy. The ideal situation would be one in which the material did not exhibit either a setting expansion or a contraction. Once the material is set, it must be dimensionally stable over time and unaffected by changes in temperature.

The strength of the material should be high to minimize the chances of accidental breakage. This is especially true in models containing teeth, which are subject to fracture. Surface hardness and abrasion resistance must be high to prevent damage to the die during the carving of the wax pattern.

Other requirements, such as the compatibility with impression materials, ease of clinical use, time involved with the procedure, and cost, must all be considered.[1]

Through the years, many people have investigated the various types of materials which may have an application for a die material. These have included dental amalgam, epoxy and acrylic resins, silicophosphate cements, and the type IV dental plasters, (previously known as the Class II stones). No single material has completely filled all the requirements for a die material for varying reasons. However, all factors considered, the type IV stones appear to be the most successful die material available.[2]

The properties of Type IV stone, (also referred to as Densite or Improved stone), are improvements over the earlier Type III stone, (hydrocal). Setting expansion is lower, and both surface hardness and compressive strength are dramatically improved.

The patent for the manufacture of improved dental stone was issued to G.A. Hagget in 1952.[3] It called for boiling gypsum in a 30% solution of calcium chloride, after which the chlorides are washed away. The remaining calcium sulfate hemihydrate is dried and ground to the desired fineness. The crystals resulting from this process are slightly denser and more compact than the Type III stones. They are either cubic or rectangular in shape.[4] The amount of water that is needed for mixing improved stone is significantly lower than that needed for either plaster or Type III stone. The water/powder ratio (W/P) ranges from 0.45 - 0.55 for plaster, 0.30 - 0.35 for Type III stone, and only 0.20 - 0.25 for the improved stone.[2] The difference in the amount of gauging water required is principally accounted for by the shape and compactness of the crystals. The dense, compact, and regular shape of the crystals of improved stone allows better packing characteristics and the improved physical properties of the Type IV stones.

It has been widely reported that deviation from the recommended W/P ratio can have an adverse affect on the physical properties of the gypsum product. Ware and McLaverty[5] noted the importance of the correct W/P ratio, saying: "...a thin stone can be weaker than a thick plaster. The strength of a plaster or stone can be judged by the amount of water required to produce a working consistency". An accompanying graph showed the inverse relationship between the W/P ratio and compressive strength.

Hollenback (1962) did an extensive study on the physical properties of gypsum materials. His data show a definite inverse relationship between the W/P ratio and compressive strength (measured at both 1 and 24 hours). The data on setting expansion were not as clearcut, however. The W/P ratio did not appear to affect the setting expansion to a significant degree.[6]

Compressive strength of stone was also tested by Overberger (1968). He measured the strength of several materials using a universal testing machine. All the data show that the highest compressive strength is reached at the recommended W/P ratio.

Deviations on either side of the recommended ratio will produce less satisfactory results.[7]

It has been observed that while the proper W/P ratio and mixing procedure are being taught in dental school, very few students actually follow the instructions and measure the correct W/P ratio. Realizing that deviations from the accepted values can have adverse effects, it was decided that the physical properties of several widely used stones, (Kerr Vel-Mix, Coe Super-Cal, and Whip Mix Silky-Rock), can be evaluated as a function of the W/P ratio. Also, noting that little work has been done in the area in the last several years, this study serves to determine whether there have been any changes or improvements in the physical properties of these improved stones over the time period. Hollenbeck stated in 1962, "We have investigated the physical properties of the better modified stones a number of times in the last six years. Our results indicate that as time goes on, the properties of these materials tend to improve.[6]

The properties of surface hardness, setting expansion and setting time of the selected materials were tested for this study. The W/P ratio was varied to determine its effect on these properties. A survey of senior dental students and dentists was conducted to determine the percentage of them who measure the W/P ratio regularly and the amount of variations of the mix in those who do not measure the W/P ratio.

All data is evaluated and correlated in order to determine the necessity of measuring the W/P ratio clinically. Comparisons of several brands of stone will also aid the practicioner in choosing a particular brand for his office use.

# CHAPTER II

## LITERATURE REVIEW

### PART I DIMENSIONAL STABILITY

As stated earlier, the ideal die material would exhibit no dimensional change during the setting process. This section will detail the studies which have been done to test the dimensional changes of stone during the setting process.

Worner (1942) stated that on theoretical grounds, one would expect plaster of Paris or hydrocal to contract on setting. He determined that, from the setting reaction, the total volume of the hemihydrate plus water entering into the reaction was 161 units, while the volume of the gypsum formed was 149 units, corresponding to a contraction of 7.5%. In fact, however, while a small contraction was often observed in the early stages of the reaction, the most marked dimensional changes in setting plasters were always in the nature of expansions. He noted that the most logical explanation of the phenomenon would seem to be the apparent expansion was due to the outward growth thrust of the crystals in the direction of their growth during hydration. He used an apparatus which consisted of a block with a highly polished V-shaped through. With a micrometer he measured dimensional changes upon setting. He found that thicker mixes yielded greater expansions.[8]

Thompson (1949) measured the setting expanion of hydrocal using a dial gauge apparatus calibrated to 0.0001 inch. He found that impressions poured immediately with hydrocal materials having a hygroscopic expansion (sic) of 0.0023 to 0.0028 inch per inch produced models sufficiently accurate to fit both the model and the mouth in a similar matter.[9]

Sweeney and Taylor (1950) presented a method for determining the dimensional changes in gypsum products, using an Electrolimit Comparator accurate to 0.0001 inch, rather than a dial gauge. They did mention that a dial gauge might also be used, but would require more care to achieve the same precision.

He noted that:

> "Methods for observing length changes by using a dial gauge in contact with a single specimen, which is not removed, restrict the number of specimens that can be measured conveniently. Also, it is sometimes desirable to maintain specimens under storage conditions which are impractical with the dial gauge."

They measured the changes in the dimensions of plaster and hydrocal casts under varying storage conditions. The results showed that no significant change in dimensions occurred as a result of storage of dental stone and plaster specimens under normal lab conditions, but that an increase in storage temperatures led to water loss and shrinkage. At 63% relative humidity and 23° C., shrinkage was at 0.019& after four days storage, and 0.024% after nine days storage.[10]

Mahler and Asgaryedeh (1953) studied the apparent contradiction of the theoretical volumetric setting contraction with the actual setting expansion. They used a set-up operating on a dilatometer principle and found that although the outer dimensions of the sample increased slightly, the true volume of the mass had decreased. However, the decrease was manifested in porosity formation within the sample, which was about equal in volume to the theoretical contraction.[11] This explanation was also postlated by Jorgenson.[12] Therefore, the true volume of the mass has decreased even though the apparent volume has increased.

Hollenbeck[6] did an extensive study to investigate the physical properties of gypsum products. He tested numerous brands of both hydrocal and densite and found that the better brands of improved stone show a normal setting expansion of from 0.05 to about 0.12%. Dimensional change was measured with a dial gauge measuring to 0.0001 inch. The accuracy of the dial gauge was checked against a pressureless comparator and against readings with a micrometer microscope. All instruments yielded the same data, indicating that the dial gauge mechanism routinely provides accurate data. Realizing the importance of the W/P ratio, Hollenbeck tested a wide range of mixes from a stiff and difficult-to-handle mix to the thinnest mix recommended by the manufacturer. He tested several brands of hydrocal and densite for normal and hygroscopic setting expansion, compressive and transverse strength, and setting time. The one-hour normal setting expansion ranged from 0.05 to 0.12%, while the hygroscopic expansion ranged from 0.10 to 0.21%.

Hollenbeck and Sullivan[13] investigated the effect of three water substitutes on the physical properties of densite and found that they all greatly increased the setting expansion of the material. For example, using a W/P ratio of 0.22 with Kerr's Velmi, the normal setting expansion was 0.11%. The hardening solution increased this figure from 0.18 to 0.27%. At two hours it increased from 0.12 to 0.22% using the gypsum hardener. Surface hardness tests indicated that the hardener had no effect on the surface hardness of the stone. Compressive strength was only slightly higher at the one-hour reading, and equal or less than the strength of water alone in the 24-hour test.

Combe and Smith[14] tested several brands of hydrocal and densite for the properties of consistency, setting time, linear setting expansion, rate of hydration, surface hardness, and compressive and transverse strength.

The widely-practiced method of mixing to a particular consistency, rather than measuring the correct W/P ratio, results in wide variations in the actual W/P ratios used due to the differences in the consistencies between brands. This variation then manifests itself in the values of the compressive strength and surface hardness. When they compared the W/P ratios needed to give a putty-like consistency, it was noted that the materials with the highest standard consistency could be mixed with a W/P ratio less than the theoretical amount (about 0.18) required for the complete hydration of the hemihydrate to gypsum. Thus, the thickest possible mix is not necessarily the best from this standpoint since incomplete hydration would give reduced strength.

Linear setting expansion was tested using the trough and dial gauge. The setting expansion of the materials they tested ranged from 0.10 to 0.30%.

(Jorgenson[12] determined that 0.20% might be considered to be the limit of error in a die or partial denture model.) They also noted that lower expansion values could be obtained through the greater addition of salts but usually only at the expense of the strength of the set mass.

Toerskog, et al.[15] made a comparative study of the physical properties of common types of material used in the die construction. Several brands of improved stone were tested using water and two types of gypsum hardener.

Dimensional change was measured by preparing a brass master die in the form of a full crown preparation with a cervical shoulder. The occlusal and cervical surfaces were polished, and reference marks were placed with a Tukon tester. An impression of the mast die was made using industrial silicone. These models were allowed to set for a minimum of one month since tests showed that there was no measurable dimensional change in this material after storage of three weeks. The impression was measured with a micrometer microscope, occlusally and cervically, just before the die material was poured into the mold. The die was then measured immediately after separation at 2 1/2 hours and at 24 hours and compared with the original impression. They found that the improved stone expanded from 0.0 to 0.13%. Use of gypsum hardener increased this figure to as high as 0.21%.

Kusner and Michman[16] examined the initial contraction often seen early in the setting of gypsum materials. Both a horizontal trough and dial gauge and a mercurcy bath method were used to measure the linear dimensional changes during setting. Results indicate that there was a lag during which no changes took place, an initial contraction that maintained its maximum for a certain period (plateau), and finally an expansion.

Beginning measurement at 3.5 min., they showed that the onset and demonstration of this initial contraction is dependent to a large extent on the methods used to measure setting expansion. Thus, on the mercury bath, the initial contraction took place immediately; whereas, in the lined trough, there was a lag before the onset of contraction. This onset of contraction corresponded to the externally observed loss of glass and also to the initial setting time as measured by the Vicat needle. The time of maximum contraction, through, appeared independent of the method of measurement. When additional water was present, allowing hygroscopic expansion, there was no initial contraction exhibited.

Hollenbeck and Smith[18] compared 18 brands of hard gypsum for cost, setting time, compressive strength, and dimensional stability at various W/P ratios. A dial gauge was used to measure dimensional stability, a universal testing machine was used for strength determinations, and a Gillmore needle was used for setting time. The gypsums used in the investigation showed an average normal setting expansion of 0.1% which they felt would have no clinical significance. The correct mixing procedure and W/P ratio was strongly stressed, and several mixes were made carelessly to show the adverse effect on the physical properties.

Lautenschlager and Corbin[17] compared the linear expansion of hydrocal using an Instron Strain Gage

Extensometer for one day at various W/P ratios. They also made calculations of the apparent density of the stone and used x-ray diffraction data to indicate the porosity of the dental stones. They found that it was highly unlikely that the expansion was accompanied by deformation of the impinging crystals and that total porosity was greater than that due simply to the loss of excess water. They theorized that the remaining porosity is due to micropores formed by the impingement of the expanding crystals. The degree of porosity due to micropores increased with increasing mixture thickness and expansion. Micropores form in the wake of impinging dihydrate crystals. Thicker mixes of stone have more impingement and hence greater expansion than thinner mixes, but they also have greater micropores to fill the expanded pores. Later in the setting process, the evaporation of water eventually accounts for the total porosity of thinner mixes being greater than that of thicker mixes.

## PART II. SURFACE HARDNESS

Mahler[19] examined the surface hardness, compressive strength and flow of plaster, and hydrocal and improved stone. He chose the Rockwell Superficial Hardness Tester using the combination of the one-half inch steel ball indenter with a 15 kg. major load (scale 15y). Hardness specimens were prepared by vibrating the mix into molds formed by 1/16 inch wall tubing having an inside diameter of 1 5/8 inches and cut to a length of 1/2 inch. Glass plates were placed at each end of the mold to insure parrallel faces as well as a good surface. The W/P ratio for the improved stones that he tested was 0.23. Realizing that this is in excess of the amount of water that is theoretically needed for the chemical reation, he correlates the surface hardness with the excess water present in the specimen at the time of the test. He found that immediately after final set, the material is relatively weak and increases in hardness to approximately RHN (15y) 68 when the excess water present is about 7% at about one hour. At the point of practically no existing excess water, he found the material is at its optimum condition of RHN (15y) 86. This point was reached in about two weeks under the average laboratory atmosphere (sic) of 23% relative humidity and 74° F. He also did a correlation between surface hardness and compressive strength and found that they were closely related, although surface hardness increases faster than compressive strength during setting. He felt that surface hardness was a much better measure of the quality of a die material than compressive strength since the two were closely correlated, and compressive strength measurements were time consuming and not applicable to the practical usage of the material.

Peyton, et al.[20] investigated the properties of hardness, strength, and abrasion resistance of various brands of both regular and improved stones when subjected to special treatments of soaking in oil and water for various periods of time. They also used the Rockwell Superficial Hardness Tester with a 15y scale. Setting time was determined with a Gillmore Needle, compressive strength was conducted using a Tinius Olsen gear and screw-type machine and weight loss or abrasion resistance on their own device. They made several conclusions: improved stone attains a maximum hardness in less time than regular die stone (three days seemed optimum); immersion in either oil or water did not increase abrasion resistance and decreased the surface hardness. Improved stone is harder, stronger, and more abrasion resistant than regular die stone, and the weight loss due to abrasion decreases with time to one week, the longest period tested.

Skinner and Gordon[21] studied the surface hardness of improved stone under various conditions. The Wilson Tukon Tester with a Knoop indenter were used with loads of 500gm or 100gm. They felt that this tested only a thin shell or layer of stone and that other hardness testers produced too great a penetration of the surface during indentation. Control specimens were allowed to set against a glass surface, while other specimens set against various types of hydrocolloid to test the effect the hydrocolloid might have on surface hardness. In all cases the samples were not separated from the gel or glass for one hour after pouring and were then conditioned at 50° C (122°F) for 72 hours before testing for surface hardness. In all cases the surface hardness was lower when the material was allowed to set against the gel than when it set against glass. Various treatments to increase surface hardness, including additions of various chemicals to the mixing water and soaking the set material in saturated Borax solution or stearic acid, failed to significantly improve the material's hardness.

Jorgensen[22] examined the surface hardness of various plasters and regular stones. One part of the study investigated the role of the W/P ratio on surface hardness. They performed a large number of readings and performed all hardness tests eight days after the preparation of the specimen; i.e. about one week after any loss of water could be shown. Using a Vicker Hardness Tester with a steel ball of diameter 5.00 mm. and a load time of ten seconds, they found that hardness was greatly affected by varying the W/P ratio.

They also found that the hardness of dry plaster model is reduced by about 60% when it is soaked, but is recovered by drying. Even very small amounts of moisture cause a considerable reduction in the hardness.

Hollenbeck and Sullivan[13] investigated the claims made for three brands of gypsum hardening solutions, and at a given W/P ratio (0.22), found that they produced a slightly, but not significantly higher surface hardness, and no increase in strength. When the solutions were substituted for water, setting expansion increased greatly as much as doubling , going from 0.12% expansion to 0.26%.

Combe and Smith[14] used a Wallace Michrohardness tester (H.W.Wallace and Company, Croydon) with a 136° pyramid diamond indentor under a minor and major load of 1g and 300g respectively, and a modified Rockwell Tester (20kg load, 0.25 inch ball) to test their specimens for surface hardness. Casts were made against glass and various impression materials for measurement. Hardness was lowest when the stone set against alginate, reflecting the alginate's effect on the density and morphology of the gypsum crystals in the surface layer. Surface hardness was also lower when the material set against the other impression materials instead of a glass surface. This was due to the physical nature of the impression surface, the possible chemical reaction with additives present in the stone, as well as absorption of consituents (e.g., oils from polysulfides) into the surface of the cast.

They found that stone reached 80 to 90% of its final hardness value after two hours. The data showed that maximum hardness was obtained only on completely hydrated and dried stone. It was noted that a lower W/P ratio will increase surface hardness but other factors were also involved (i.e., humidity and temperature). Similarly, they noted that abrasion resistance is not necessarily related to hardness. They concluded by saying that the material which provided adequate working time coupled with good fluidity for a low W/P ratio represented the best combination of properties.

Toreskog, et al.[15] compared several types of die materials including improved stone. Hardness was measured by both Baby Brinell hardness and Knoop hardness tests on cylindrical specimens 12mm by 18mm. The dies were stored for 24 hours before they were tested. The flat surface of the die which had dried in contact with the silicone mold was employed for the test. They also tested abrasion resistance using an apparatus they had constructed. They found there is an apparent correlation between hardness and abrasion resistance when they plotted the Knoop hardness data with their abrasion resistance results. It was noted, however, that a higher hardness number for one die stone does not invariably give an indication that the resistance to abrasion is also greater.

Askinas, et al.[23] studied the effects that various setting environments might have on the surface hardness of hydrocal casts. Using the Knoop hardness tester, their group concluded that the greatest surface hardness was obtained by allowing the final set to take place in the ambient room environment (room temperature 78F=55%R.H.) comparing their data from both the hardness and strength, they felt that the correlation testing was low, differing from the opinion of Mahler.[19]

Johansson, et al.[24] measured the effects that various stone mixing agents, impression materials, and lubricants had on the surface hardness and dimensions of a dental stone die material. The study also evaluated the Brinell, Vickers, and Knoop hardness test methods. Data indicates that the Brinell had the lowest standard deviation in its measurements followed by the Vickers. There was no significant difference between these two, however, as measured by variance analysis (F test). The Knoop tester, however, had a much higher standard deviation in its measuring and was significantly different from the other two testers.

The surface hardness of casts was compared when they set against glass, agar-agar, polyether, polysulfide, and silicone impression materials. Specimens were stored for one month in room atmosphere in order to ensure equalization. It was found that agar-agar, polyether, and silicone materials gave a significant reduction of the surface hardness for stone mixed with water. Lubrication of the stone with mineral oil, water soluble lubricant, or a combination of the two resulted in significantly decreased surface hardness in most cases. Gypsum hardener, when evaluated as a water substitute, increased the surface hardness of stone except when set on a silicone impression material. Gypsum hardener also increased the hardness for the stone which set against the various materials (except for silicone) more than the hardness of the material which set against glass. Dimensions of the stone die were reported to be unaffected by the use of gypsum hardener rather than water.

Kaiser and Nichols[25] studied the surface hardness of die stone using the Rockwell hardness tester with the 15x scale. They tried to determine if there was a difference in surface hardness between the single pour (inverted) and double-pour (non-inverted) techniques. They also determined the effect that substituting slurry water for distilled water might have. It was found that double-pour casts showed a significantly harder surface than found on single-pour specimens according to the statistical "t" test. Analysis of the slurry data indicate slurry specimens had surfaces significantly harder than those of specimens made with distilled water, but not significantly harder than those of specimens of the double-pour technique.

## PART III. RATE OF REACTION:

Combe and Smith[14] measured the temperature rise of setting gypsum products and related this data to the rate of hydration of the material. The graph of temperature rise vs. time shows the characteristic sigmoid shape with an initial 'induction' period, when there is little crystalline growth, a rapid rise during crystalization followed by a gradual slowing down as the reactants were depleted. The length of induction period (defined as the time needed to exceed 0.4° C/min.), rate of temperature rise over the linear portion of the graph, and time to reach maximum temperature were all described as being characteristic of a particular brand.

Their results indicated that die stones in particular show a large variation in the rate of hydration. It was also noted a stone with a long induction period may show rapid crystallization once the process begins.

Docking[26] described work that had been done on the heat evolved on the setting of plaster. Graphed on standard paper, the typical sigmoidal curve was seen. A comparison was made between standard plaster, plaster with an addition of sodium chloride, and one with "killed" plaster added. Both additions increased the rate of temperature rise.

## PART IV. COMPRESSIVE STRENGTH:

Compressive strength of improved stone was tested by many researchers over the years. Mahler[27], Docking[28], Ware & McLaverty[5], Fairhurst[29], and Overberger[7] all conducted investigations into the strength properties of gypsum products and improved stone in particular. It was generally found that the W/P ratio used had a profound effect on the strength of the material with the higher ratio resulting in decreased strength.

# CHAPTER III

## METHODS AND MATERIALS

It was decided to test three widely used brands of improved stone which were believed to be representative of the market. The three brands were: Super-Cal* (Lot #011276), Vel-Mix Stone** (Lot # 020477, 8678HO), and Silky-Rock***(Lot #0285712). (See Figure I) Complimentary samples were obtained from the manufacturers and stored in sealed containers until used.

It was felt that, although dental students were instructed in the proper mixing procedure and W/P ratio for gypsum materials, they seldom practiced what they had been taught. For this reason, a survey was conducted among a group of upperclass dental students and dentists at Loyola University School of Denistry. The purposes of this survey was to

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*Coe Laboratories, Inc., Chicago, Illinois.

**Kerr Company, Romulus, Michigan.

***Whip-Mix Corporation, Louisville, Kentucky.

FIGURE I. MATERIALS TESTED

FIGURE II. SURFACE HARDNESS SAMPLE IMMEDIATELY AFTER POURING determine the number of people who normally measured the recommended W/P ratio in clinical practice and the amount of variation in the mixes of the people who do not measure the W/P ratio. This information was also used to set the limits for the various W/P ratios to be tested.

The survey was conducted by approaching upperclass dental students in the laboratory of the dental school. They were presented with a rubber mixing bowl and spatula, a pre-measured envelope containing 50 gms. of Kerr Vel-Mix, and a pre-measured vial of water containing a large excess of the amount of water needed for a satisfactory mix. It was requested that the individual, using all of the powder and as much of the water as he desired, make a mix of the stone as he normally would. If the student measured the correct amount of water with an available graduated cylinder, it was noted. Those who did not usually measure the W/P ratio, made a mix to the consistency they desired. The excess water which was not used in mixing was measured in a graduated cylinder to determine the amount of water used in the mix, and hence, the W/P ratio. The survey was conducted on 25 students and 5 dentists. Of that number, five students and none of the dentists regularly measured the recommended W/P ratio. Of the remaining people surveyed, the actual W/P ratio used in making the mix ranged from a low of 0.19 to a high of 0.30 with the average being 0.23 with a standard deviation of 0.0275. (According to the Kerr directions, the recommended W/P ratio should be 0.22 to 0.25.) From this information it was decided to test the materials at W/P range of 0.20 to 0.30 in 0.02 increments.

## MIXING PROCEDURE:

Before measuring, the container of material was agitated to insure even distribution of the material. The stone was weighed to the nearest 0.5 gm on a balance. Distilled water at room temperature was used for all mixes and measured to the nearest 0.1 ml. in a graduated cylinder. All tests were performed a minimum of five times. The measured amount of water was placed in the mixing bowl, and the powder was sifted in over a period of ten seconds. The mix was then mechanically mixed for 15 seconds in a Whip-mix Power mixer under vacuum of 28 inches of mercury. The material was then vibrated (Buffalo Vibrator No. 2, Brooklyn, New York) into the molds.

## SURFACE HARDNESS:

The Rockwell Hardness Tester, (Acco, Wilson Instrument Division, New York, New York ), with the 15y scale (one-half inch ball indentor and 15 kg. load) was used to obtain data of the surface hardness. The mixing procedure, outlined above, was rigorously followed, and the material was vibrated into a plastic ring mold measuring 1.0 inch inside diameter and a 0.25 inch high. The ring had been previously waxed to a 2 X 2 inch of glass plate using red boxing wax. Another piece of glass was then placed on the top of the ring. (See Figure II) This insured flat, parallel surfaces. This upper piece of glass was removed after 30 minutes to allow trapped water to escape and to more closely reproduce laboratory conditions. Samples were allowed to dry at room conditions of 21± 1°C, and R.H. of 40 to 65%. Specimens were tested at both 1 hour and 24 hours after the start of the mix. All hardness tests were performed on the lower side of the mold which had dried against the glass surface. (See Figure III) A minimum of ten readings were made on each sample and the data averaged. The series of mixes and hardness readings were all repeated five times.

## SETTING EXPANSION:

Linear setting expansion was measured with the use of a horizontal trough and dial gauge. (See Figures IV and V) The trough was stainless steel and measured off at 200 mm. length. The spring dial gauge, (B.C. Ames Company, Waltham, Massachusetts), mounted on a heavy slate base and graduated in increments of 0.01 mm., allowed readings to be reasonably made to the nearest 0.001± .001 mm. The trough was lined with three overlapping sheets of (0.001 inch) polyethylene to lower the coefficient

FIGURE III. HARDNESS SAMPLE AND INDENTER BALL.

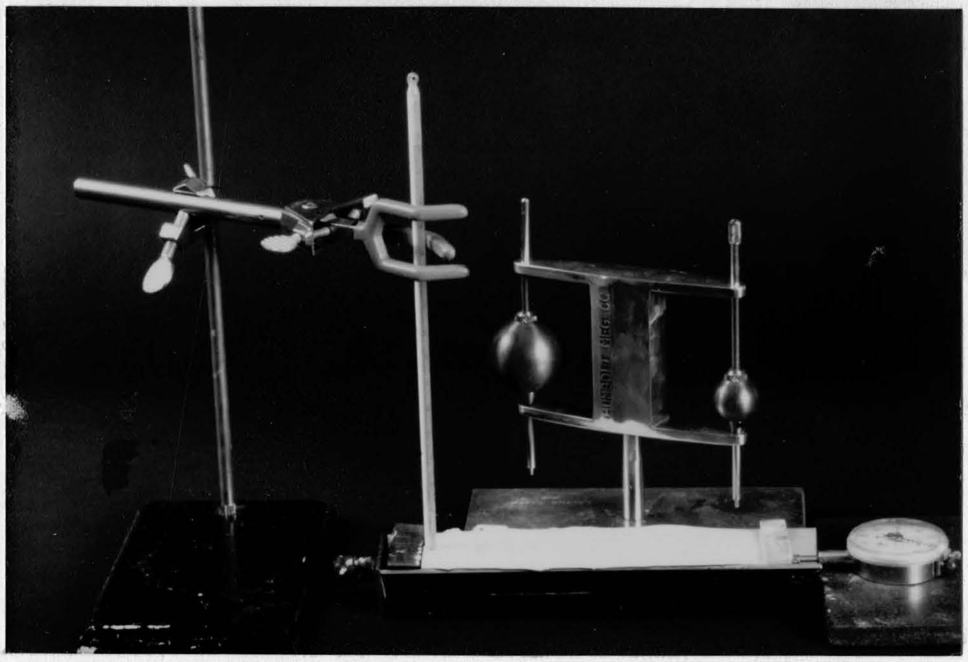


FIGURE IV. TROUGH AND DIAL GAUGE ARRANGEMENT FOR SETTING EXPANSION AND MEASUREMENT.

FIGURE V. CLOSE-UP VIEW OF DIAL AND TROUGH FOR MEASUREMENT OF SETTING EXPANSION of friction. The dial of the gauge was in contact with a freely-moving piece of plastic in the open end of the trough. (250 g. of powder were then mixed with the appropriate amount of water and vibrated into the trough.) In the early trails, readings of the gauge were made at five minute intervals. The intervals were soon changed to thirty seconds apart for the first 30 minutes, and then readings were taken every minute for the next thirty minutes. Final expansion was then calculated at one hour from the start of the mix. Five repetitions were made for each series, and the data averaged.

## SETTING TIME:

Initial and final setting times were determined using a Gillmore needle. Setting time was determined at the same time as setting expansion, indenting the material in the trough to determine setting times. Setting times were determined to the nearest 30 seconds and repeated five times.

## TEMPERATURE RISE OF THE SETTING REACTION:

One series of data included a measurement of the temperatures of the setting material. A lubricated thermometer was supported in the far end of the setting expansion trough, and the temperature change was monitored at 30 second invervals for one hour.

# CHAPTER IV

## RESULTS

Of the thirty individuals surveyed, six of them claimed to always weigh the stone to achieve the desired W/P ratio. The remainder of the people mixed improved stone with W/P ratios ranging from 0.19 to 0.30. The manufacturer recommends a W/P ratio of 0.22 to 0.25. Fourteen out of these twenty-four individuals made a mix which fell within this range. Seven people used a lower W/P ratio, and four individuals made a mix with a W/P ratio higher than the recommended range.

A summary of the surface hardness data appears in Table I. These data points are also represented in Figure VI, One-hour Surface Hardness vs. W/P ratio, and in Figure VII, 24-hour Surface Hardness vs. W/P ratio.

The data for the one-hour setting expansion of the various materials at the different W/P ratios are shown in Table II. A series was not done at a W/P ratio of 0.20 as originally scheduled. At

## TABLE I. SURFACE HARDNESS DATA (RHN 15Y SCALE):

## COMPARISON OF BRANDS AT VARIOUS W/P RATIOS AND DRYING TIMES

WATER/POWDER RATIOS

| BRAND | 0.20 | | 0.22 | | 0.24 | | 0.26 | | 0.28 | | 0.30 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ |
| Silky-Rock | | | | | | | | | | | | |
| 1 Hour | 85.64 | 1.40 | 79.91 | 1.25 | 71.16 | 1.35 | 67.60 | 2.88 | 59.49 | 3.33 | 52.76 | 3.07 |
| 24 Hours | ---- | | 86.83 | 1.79 | 84.92 | 2.25 | 80.18 | 3.14 | 74.86 | 4.07 | 69.74 | 1.62 |
| Super-Cal | | | | | | | | | | | | |
| 1 Hour | 86.30 | 1.29 | 80.57 | 0.74 | 76.83 | 1.63 | 74.60 | 2.42 | 68.72 | 1.83 | 66.96 | 1.01 |
| 24 Hours | 89.94 | 1.09 | 84.03 | 2.27 | 79.44 | 0.95 | 78.01 | 3.23 | 75.52 | 2.48 | 74.96 | 7.14 |
| Vel-Mix | | | | | | | | | | | | |
| 1 Hour | 84.18 | 1.27 | 81.99 | 1.63 | 79.00 | 2.14 | 78.38 | 1.39 | 74.72 | 0.48 | 71.73 | 3.10 |
| 24 Hours | 88.91 | 0.34 | 88.14 | 0.81 | 87.84 | 0.81 | 86.72 | 1.01 | 85.70 | 1.52 | 77.80 | 3.76 |

FIGURE VI. CORRELATION BETWEEN SURFACE HARDNESS (RHN 15Y SCALE) AND WATER POWDER RATIO

TIME = 1 HOUR

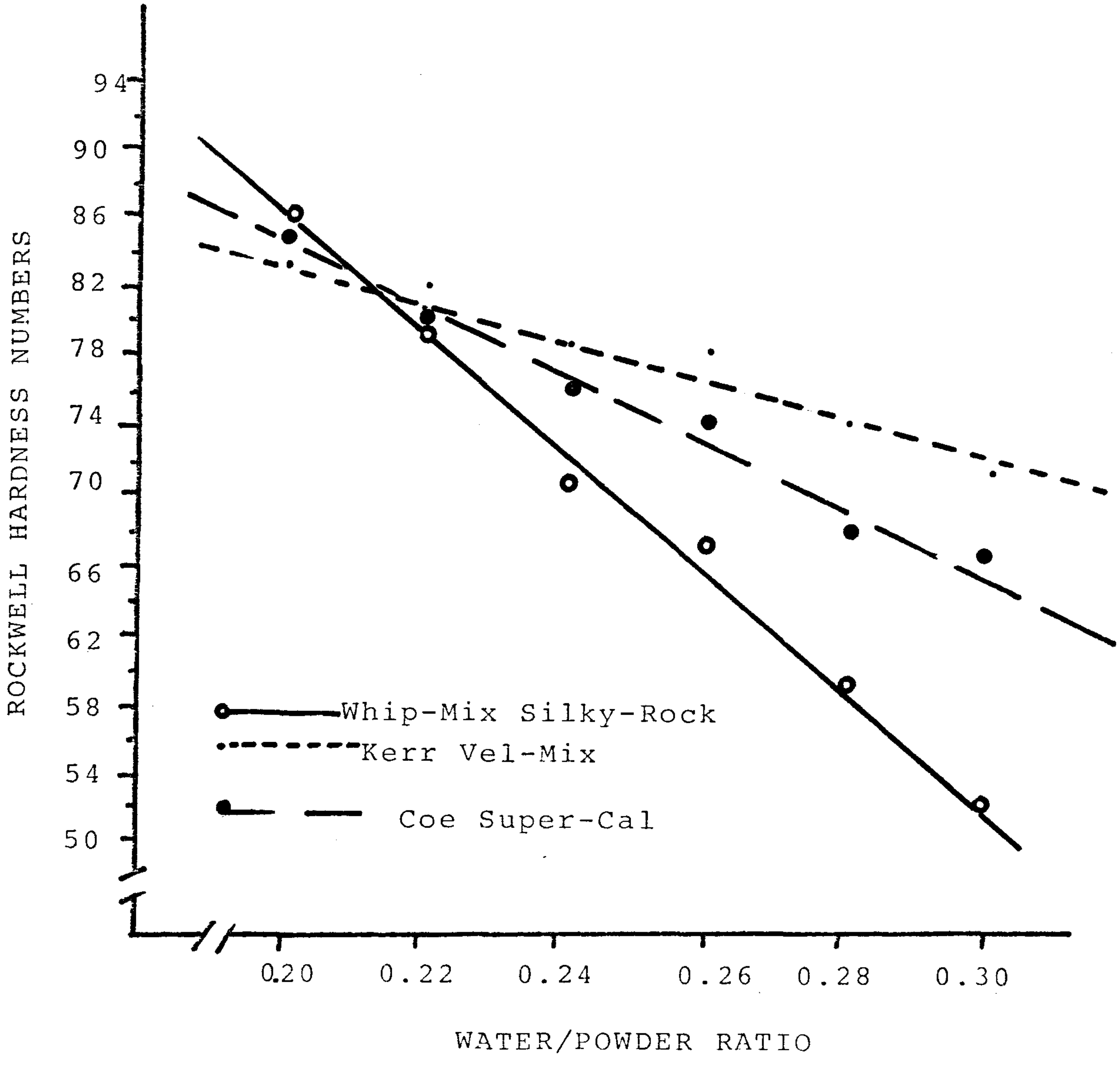
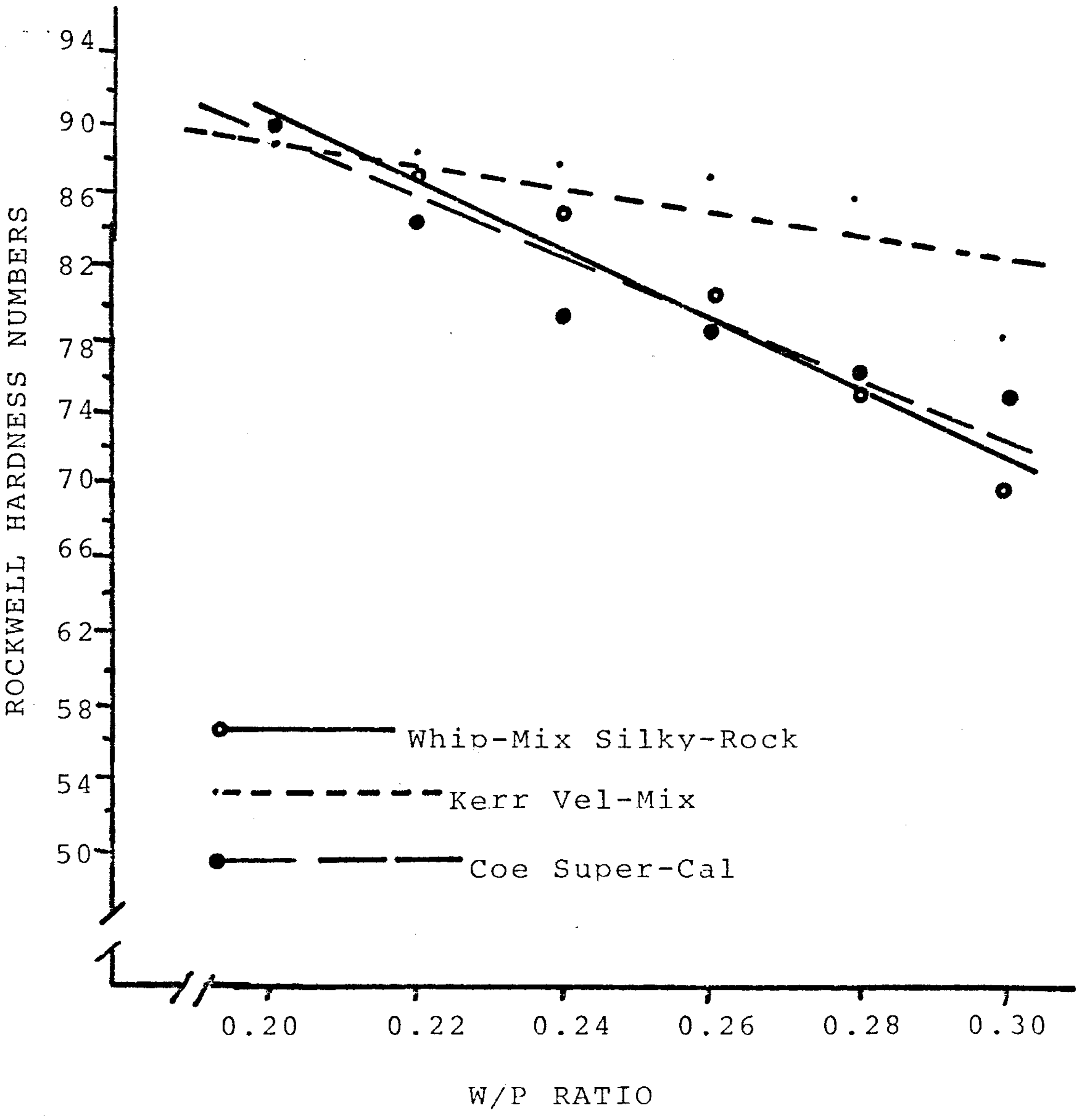


FIGURE VII. CORRELATION BETWEEN SURFACE HARDNESS (RHN L&Y SCALE) AND WATER/POWDER RATIO

TIME = 24 HOURS



# TABLE II. COMPARISON OF ONE-HOUR SETTING EXPANSION (%) AS A FUNCTION OF THE WATER/POWDER RATIO

| | Materials | | | | | |
|---|---|---|---|---|---|---|
| | Silky-Rock | | Super-Cal | | Vel-Mix | |
| W/P Ratio | $\bar{X}$ | $\sigma$ | $\bar{X}$ | $\sigma$ | $\bar{X}$ | $\sigma$ |
| 0.22 | .0705 | .0071 | .0985 | .0075 | .0642 | .0230 |
| 0.24 | .0690 | .0048 | .0952 | .0089 | .0760 | .0204 |
| 0.26 | .0903 | .0110 | .1085 | .0288 | .0954 | .0116 |
| 0.28 | .1012 | .0113 | .1081 | .0126 | .0873 | .0206 |
| 0.30 | .1083 | .0085 | .1080 | .0121 | .1240 | .0204 |

this ratio, the material was too viscous to pour smoothly into the trough. Figure VIII shows a typical curve of the setting expansion plotted as a function of time. It should be noted that all of the expansion occurs after the material has reached its final set as determined by the Gillmore needle.

Initial and final setting times as measured by the Gillmore needle are shown in Table III. The data is also presented graphically in Figure IX.

A typical curve of the temperature rise as a function of time is presented in Figure VIII.

Subjective observation of the three materials revealed that Silky-Rock had a creamier and less viscous consistency than the other two materials at a particular W/P ratio. This fact allows Silky-Rock to be mixed at a slightly lower W/P ratio to produce a satisfactory consistency. This was especially evident during the setting expansion tests when a film of water rose to the surface of Silky-Rock at higher W/P ratios. This film of excess water was not seen on the samples of either Vel-Mix or Super-Cal.

FIGURE VIII. A PLOT OF TEMPERATURE RISE AND SETTING EXPANSION AS A FUNCTION OF TIME

EXAMPLE: SILKY-ROCK, W/P RATIO = 0.24

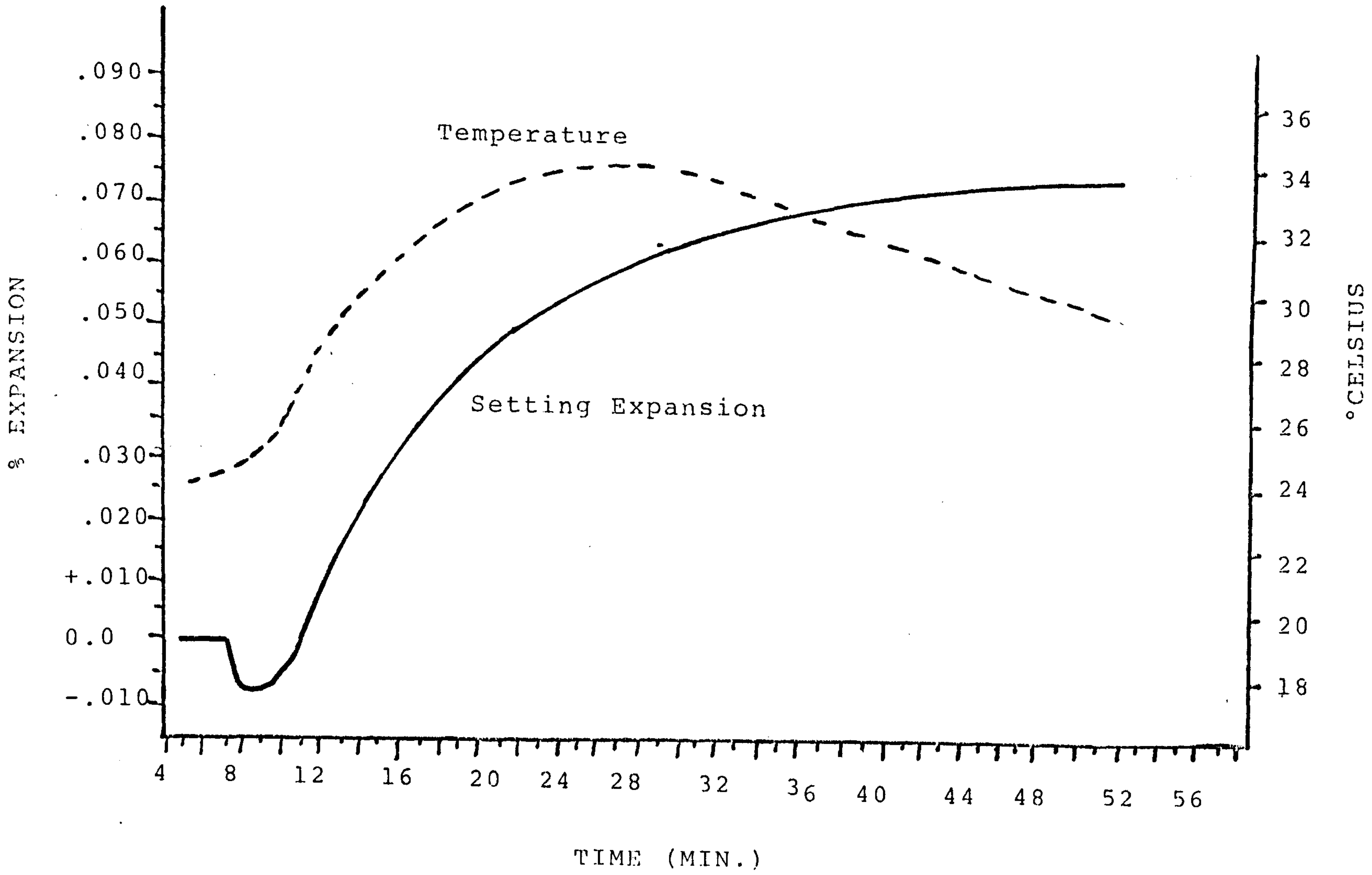
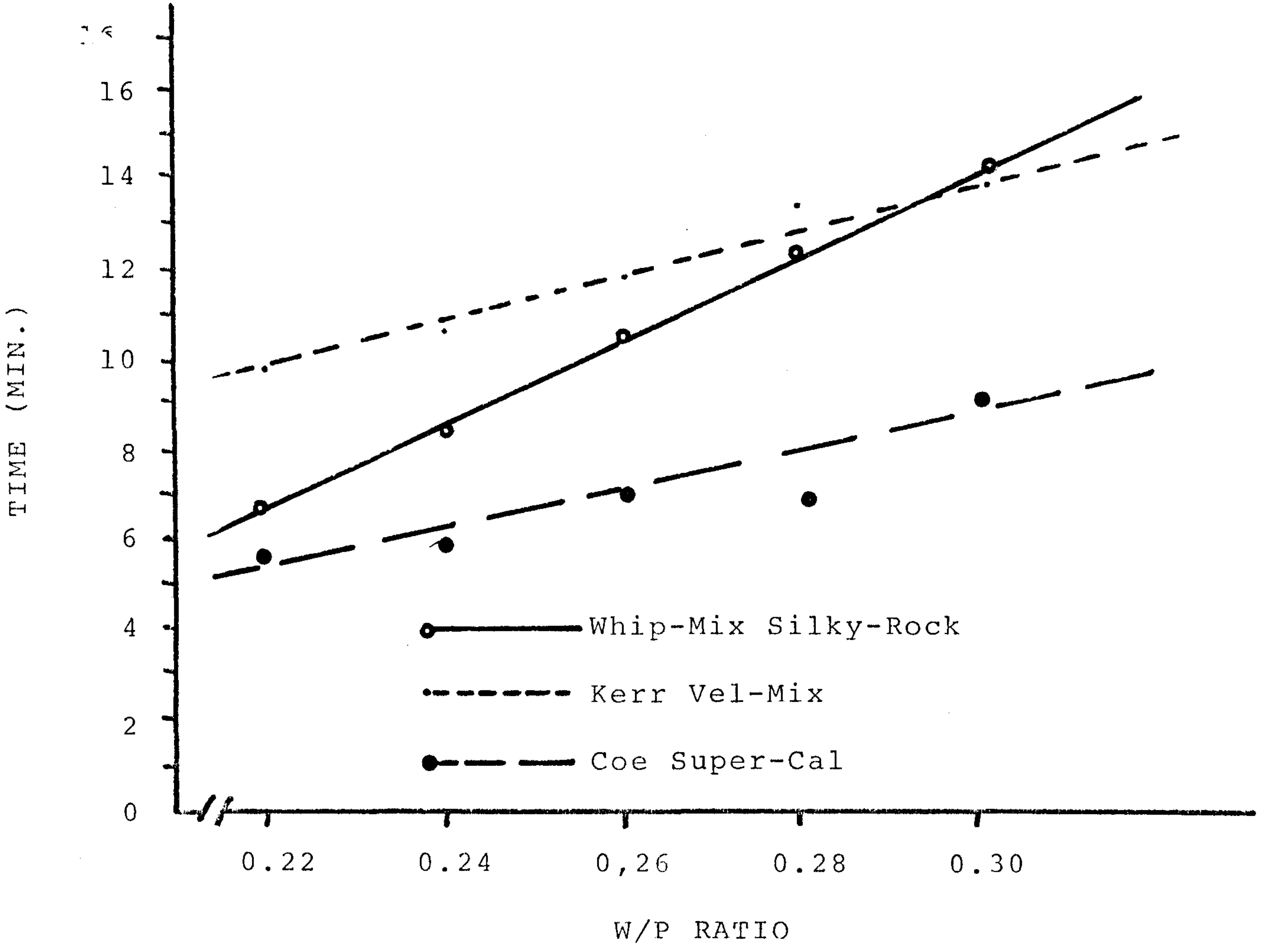


TABLE III. COMPARISON OF SETTING TIMES (MIN.) OF MATERIALS AS A FUNCTION OF THE WATER/POWDER RATIO

Materials

| W/P RATIO | Silky-Rock | | Super-Cal | | Vel-Mix | |
|---|---|---|---|---|---|---|
| | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ | $\overline{X}$ | $\sigma$ |
| 0.22 | | | | | | |
| Initial | 6.6 | 0.63 | 5.5 | 0.71 | 9.8 | 0.21 |
| Final | 8.0 | 0.71 | 7.2 | 0.76 | 11.9 | 0.42 |
| 0.24 | | | | | | |
| Initial | 8.2 | 0.29 | 5.9 | 0.75 | 10.6 | 0.54 |
| Final | 9.9 | 0.48 | 7.1 | 0.95 | 13.1 | 0.67 |
| 0.26 | | | | | | |
| Initial | 10.6 | 0.42 | 7.0 | 1.18 | 11.8 | 0.57 |
| Final | 12.7 | 0.45 | 9.1 | 1.29 | 14.5 | 0.41 |
| 0.28 | | | | | | |
| Initial | 12.1 | 0.75 | 6.8 | 0.67 | 13.5 | 0.65 |
| Final | 15.1 | 1.25 | 9.4 | 0.39 | 15.9 | 0.97 |
| 0.30 | | | | | | |
| Initial | 14.3 | 0.58 | 9.1 | 2.04 | 13.9 | 1.68 |
| Final | 16.3 | 0.26 | 12.5 | 2.81 | 17.3 | 0.76 |

FIGURE IX. COMPARISON OF INITIAL SETTING TIME OF MATERIALS AS A FUNCTION OF THE W/P RATIO



# CHAPTER V

# DISCUSSION

## PART I. SURFACE HARDNESS

Analysis of the surface hardness data reveals several facts. When surface hardness is compared as a function of drying time, the 24-hour hardness value is always greater. Using the student "t" test at a 95% confidence level, all of the 24-hour surface hardness values were significantly greater than the comparable one-hour value. This would indicate that one hour is insufficient time to allow adequate drying, even with the relatively small physical size of the die used for the samples. The time necessary for complete drying has been reported in the literature to be as long as one week. However, Peyton, et al.[20] concluded that three days is sufficient to attain maximum hardness for improved stone materials. Regular stone required a longer drying period to reach maximum hardness. The one and 24-hour time periods were selected to measure the hardness at times which a die would often be used clinically.

Allowing all samples to dry in ambient room conditions reproduces the practice routinely seen in dental offices. A study by Askinas, et al.[23] determined that "the most desirable combination of strength and hardness properties was obtained by allowing final set to take place in the ambient room environment".

Figures VI and VII show the strong inverse relationship between surface hardness and the W/P ratio. When the "best line" is calculated to fit each data series, it closely followed the actual data points. The correlation coefficient was calculated for each line. With a value of ± 1 indicating perfect correlation, the computed values ranged from a low of -0.8335 for the 24-hour series of Vel-Mix to approximately -0.9800 for the other series of data. These values indicate that nearly all of the change in surface hardness can be attributed to changes in the W/P ratio, rather than to external causes of experimental error.

Figure X is a photograph of two hardness samples which had been tested with the Rockwell hardness tester.

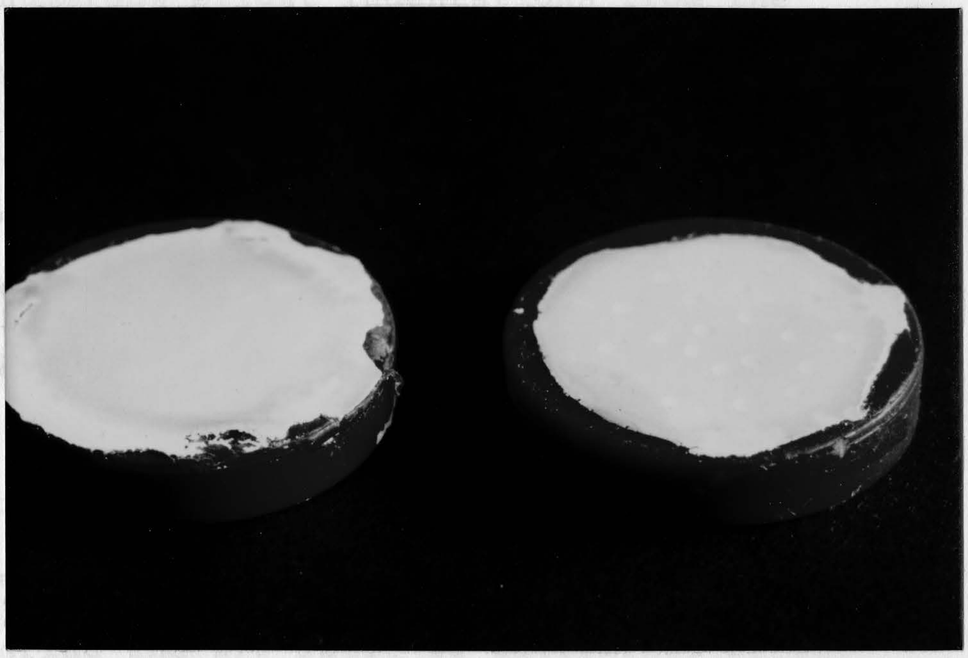


FIGURE X. COMPARISON OF TWO HARDNESS SAMPLES AFTER TEST

The sample in the left of the figure was mixed with a low W/P ratio and retains its smooth surface. The sample in the right of the photograph shows numerous slight indentations from the pentrator ball of the hardness tester. This second sample was mixed at a highwer W/P ratio and was found to have a low hardness value. This illustrates the fact that differences in the hardness values could probably be detected clinically, although the design of this study did not investigate that possibility.

The degree that a particular brand is affected by altering the W/P ratio is determined by the slope of the line for that series of data. The steeper the slope of the line, the greater is the importance of measuring the correct W/P ratio. This can be seen, for example, in Figure VI. At a W/P ratio of 0.20, there is no statistical difference in hardness between Silky-Rock and Vel-Mix. However, when the W/P ratio is increased to 0.24, there is a relatively large difference between the two with Vel-Mix significantly harder. The difference between them becomes even greater at increasing W/P ratios. To summarize, at one hour, the surface hardness of Vel-Mix is least affected by changes in the W/P ratio; Super-Cal is moderately affected; and Silky-Rock affected to the greatest degree.

The situation remains unchanged at 24 hours with the three materials maintaining their respective positions to one another. Poor mixing technique, with a large amount of excess water in a high W/P ratio can make a substantial difference in the quality of the surface of the cast.

Again, using the student "t" test at the 95% confidence level, it was found that there was very little difference between brands when the recommended W/P ratios were used. For example, when the W/P= 0.22, at one hour, there is no significant differences in surface hardness between materials. At the same W/P ratio and 24 hours, there is a statistical difference only between the two extremes, i.e., Super-Cal with RHN 15y= 84.03, and Vel-Mix with RHN 15y= 88.14. It was not determined whether this amount of difference in hardness was clinically signficant, i.e., a technician or dentist could determine whether one was noticeably harder or softer. At W/P ratios of 0.24 or greater, the surface hardness values at 2-hours are significantly different between the materials. At both a W/P of 0.26 and 0.28, Vel-Mix is harder than the other two, and there is no statistical difference between Silky-Rock and Super-Cal. At a W/P of 0.30, there was no significant difference between Super-Cal and Vel-Mix, and both were signficantly harder than Silky-Rock.

The surface hardness data collected in this investigation can be directly compared to other studies which utilized the Rockwell 15y scale as their index of surface hardness. Mahler[19] also used the Rockwell 15y scale to evaluate surface hardness. His one-hour data for Vel-Mix (W/P= 0.22) was nearly identical to the results found in this study. (RHN= 82.30 for his study; 81.99 for this one) Curiously, when he monitored hardness as a function of storage (drying) time, he reported a hardness drop after 24 hours to RHN 78.4. Hardness again increased with longer storage time with

RHN 88.9 reported after three days and RHN 91.3 reported after seven days storage. He concluded that three days storage is sufficient time for improved stone to reach its maximum hardness. He offered no explanation of the hardness drop seen in the 24 data, and statistics and standard deviation of his data were not reported. It is impossible to determine from this viewpoint whether the hardness drop he reported was significant.

The use of the Rockwell hardness tester with the 15y scale for evaluation of surface hardness appeared to be valid and useful. It gave consistent results within a rather narrow range. In the initial set-up of this investigation, several samples were tested on the Knoop hardness tester which was widely used for the evaluation of surface hardness. Accuracte readings were difficult to obtain using the Knoop tester since the border of the indentation was somewhat jagged and uneven. It was more time consuming and subject to greater error from the operator's readings. Doctor Wilmer Fames from Emory University Dental School evaluated the means of testing the surface hardness of gypsum materials, and he essentially agreed with the use of the Rockweel hardness tester for the reasons just stated.[30]

## PART II. SETTING EXPANSION

Analyzing the setting expansion data, it appears that the role of the W/P ratio is rather small. Within a single material series, although the setting expansion data appears to increase slightly with an increasing W/P, this difference cannot be detected statistically for either Super-Cal or Vel-Mix. (Student "t" test and 95% confidence level again used for statistical analysis.) Within the scope of this study, there was no significant differences found in any of the setting expansion data for Super-Cal. For Vel-Mix, there was a statistical difference found in the data only between the two W/P ratio extremes, 0.22 and 0.30. Comparing the setting expansion at these two ratios, it was found that the setting expansion increased in direct proportion to the W/P. Several statistically significant differences could be found within the series of Silky-Rock. While there was no significant difference between the values at W/P= 0.22 and W/P= 0.24, these two values were both significantly different from all the values at the higher W/P ratios. In this series too, when a significant difference was found between the data of different W/P ratios, the trend of the data was in direct proportion to the W/P.

The one-hour setting expansion data compares favorably with the reports found in the literature. The ADA Guide to Dental Materials reports that the linear setting expansion for Type IV Dental plaster ranged from 0.08 to 0.13%.[31] Hollenback, et al. (1967)[18] reported a normal setting expansion of from 0.05 to 0.12% for the "better densite materials". His 1967 evaluation of various materials included Vel-Mix and Super-Cal. He varied the W/P ratio in the range of 0.20 to 0.26 to 0.02 unit intervals, and could not detect a difference in setting expansion as a function of the W/P ratio. His data showed a one-hour setting expansion of 0.08% for Vel-Mix and 0.09% for Super-Cal. He also noted that the average normal setting expansion of 0.10% would have no clinical significance whatsoever.

Toreskog, et al.[15] included Vel-Mix and Silky-Rock in an evaluation of die materials and found a setting expansion of 0.09% and 0.12% respectively. This setting expansion was computed by comparing the occlusal measurement to a steel die at 2.5 hours after mixing. They concluded that of the eight classes of die materials they evaluated, the densite materials were superior from the standpoint of dimensional accuracy. Surveying the literature, it can be concluded that the amount of setting expansion with improved stone is not clinically significant.

The slight trend of setting expansion increasing in direct proportion to the W/P ratio that was found in the Silky-Rock and Vel-Mix is counter to the results in the literature.[12,17] It was concluded that the amount of setting expansion in gypsum materials was inversely proportional to the W/P. Jorgensen[12] noted that the W/P ratio has a "relatively slight influence on commercial dental stones and is clearly controlled by the addition of chemicals; the concentration of these salts is reduced by mixing the plaster with more water, but their anti-expansion effect is not reduced accordingly".

Concerning hygroscopic expansion, Jorgensen[12] goes on to say, "Supplementary experiments have established that the expansion of plaster is increased if a few drops of water are added during setting or if the loss or water by evaporation while setting is restricted".

Lautenschlager and Corbin hypothezied that setting expansion is caused by impinging dihydrate crystals leaving micropores in their wake. Thicker mixes of stone have more impingement, and hence, greater expansion than thinner mixes.

The anomalous data reported in this study should be viewed in terms of the material which exhibited the phenomena; i.e., Silky-Rock. As part of the pilot study for this investigation, the physical properties of Vel-Mix were tested with Whip-Mix Gypsum Hardener substituting for water. Use of Gypsum Hardner (Whip-Mix Corporation, Louisville, Kentucky) did improve the consistency of Vel-Mix and allowed a smooth mix to be made at a slightly lower Liquid/Powder ratio. Substitution of gypsum hardner for water also had an effect on the physical properties. Setting expansion (W/P= 0.24) increased from 0.09% for Vel-Mix with water to 0.14% when Gypsum Hardener was substituted. In the Hollenback & Sullivan of study of gypsum hardener, (1964)[13], they reported the one-hour setting expansion of Vel-Mix to be 0.11% (W/P= 0.22). This increased to 0.18% when gypsum hardener was employed.

It was earlier reported in this investigation that Silky-Rock had a thinner consistency than the other materials. It would lead one to conclude that Whip-Mix Corporation is employing the same salts as additives to both its Silky-Rock and its Gypsum Hardener. The large amount of excess water seen on the surface of the setting expansion test for Silky-Rock, especially at the higher W/P ratios, helps to explain the apparent anomoly. The increased expansion in direct proportion to the W/P ratio that is reported for Silky-Rock can be explained by the combination of additives and larger amount of excess water, leading to hygroscopic expansion.

When the three materials are compared to one another at W/P = 0.22, there is no significant difference between Vel-Mix and Silky-Rock, although Super-Cal had a significantly higher setting expansion than the other two. When the materials were compared at the highest W/P ratio (0.30), there were no statistical differences found between them. It is important to note, however, that although a statistical difference may be found in this investigation, the differences have been shown to be clinically insignificant.

A typical curve of setting expansion as a function of time is reported in Figure IX. Kusner & Mitchem[16] determined the expansion of plaster of Paris by several methods. Their curve of the rate of setting expansion vs. time compares very favorably with the results obtained in this investigation. They had also compared the horizontal trough with a plastic film and dial gauge to one using a mercury bath to reduce friction. There were no significant difference in the measurement of final setting expansion between the two methods, although the mercury bath arrangement showed a smaller lag period before the onset of the initial contraction.

There are several interesting portions of the graph in Figure IX to consider. From the start of measurement (T=5min.) to 7 min., there is no detectable change registered on the dial gauge. At seven minutes, the dial gauge detects a contraction which reaches its maximum of 0.10% at eight and one-half minutes. Expansion then begins and continues until it tapers off at about 50 minutes. It is also interesting to note that the initial and final setting times were 8.0 and 9.5 minutes respectively. Therefore, setting expansion occurs even though the material has reached its final set.

## PART III. SETTING TIME

Table III summarizes the data on initial and final setting times of the materials as a function of the W/P. When the setting times between the three materials are compared, it is found that they are all statistically different. Figure X represents the data in graphic form. Super-Cal was the fastest setting material followed by Silky-Rock and finally Vel-Mix. Whether or not this faster setting time seen in Super-Cal would allow earlier separation of the cast and impression was not determined. That would have to be determined by compressive strength tests performed as a function of time. The fast setting time of Super-Cal did not act to increase surface hardening at one hour, however.

Setting time was found to be directly proportional to the W/P. As the amount of excess water increases, it logically takes longer for the material to dry. It was earlier noted that at higher W/P ratios, there was often a layer of water formed on the upper surface of the material in the trough. This tended to give the material a chalky appearance and to make the determination of setting time more difficult.

The use of the Gillmore needle for the determination of setting time is highly subjective and prone to operator error. It is useful as a rough guide to setting times, but more exact determination should be made through the use of an impartial machine such as a rheometer.

## PART IV. TEMPERATURE RISE OF THE SETTING REACTION

A typical curve of the temperature rise as a function of time can be seen in Figure X. Note that there is only a slight temperature increase seen before the initial setting time. It then reaches its maximum rate of rise almost immediately after the final setting time. Due to the large bulk of material, it is theorized that this temperature graph actually lags slightly behind the actual heat of the reaction.

The temperature rise was responsible for a very small change, if any, in setting expansion due to thermal expansion. The setting expansion continues even after the temperature has peaked and fallen.

# CHAPTER VI

## SUMMARY

It has been shown that a majority of the individuals surveyed are fairly accurate in determining the correct W/P ratio by judging the consistency of the improved stone. However, a significant number of people vary from the recommended W/P ratio. The results of this investigation have shown that careless mixing can produce a significant reduction in the surface hardness of the material due to excess water. In general, low surface hardness is the biggest drawback of improved stone when compared to other die materials. Careless mixing makes this problem even more pronounced. When mixed correctly, the three brands of materials produce results which are completely acceptable.

Very slight, if any, differences in setting expansion can be attributed to differences in the W/P ratio. Again, the one-hour setting expansion data revealed that the three brands tested were comparable. The amount of setting expansion found in these materials was found by others to be clinically insignificant. It was also interesting to note that setting expansion continued long after the final setting time of the material was recorded.

Measurement of the correct W/P ratio is very important in order to obtain the highest potential of desirable properties that the materials can offer. Improper mixing procedure can reduce a perfectly acceptable material to one which is clearly inferior, especially in terms of surface hardness. Since relatively low surface hardness is the biggest disadvantage of improved stone when compared to other die materials, every effort must be made to follow the recommendations of the manufacturers in measuring the correct amount of powder and water.

This study has prompted several questions. Further investigation into the heat of setting reaction is needed to determine whether the heat evolved is due to the heat of crystalization or to energy released due to frictional forces of setting expansion. A determination of the length of the crystalization period would also be useful.

The anomoly of the direct relationship between the setting expansion and the W/P ratio that was seen in Silky-Rock also deserves further study to determine the role that the additives play on the setting expansion.

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# APPROVAL SHEET

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The thesis is therefore accepted in partial fulfillment of the requirement for the degree of Master of Science.

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