Influence of stone mixing agents, impression materials and lubricants on surface hardness and dimension of a dental stone die material

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The influence of different stone mixing agents, impression materials and lubrication methods on the surface hardness of a stone die material has been evaluated. For one impression material the dimensional effect of the mixing agents and lubrication on the dies was also studied. The stone die material was mixed with water or a gypsum hardener and allowed to set on surfaces of glass, agar-agar, polyether, polysulfide and silicone impression materials. The lubrication methods for the stone were mineral oil, water soluble lubricant and mineral oil followed by water soluble lubricant. The surface hardness was measured according to the Brinell test. The Brinell test was chosen after a comparative study of the Brinell, Vickers and Knoop hardness test methods. The results showed that gypsum hardener was preferable to distilled water. The impression materials appear to have influence on the surface hardness of stone. The effect differed on water mixed and hardener mixed stone which emphasizes the importance of the mixing agent. All lubrication decreased the surface hardness of stone. With hardener mixed stone the combination of mineral oil followed by water soluble lubricant seemed preferable. Neither the gypsum hardener nor the lubrication influenced the dimension of the stone die material.

Key-words: Dental materials; hardness; dental stone

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Dental stone die materials exhibit acceptable dimensional and detail reproducing properties when used with various impression materials (*Fusayama et al.*, 1956, *Toreskog et al.*, 1966, *Johansson et al.*, 1974). One of the problems with dental stone materials is the inferior surface hardness and resistance to wear. The adverse effects of agar-agar (*Skinner & Gordon*, 1956) and silicone impression materials (*Finger & Lockowandt*, 1971) upon surface hardness of stone further emphasizes this shortcoming. Different methods have been suggested to remedy this (*Fusayama et al.*, 1956, *Skinner & Gordon*, 1956, *Hosoda et al.*, 1962).

Since calcium sulphate dihydrate, dental stone, is soluble in water to the extent of 0.2 gr per 100 gr water at 20°C (*Jörgensen*, 1969), water soluble lubricants may reduce the surface hardness by dissolving the surface of the stone (*Peyton & Craig*, 1971). Lubricants on the order of mineral oil may not have this effect and conse-

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quently should not impair the surface hardness but are on the other hand considered to disolve the surface of a wax model thereby setting off a stress release that may cause warpage of the wax pattern and that also may impair the wetting of the wax during investing. By first subjecting the stone model to impregnation with mineral oil and then applying a water soluble lubricant it was thought that the problems of hardness reduction of the stone dies, the stress release and the impaired wetting of the wax could be avoided.

One method of increasing hardness of dental stone dies is to substitute a liquid gypsum hardener for the water (*Toreskog et al.*, 1966). *Hollenback & Sullivan* (1964) found no such increase. Both, however, reported a dimensional increase in connection with the employment of gypsum hardeners.

The aim of the present investigation was to study the influence on surface hardness of a dental stone die material of two stone mixing agents, four impression materials and three lubrication methods. The surface hardness of stone set on glass was measured for the purpose of comparison. The influence of the two mixing agents and three lubrication methods on dimension of stone dies was also studied. Furthermore a comparative study between the Brinell, Vickers and Knoop hardness tests was made in order to find the preferable method for this investigation.

MATERIAL AND METHODS

Hardness

Impression material surfaces were rendered »equivalent» to glass in regard to smoothness and gloss by making impressions of a glass surface. This was accomplished in the following way. For the elastomer impression materials adhesive solution was applied to the frosted side of a glass slab and a small piece of sheet wax was attached to each corner to secure an even (2 mm) layer of impression material. For the agar-agar material metal trays provided with mechanical retention were made allowing 4 mm thickness of impression material. Impression materials were prepared according to specifications and spread on slabs or trays. A glass plate was then placed on top of the impression material and gently pressed down in contact with the stops. Elastomers were allowed to polymerize for 30 minutes in room atmosphere. Agar-agar impressions were immediately transferred to a humidor where they were allowed to gel for 40 minutes. Copper tubes (No 20) were fixed to elastomer impression materals with each specific adhesive solution. To agar-agar impressions copper tubes were attached through mechanical retention obtained by making funnel shaped perforations around the edges of each tube which was then pressed down into the gel. To the glass surface the copper tubes were sealed with wax.

The stone die material[1]) was mixed according to specification by the manufacturer. In order to avoid systematic errors from the mixing procedure specimens were randomized and numbered. In odd numbered series the stone hemihydrate was mixed with distilled water (v/p-ratio 0.22) and in even numbered series the stone was mixed with a gypsum hardener[2]) (v/p-ratio 0.22). Each series consisted of 10 cylindrical specimens with a diameter of 12 mm and a height of 10 mm. Specimen series were made with

[1]) Vel Mix Stone, Kerr Mfg Co, Detroit, Mich., USA

[2]) Gypsum Hardener, Whip Mix Corp., Louisville, Ky., USA

stone hardened on glass surface, agar-agar[3]), polyether[4]), polysulfide[5]) and silicone[6]) impression materials. The stone was mixed and poured immediately after the copper tubes had been attached to the impression material. In the case of agar-agar impressions the stone was allowed to set in a humidor while specimens cast on glass and elastomers set in room atmosphere. All specimens were stored for 1 month in room atmosphere in order to ensure equalization.

Control series received no lubrication treatment. Series treated with mineral oil were immersed and kept under vacuum for 5 minutes whereafter excess oil was wiped off. Series treated with water soluble lubricant were immersed for 10 minutes whereupon the excess lubricant was wiped off. Series treated with mineral oil in combination with water soluble lubricant were first immersed in mineral oil and kept under vacuum for 5 minutes whereafter the excess oil was wiped off and the specimens immersed in water soluble lubricant for 10 minutes whereupon the excess lubricant was wiped off. The surface hardness tests were performed immediately after removal of excess lubricant except in those series where hardness tests were delayed for 60 minutes. A randomized lubrication schedule was used in which the control series were included.

In order to decide which one of three surface hardness testing methods to use a comparative study was performed between the Brinell, Vickers and Knoop tests. The Brinell macro hardness tests were performed in a SPV Durometer (Alfa D 11). The diameter of the indenter steel ball was 2.5 mm and the load (15,625 kp) was maintained for 30 seconds. The Vickers tests were carried out in the same Durometer with a Vickers Diamond Pyramid (136°) and the load (15,625 kp) was maintained for 30 seconds. The Knoop tests were performed in a Tucon testing instrument with a load of 1 kp maintained for 30 seconds. The specimens selected for this study, stone set on agar-agar, were chosen at random and did not receive any lubrication treatment. Each specimen received 4 indentations. After indentation the stone surface was dusted with silver powder in order to facilitate the reading. The Brinell and Vickers indentations were measured with a Leitz linear measuring microscope (TBS-5C). The average of two diameters was recorded for the Brinell test while the average of two diagonals was recorded for the Vickers test. In the Knoop test the long diagonal was measured directly in the instrument. Two series of ten specimens each were submitted to the three hardness testing methods.

Dimension

A steel master die (Gauge Block[7]) no. 1, 6,500 mm between the measurement surfaces) was mounted in an impression device. An acrylic tray was made in such a way that it permitted only one position. The space between each of the five surfaces of the master die and the corresponding surfaces of the tray allowed a uniform (3 mm) layer of impression material. Impressions were made with a silicone[6]) elastomer, selected at random. Stone dies were cast immediately upon separation from the master die. In this study 14 series each of 5 specimens were used. Before being subjected to the lubrication treat-

[3]) Surgident, Lacotna Corp., Philadelphia, Penn., USA

[4]) Impregum, ESPE, Seefeld, Oberbay., B.D.

[5]) Permlastic Lightbodied, Kerr Mfg Co., Detroit, Mich., USA

[6]) Xantopren Blue, Bayer, Leverkusen, B.D.

[7]) C. E. Johansson, Co, *Eskilstuna, Sweden*

ment all stone dies were measured twice each by two observers using a micrometer no. 170[7]) which had been calibrated to the master die. After lubrication treatment the dies were measured in the same way. The control series were included in this schedule although they had not been subjected to lubrication treatment.

Statistical methods and significance levels

The t-test was used to establish the significance level between observed means.

Variance analysis was performed (F-test) to compare the hardness test methods.

Significance levels		Probability
xxx	highly significant	$p \leq 0{,}001$
xx	significant	$0{,}001 < p \leq 0{,}01$
x	almost significant	$0{,}01 < p \leq 0{,}05$

RESULTS

Hardness

The result of the comparative study between the Brinell, Vickers and Knoop hardness test methods is shown in Table I. The standard deviation values for the Knoop test method are higher than for the other two. Variance analysis (F-test) indicates a significant difference ($p < 0.001$). No significant difference could be observed between the Brinell and Vickers

Table I. *Comparison between Brinell, Vickers and Knoop hardness test methods*

Hardness test	Mixing agent for dental stone			
	Distilled water		Gypsum hardener	
	$\bar{x}$	S.D.k	$\bar{x}$	S.D.k
Brinell	29.7	1.8	51.8	3.3
Vickers	30.9	2.4	55.0	2.6
Knoop	39.3	7.4	56.0	10.8

7) C. E. Johansson, Co, Eskilstuna, Sweden

Table II. *Surface hardness of a dental die stone expressed in Brinell hardness numbers. Hardness tested immediately after lubrication*

Mixing agent	Surface lubrication method	Stone set on surface of											
		Agar-agar			Polyether			Polysulfide			Silicone		
		$\bar{x}$	S.D.k	S.E.M.	$\bar{x}$	S.D.k	S.E.M.	$\bar{x}$	S.D.k	S.E.M.	$\bar{x}$	S.D.k	S.E.M.
Distilled water	none	29.7	1.8	0.6	26.3	1.9	0.6	42.8	1.9	0.6	39.6	2.4	0.8
»	mineral oil	30.3	3.2	1.0	19.0	1.6	0.5	43.8	1.8	0.6	38.9	1.8	0.6
»	water soluble lubricant	24.9	2.1	0.7	16.9	0.9	0.3	29.2	1.7	0.5	23.6	0.7	0.2
»	mineral oil and water soluble lubricant	20.4	1.1	0.3	18.7	0.9	0.3	29.7	1.6	0.5	26.3	1.3	0.4
Gypsum Hardener	none	51.8	3.5	1.2	55.8	1.6	0.5	53.6	3.1	1.0	39.8	2.1	0.7
»	mineral oil	43.7	5.9	1.9	54.2	3.2	1.0	53.6	2.1	0.7	39.8	1.6	0.5
»	water soluble lubricant	37.8	4.5	1.4	47.7	4.1	1.3	44.2	1.8	0.6	26.5	1.9	0.6
»	mineral oil and water soluble lubricant	47.0	4.8	1.5	51.0	2.2	0.7	42.8	3.6	1.1	30.6	1.1	0.3

tests. The results of the surface hardness tests on stone die material are listed in Tables II and III. The mean values exhibited significant differences for several variables studied. Thus the gypsum hardener significantly increased the stone surface hardness except for stone set on silicone. For the nonlubricated stone the increase varied between 18 and 112 per cent. (Fig. 1). Surface hardness of stone set on impression materials and glass are compared in Fig. 3. Compared with glass agar-agar, polyether and silicone materials gave a significant reduction of the surface hardness for stone mixed with water while on the other hand the hardness of hardener mixed stone was improved on polyether and polysulfide whereas silicone inflicted a decrease. The lubrication of the stone with mineral oil, water soluble lubricant or

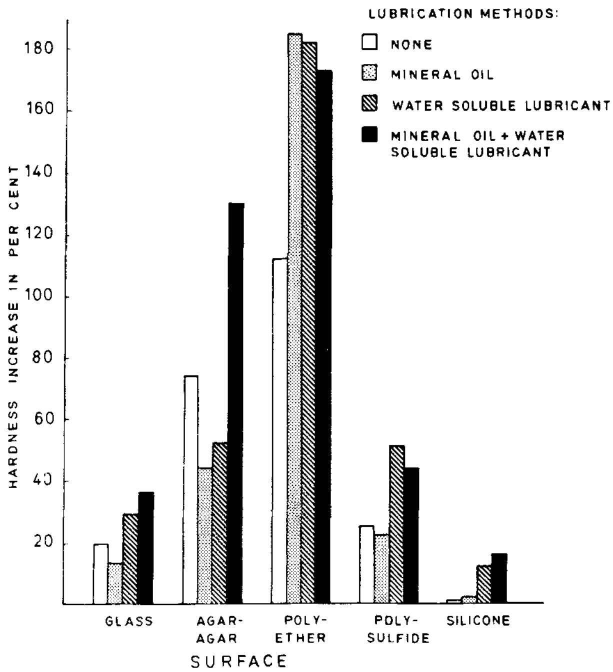

Fig. 1. Per cent increase in surface hardness of stone mixed with *gypsum hardener* compared with stone mixed with *distilled water.*

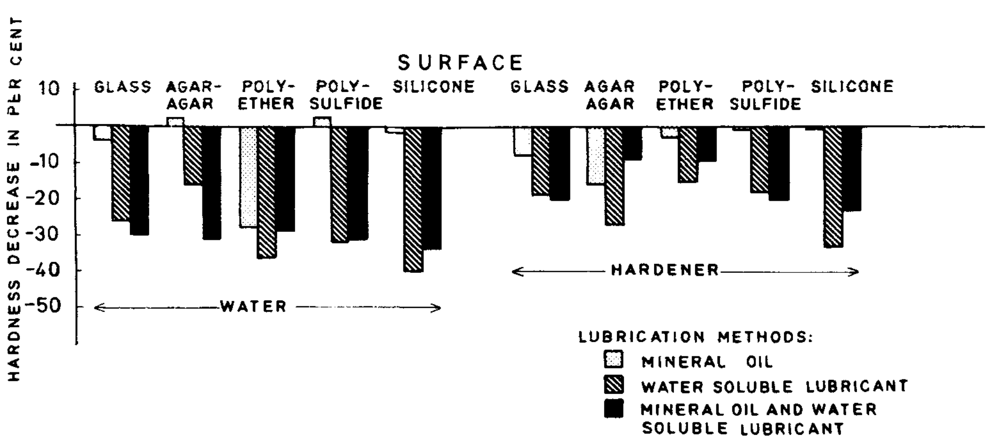

Fig. 2. Per cent decrease in surface hardness of lubricated stone compared with stone not lubricated.

a combination of the two resulted in significantly decreased surface hardness in most cases (Fig. 2). Mineral oil on the other hand reduced the hardness only for water mixed stone set on polyether and for hardener mixed stone set on glass and agar-agar. In the other series the mineral oil did not appear to reduce the hardness. This, however, seems to be only of temporary nature and eventually hardness reduction will result (Table III). The water soluble lubricant significantly reduced the hardness of stone set on all impression materials studied. Also when the stone was treated with both oil and water soluble lubricant a significant reduction was

Table III. *Surface hardness of dental die stone set on glass. Hardness (B.H.N.) tested immediately and one hour after lubrication*

Mixing agent	Surface lubrication method	Hardness Immediately $\bar{x}$	S.D.k	S.E.M.	After 1 hour $\bar{x}$	S.D.k	S.E.M.	Difference
Distilled water	none	42.5	1.4	0.4	—	—	—	—
»	mineral oil	41.0	3.1	0.8	27.2	3.3	1.1	13.8***)
»	water soluble lubricant	31.5	0.9	0.3	30.8	2.0	0.6	0.7
»	mineral oil and water soluble lubricant	29.8	2.8	0.9	28.6	1.5	0.5	1.2
Gypsum Hardener	none	50.5	1.8	0.5	—	—	—	—
»	mineral oil	46.3	0.9	0.3	32.3	1.5	0.5	14.0***)
»	water soluble lubricant	40.7	1.6	0.5	40.7	2.2	0.7	0.0
»	mineral oil and water soluble lubricant	40.5	2.8	0.9	40.5	2.7	0.9	0.0

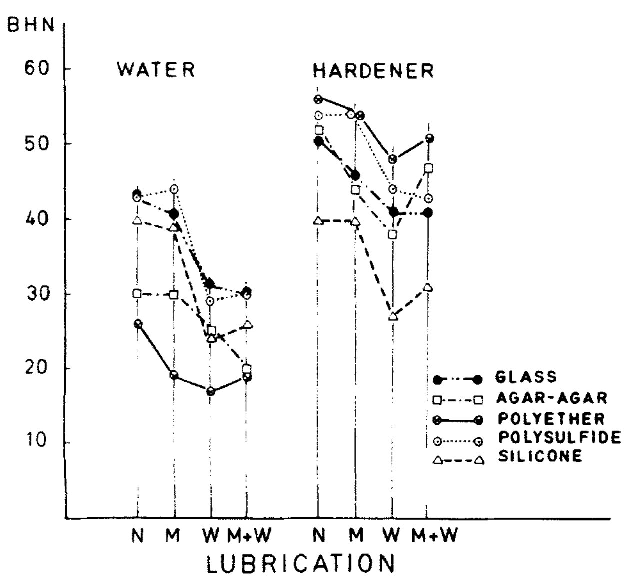

Fig. 3. Influence of impression materials and lubrication methods on surface hardness of stone material. N = none, M = mineral oil, W = water soluble lubricant, M+W = mineral oil and water soluble lubricant.

Table IV. *Comparison in per cent between two lubrication methods: water soluble lubricant only, and a combination of mineral oil and water soluble lubricant. Positive values indicate greater surface hardness of stone treated with the combination method*

Mixing agent	Stone set on surface of Glass	Agar-agar	Polyether	Polysulfide	Silicone
Distilled water	—5.4	—18.1***)	+10.7***)	+1.7	+11.4***)
Gypsum Hardener	—0.5	+25.3***)	+ 6.9*)	—3.2	+15.5***)

Table V. *Influence of mixing agents and lubrication methods on the dimension of dental stone dies*

Mixing agent	Surface lubrication methods	Dimension (mm) Before lubrication	Immediately after lubrication	1 hour after lubrication
Distilled water	none	6,515	6,515	
»	mineral oil	6,521	6,522	
»	»	6,507		6,507
»	water soluble lubricant	6,509	6,512	
»	»	6,515		6,519
»	mineral oil and water soluble lubricant	6,523	6,525	
»	»	6,522		6,525
Gypsum Hardener	none	6,520	6,519	
»	mineral oil	6,515	6,515	
»	»	6,524		6,524
»	water soluble lubricant	6,512	6,513	
»	»	6,521		6,524
»	mineral oil and water soluble lubricant	6,523	6,523	
»	»	6,518		6,519

obtained. Table IV presents a comparison between the two lubrication methods: water soluble lubricant only and the combination between mineral oil and water soluble lubricant.

Dimension

Measurements of the stone die series are listed in Table V. Neither the gypsum hardener nor the lubrication appears to have any significant influence on the dimension of the stone dies.

DISCUSSION

Hardness may be defined as resistance to indentation. But since indentation will cause both plastic and elastic deformation, physical properties such as compressive and tensile strength and ductility will be encountered. Because of the complex nature of hardness, different materials will behave quite differently to indentation, making comparison between them more or less irrelevant and even erroneous. Comparative hardness studies of one material subjected to different handling procedures, on the other hand, make comparative investigations more relevant.

The hardness tests most commonly used are the Brinell, Vickers and Knoop methods. Unfortunately hardness test of materials such as plaster and dental stone have poor reproducability probably because of the heterogenous material (*Jörgensen*, 1969). In many respects a scratch test more adequately simulates the forces excerted on a die and would consequently be a more satisfactory way of testing. There is, however, no record of better reproducability on plaster of such a method than of the established hardness tests.

The comparative study of the three indentation methods for this investigaticn showed the Knoop method to be the least suitable. The considerably greater variance values of the Knoop test must in this case be attributed to difficulties in the reading of indentations. These difficulties were even more accentuated in the micro hardness tests which were attempted but abandoned due to insurmountable problems of reading the indentations. Furthermore the micro hardness recordings may vary considerably depending on whether the indentor hit solidly on a crystal or in a pore. Consequently micro hardness tests do not seem very suitable for porous materials such as plaster and stone. No ranking should be done between the Brinell and Vickers methods. Vickers values, however, were consistantly higher than the Brinell values, which corresponds to the results of a somewhat similar comparative test on gold alloys by *Barton et al.* (1973), who also found the coefficient of variation to be slightly less for the Brinell test than for the Vickers test. The common assumption that the Vickers and Knoop tests are more precise than the Brinell test has not been verified in this investigation.

The mixing agent Gypsum Hardener, compared to distilled water, increased the surface hardness of stone except when set on a silicone impression material. After lubrication, however, the hardness of the hardener mixed stone significantly exceeded that of the water mixed stone also when set on silicone although the difference was not as large as for stone set on other impression materials and on glass. The results of this study in regard to the mixing agents corroborate the conclusions of *Toreskog et al.* (1966).

The influence of impression materials on the hardness of stone is quite clear but rather complex. With water mixed stone most impression materials gave less hardness to the stone than a glass surface corroborating the findings of *Finger & Lockowandt* (1971). With hardener mixed stone most impression materials gave equivalent or greater hardness to the stone than what a glass surface did.

Lubrication of the stone dies caused a significant decrease in surface hardness. The absence in some series of this immediate effect from mineral oil seems to be only temporary. It is interesting to note that hardener mixed stone in regard to surface hardness was less influenced by lubrication than water mixed stone. This further emphasizes the positive effect of the gypsum hardener.

Neither gypsum hardener nor lubrication influenced the dimension of stone dies in this study. This is contradictory to the conclusions of *Toreskog et al.* (1966), who reported gypsum hardener to increase the dimension of stone dies. One explanation for this may be their use of different water-powder ratios when mixing with water (0.23) and with gypsum hardener

(0.21). In the presented study a water-powder ratio of 0.22 was used for both mixing agents.

Conclusions

1) The mixing agent Gypsum Hardener is preferable to distilled water. It gives superior surface hardness to dental stone in combination with all tested impression materials and lubrication methods.

2) The two presumably most commonly used lubrication methods: water soluble lubricant only and the combination of mineral oil followed by water soluble lubricant both decrease surface hardness of stone. With hardener mixed stone the combination method seems preferable.

3) The dimension of stone dies is not affected by gypsum hardener and/or lubrication.

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