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THIOKOL AS A DENTAL IMPRESSION MATERIAL

by

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About two years ago a new type of elastic impression material, based on the synthetic rubber Thiokol, was placed on the market. The material is supplied in two tubes, the contents of which are mixed to a homogeneous paste before use. At or above room temperature the mix will quickly polymerize to form a rubbery mass. The manufacturers assert that the material is strong, very elastic, and undergoes little dimensional change during polymerization and subsequent storage.

So far, this material has only been briefly and preliminarily mentioned in the dental literature (*Jørgensen,* 1954, *Pearson,* 1955, *Rosenstiel,* 1955, *Schwindling,* 1955, *Tylman,* 1954, and *Östlund,* 1954). According to this literature Thiokol seems to be suited for dental impression work. The physical properties of the material and of the various commercial products are, however, only briefly described.

CHEMISTRY

The technical literature contains full information about the manufacture, chemical structure, reaction chemistry and physical properties of Thiokol *(Fettes & Jorczak,* 1950. *Thiokol Chemical Corporation).*

The manufacture of Thiokol (the name registered at U.S. Pat. Off.) is patented and takes place only at the Thiokol Chemical Corporation in New Jersey. The substance is a polysulfide poly-

mer, and in the form in which it is used as a dental impression material (Thiokol LP 2) its average formula is,

$$HS - (C_2H_4 - O - CH_2 - O - C_2H_4 - S - S)_{23} - C_2H_4 - O - CH_2 - O - C_2H_4 - SH$$

This macro-molecule has sometimes mercaptan (—SH) side groups. LP 2 is a brownish, syrupy liquid with a molecular weight of about 4000. When heated it becomes definitely thinner. The viscosity is, for example, 44000 cp at 25° C, and 22000 cp at 37° C.

The mercaptan groups form salts with metallic oxides, and it has been found that especially lead peroxide. (PbO_2) reacts very quickly with these groups, also at room temperature. If the group ($C_2H_4 - O - CH_2 - O - C_2H_4$) is called R, the formula of reaction may be written as follows,

$2HS - (RSS)_{23} - R - SH + PbO_2 \rightarrow - S - (RSS)_{23} - R - S - Pb - S - R - (RSS)_{23} - S - + 2H_2O$. On reaction of LP 2 with PbO_2 the molecular size is increased at the same time as the viscosity becomes higher. If a sufficient amount of lead peroxide is present, the mix is converted into a rather soft rubber compound. The usual ratio is 8 parts PbO_2 to 100 parts LP 2; lower proportions of PbO_2 result in incomplete polymerization.

The rate of reaction between LP 2 and PbO_2 can be controlled by the following factors inter alia,

(1) The particle size of the lead peroxide. The smaller particle size, the faster and more complete polymerization.

(2) Temperature. The rate of reaction is approximately doubled with every temperature rise of 10 C°, at least within the range 20—70° C.

(3) Relative humidity. At high degrees of humidity the reaction is much quicker than at low degrees, provided that LP 2 is in equilibrium with the humidity at the time it is mixed with PbO_2. Incorporation of small quantities of water during mixing will also accelerate the reaction.

(4) Retarders. Stearic and oleic acids in small amounts (1—3 per cent) retard the cure considerably. The solid stearic acid is insoluble in LP 2 and is therefore difficult to mix with the latter without a special apparatus. The liquid oleic acid can without difficulty be mixed with the polymer.

Several substances besides PbO_2 are capable of polymerizing LP 2, but as PbO_2 seems to be used in all the dental brands, they are of minor importance in this connection.

CONSISTENCY

It is rather difficult and inconvenient for the dentist to mix powdered PbO_2 with Thiokol, and the mix obtained is too thin for the majority of clinical applications, especially for taking impressions of teeth. The manufacturer can to a large extent control the consistency of the paste by (1) mixing the Thiokol with chemically inactive powders, such as plaster of Paris, kaolin and chalk, and (2) dispersing the PbO_2 powder in an inactive oil as dibultyl phthalate or others. The powder tends to separate from the oil and render the mix inhomogeneous. Some brands of dental Thiokol impression materials exhibit this tendency to inhomogeneity, which makes it impossible or at any rate difficult to dose the proper quantity of accelerator (i.e. PbO_2 paste). Other brands contain special carriers in the lead peroxide paste and seem to be quite homogeneous (Table 1).

Table 1

No.	Name	Manufacturer	Homogeneity of the accelerator
1	Coe-flex	Coe Laboratories Inc., U.S.	good
2	Duro-Flex	Tanrac Ltd., Sweden	fair
3	Flexico	Flexico Developments Ltd., England	fair
4	Momflex	Swedia Dental-Industri AB, Sweden	good
5	Permaflex A[1]	Dentax Dental, Germany	bad[3]
6	Permaflex B[2]	» » »	bad[3]
7	Permlastic	Kerr Manufacturing Co., U.S.	good
8	Rubber Base	Scania Dentalmaterial AB, Sweden	fair
9	Soft-flex	M. Laserow, Sweden	fair
10	Sta-tic	Stalite Inc., U.S.	good
11	Sta-tic X	» » »	good

[1] Dark PbO_2 paste.
[2] Light PbO_2 paste.
[3] Screw cap partly dissolved.

The consistency of the various commercial products were tested in the following way: the paste was mixed according to the manufacturer's directions; 0.5 ml of the mix was measured in a syringe of a special design (described in A.D.A. specification No. 8) and placed in the middle of a glass slab. 90 seconds after start of mix the paste was subjected to a load of 150 g, so that it was squeezed out to form an almost circular disc; at the end of 10 minutes its size was measured as the average of two diameters at right angles to each other. All measurements were

Table 2

Brand No.	Consistency mm			
	Individual measurements			Average
1	23.25	— 25.0	— 25.0	24.4
2	24.0	— 24.5	— 26.0	24.8
3	24.0	— 25.0	— 25.0	24.7
4	21.5	— 21.5	— 22.0	21.7
5	30.5	— 29.75	— 29.0	29.7
6	26.25	— 24.5	— 27.5	26.1
7	36.0	— 36.0	— 36.25	36.1
8	21.5	— 23.5	— 24.0	23.0
9	27.0	— 27.5	— 28.25	27.8
10	29.0	— 29.25	— 29.5	29.3
11	33.0	— 33.5	— 34.0	33.5

taken at room temperature ($22 \pm 1°$ C) after the pastes had been stored for at least a week at a relative humidity of 80—85 per cent. In case of the quick-curing brand No. 4 the load was applied 45 seconds after spatulation was commenced, and in case of No. 11, which is to be stirred for 120 seconds, after 150 seconds. For each brand three consistency tests were made from three different packages, which as far as possible were bought at different times over a period of 6 months. Exceptions from this rule were made in these and the subsequent tests for No. 3 and 4, which are new on the market, and No. 9, which is not yet obtainable.

Table 1 contains a list of the commercial products tested, together with an evoluation of the homogeneity of the PbO_2 paste

(accelerator), in most cases based on samples from at least 10 different packages. Table 2 shows the results of the consistency tests.

The consistency for the brands No. 1, 7, and 8 were also tested in other mixing proportions than those stated as normal by the manufacturers. In one experimental series the amount of accelerator was halved, in another it was doubled. Table 3 shows the values for the latter tests (column 2 and 4 respectively) as well as for those with normal proportioning (column 3).

Table 2 shows rather considerable differences between the viscosity of the various brands in a freshly mixed condition. The most viscous products (No. 1, 2, 3, 4 and 8) are probably better

Table 3

Brand No.	Consistency mm		
	1/2 portion accelerator	1 portion accelerator	2 portions accelerator
1	26.8	24.4	21.3
7	36.4	36.1	34.3
8	25.4	23.0	22.1

suited for impressions for inlays and crowns, since they are capable of removing air-bells from the preparation surfaces more easily than thin mixes. The thin products (especially No. 7 and 11) are perhaps best suited for mucostatic denture impressions. On the other hand, this difference between the brands does not seem to be of much clinical importance within this field of application, inasmuch as all the Thiokol impression materials are mucostatic in nature.

Table 3 seems to show that the higher the proportion of accelerator is, the thicker will be the pastes. It must be taken into account, however, that an acceleration of the cure will reduce the time during which the mix is allowed to flow between the glass slabs. The values in the second and third columns in Table 3 are therefore somewhat too high in proportion to the corresponding values in the fourth column, just as those in the second column are somewhat too high in proportion to those in the third column. Subjectively, no material difference was found between the differently proportioned mixes.

CURING TIME

It is of considerable interest for practice to establish the manipulation time of the Thiokol pastes, i.e. the time elapsing from spatulation is commenced until the polymerization has rendered the mix too stiff to be used as an impression material. No objective method is known by which it is possible to determine the consistency of the mix at the stage where it can no longer be used for taking impressions. Subjectively, this stage can be established with fair accuracy as far as the homogeneous brands are concerned: ± 10 seconds for the quick-curing brands, ± 40

Table 4

Brand No.	Manipulation time. Minutes. Seconds		
	½ portion accelerator	1 portion accelerator	2 portions accelerator
1	6.30	4.00	3.00
2	4.00	3.30	1.50
3	3.30	2.20	0.30
4	1.45	1.00	0.30
5	3.00	2.30	1.20
6	2.00	1.40	0.30
7	6.00	5.30	3.30
8	4.00	3.15	2.30
9	4.00	2.00	0.45
10	5.00	3.00	0.30
11	9.00	8.00	5.00

seconds for the slow-curing brands, and ± 20 seconds for those with medium curing time (approximate values). The end of the stage of clinically suitable consistency is characterized as follows: (1) the paste is no longer flowing from the spatula to form part of the paste remaining on the mixing slab, (2) the spatula can no longer be drawn slowly through the paste without appreciable resistance, (3) slow withdrawal of the spatula from the paste does no longer form unbroken strings, several centimeters in length.

The manipulation time was determined after storage of the pastes for at least 14 days at a relative humidity of 80—85 per cent. The experiments were performed at room temperature

(22 ± 1° C). The samples were drawn from different packages as described above, and each brand submitted to at least 5 tests. Further, the manipulation time was determined for mixes with half and twice the amount of accelerator indicated by the manufacturers as the standard dose. The results appear from Table 4.

As expected the findings show that the manipulation time of the Thiokol pastes may be varied within a relatively broad range by altering the proportions of the mix, since increased amounts of PbO_2 paste promote the cure. The inhomogeneous pastes showed much greater fluctuations in the manipulation time than

Table 5

Brand No.	Manipulation time. Minutes. Seconds.	
	80—85 % relative humidity	45—50 % relative humidity
1	4.00	4.30
2	3.30	4.45
3	2.20	2.20
4	1.00	1.15
5	2.30	3.00
6	1.40	1.45
7	5.30	6.00
8	3.15	4.30
9	2.00	2.20
10	3.00	9.00
11	8.00	9.00

did the homogeneous. Thus brand No. 5, having an average manipulation time of 2^{30} minutes, varied between 1^{45} and 3^{00} when mixed in normal proportions, while No. 3, a homogeneous paste with an average manipulation time of 2^{20} minutes, varied no more than from 2^{05} to 2^{30}. In other words, the dosing method used in mixing these pastes — squeezing out strings of a given length — is not accurate except for homogeneous products.

As it appears from the technical literature (see above) that the Thiokol-PbO_2 mixes polymerize more slowly at low degrees of humidity, the determinations of the curing time for normally proportioned mixes were repeated for the various brands after the relative humidity had fallen to 45—50 per cent. The experi-

ments were carried out after the products had been stored for a week at that degree of humidity, three curing tests being made for each brand from different tubes. The results are shown in Table 5.

Table 5 shows that the tested group as a whole demonstrates a clear tendency toward prolongation of the manipulation time with decreased humidity. For several brands the variations are negligible, but for a single brand (No. 10), very considerable. Immediately after squeezing out the sample that showed a mani-

Table 6

Brand No.	Manipulation time. Minutes. Seconds.	
	46—48 % relative humidity	100 % relative humidity
1	4.15	2.00
2	5.00	1.50
3	2.10	3.30
4	1.15	0.45
5	6.00	2.50
6	5.00	1.40
7	7.00	2.30
8	6.00	2.00
9	—	—
10	15.00	3.00
11	13.00	7.30

pulation time of 9^{00}, another sample was taken from the same tube and showed a manipulation time of 6^{30}; subsequent samples gave the times 5^{00}, 4^{00} and 3^{30}. It is unknown why this particular brand is more sensitive than the others.

In order to examine more closely the influence of the relative humidity on the manipulation time for the Thiokol pastes, samples made up in normal proportions were placed on mixing slabs, where they were left for 18 hours in a humidor at 100 per cent humidity, and in the open air at 46—48 per cent humidity, respectively. Then mixing was carried out and the time of manipulation determined. The results of this experimental series appear from Table 6.

The experiments were repeated twice for the brands No. 3, 10

and 11. The repeated tests confirmed the results in Table 6. Once again the curing time of the pastes was found to be strongly dependent on the atmospheric humidity. It is unknown why brand No. 3 reacts in a way contrary to the behaviour of the other brands. If small amounts of water are incorporated with the pastes during spatulation their manipulation time is materially shortened: Pastes with a manipulation time as stated in Table 4 for normal proportions were stirred with water in the approximate ratio of 2 ml paste to 1 drop of water. This resulted in a considerable reduction of the manipulation time for all the brands except No. 10. For example: No. 2 from 3^{30} to 0^{50}, No. 3 from 2^{20} to 0^{45}, No. 7 from 5^{30} to 1^{40} and No. 10 from 3^{00} to 3^{00}.

The influence of temperature on the manipulation time was examined only for the very quick-curing brand No. 4, and for brand No. 1. Both tubes were left for 20 minutes in water at 10° C. At the end of this time about 2 ml of their contents were mixed on a paper pad at room temperature (22° C), no water from the cooling bath being incorporated with the mix. This changed the manipulation time for No. 1 from 4^{00} to 6^{00} minutes, and for No. 4 from 1^{00} to 1^{30} minutes.

The retarding action of oleic acid on No. 4 was shown by the following experiments: 1, 2 or 5 drops of oleic acid were added to about 2 ml unmixed paste. The manipulation times of the mixes were thereby altered from 1^{00} to 1^{20}, 2^{20} and 6^{00} minutes respectively. The oleic acid renders the mix definitely less viscous.

EVOLUTION OF HEAT

The chemical reaction between Thiokol and PbO_2 is an exothermic (i.e. a heat-producing) process. It is therefore of clinical interest to know the rise of temperature during polymerization.

Pastes with a manipulation time as stated in Table 4 were mixed in normal proportions as specified by the manufacturers. Immediately after the mix was completed the material was placed in a brass cylinder (diameter 15 mm, height 20 mm) and the temperature rise measured with a small mercurial thermometer.

Only one brand (No. 4) showed a relatively high increase of the temperature, viz. about 13 C°. For all the other brands the increase ranged from 3.4 (No. 11) to 5.5 (No. 3) C°. Part of this

temperature rise is due solely to the mechanical manipulation of the material on the mixing slab. The spatulation of the Thiokol paste raised the temperature about 3 C°.

Considering the low thermal conductivity and specific heat characterizing the synthetic rubber materials, temperatures of the abovementioned magnitudes are hardly likely to cause any inconvenience in the clinical work. — Their chief importance is connected with the measuring technique, as described below, for the determination of linear changes during polymerization.

LINEAR CHANGES DURING POLYMERIZATION

It is the rule that polymerization processes involve a linear contraction in the polymerizing materials. To determine the degree of this contraction is of essential importance in assessing the precision of the Thiokol pastes as impression materials.

The tests were carried out by the mercury-bath method developed by *Worner* (1942) and *Docking* and co-workers (1948). According to this method the test piece is floating on the mercury surface, secured at one end. At the other end is placed a suitable gauge point, the position of which can be determined at any time by means of a measuring microscope. In the tests for determining the contraction of the Thiokol pastes the length of the test specimens was from 20 to 50 mm. Immediately after being mixed the paste was placed in the mercury bath. At its free end was placed a ball of tin-foil (diameter about ¼ mm), in the surface of which a well-defined reference point was chosen under the microscope. The test piece was placed in such a way that the surface of the free end, the movements of which were recorded, was lower than any part of the surface nearer to the attached end. Under these conditions the observations under the microscope always showed (1) an initial movement of the material away from the secured end, (2) a stationary position of the ball and (3) a contraction causing the ball to move toward the attached end of the test specimen. The findings, which are set forth in Table 7, show the contraction after 24 hours. The contraction during the following 24 hours was in each case less than 0.02 per cent. The measuring microscope permitted reliable readings of 1 micron. On completion of the experiments the length of the

test specimens was determined with an accuracy of 0.1 mm. At least three measurements were carried out for each commercial product.

A small part of the measured contraction undoubtedly represents thermal contraction, especially in case of brand No. 4. This material has a contraction coefficient of about $140 \cdot 10^{-6}$ (see below), shows maximum temperature almost at the beginning of the measurements, and does not reach room temperature until about 30 minutes later. It is estimated that roughly ⅓ of the contraction recorded for this brand is due to thermal conditions. For the other, less heat-producing materials the correction for temperature is of a much lower order, presumably 0.02—0.04 per cent. — When using the materials for impressions it is perhaps possible to compensate for a small part of the measured

Table 7

Brand No.	1	2	3	4	5	6	7	8	9	10	11
Contraction	0.17	0.30	0.41	0.17	0.10	0.34	0.19	0.32	0.37	0.34	0.28
in % after	0.20	0.33	0.37	0.21	0.15	0.40	0.23	0.34	0.34	0 30	0.30
24 hours	0.19	0.29	0.38	0.18	0.13	0.36	0.21	0.32	0.34	0.30	0.31
Average	0.19	0.31	0.39	0.19	0.13	0.37	0.21	0.33	0.35	0.31	0.30

contraction by holding them at a slight over-pressure, since an initial contraction occurs already at a curing stage where the materials are in a semi-fluid condition. However, even after allowance for thermal contraction several materials undoubtedly show a serious shrinkage during polymerization.

At the curing stage where the materials are removed from the mouth in practice they still showed a considerable contraction, which proceeded during the following hours. In order to get an impression of this extraoral shrinkage the hardness was measured in materials which after expiration of the manipulation time had been cured at mouth temperature (37° C) for the duration of the time stated by the manufacturers. Further the hardness was measured of the materials when cured at room temperature. The extraoral contraction was then reckoned from the time when the room temperature cured material had attained the same hardness as that cured at 37° C. Although these measure-

ments were not found to be of perfect accuracy, it was possible in this way to estimate with reasonable certainty the magnitude of the extraoral contraction. For several brands it was found to constitute between ½ and ⅔ of the total contraction stated in Table 7.

The polymerization contraction was determined only for normal mixing proportions as specified by the manufacturers.

THERMAL CONTRACTION

The thermal contraction coefficient was determined in a mercurial dilatometer on at least 24 hours old test specimens, measuring 7.0 · 7.0 · 30.0 mm. The temperature interval was roughly

Table 8

Brand No.	1	2	3	4	5	6	7	8	9	10	11
Temperature coefficient $c \cdot 10^{-6}$ cm/cm/C° about 37°—22°	157	148	167	137	160	153	149	137	151	153	148
	142	143	174	134	174	149	163	140	138	145	150
	146	150	174	145	159	143	150	133	140	150	139
Average	148	147	172	139	164	148	154	137	143	149	146

15 C°, viz. from about 37° to 22° C. The measuring error wih this apparatus was found to be ± 1 per cent.

From each brand were prepared at least three test specimens mixed in the proportions recommended by the manufacturers. On each test specimen was made one determination of the thermal contraction displayed by the materials. A few control measurements confirmed the accuracy stated above. All the brands have a practically straight thermal contraction curve within the investigated temperature range, and therefore only one value is given in Table 8 for the temperature coefficient.

There is a remarkable variation in the findings for the different brands. This is probably caused by the inevitable and varying contents of small air bubbles in the test specimens. Such bubbles will result in higher values than would have been found for test specimens without air bells; but as the rubber also contains air bells in clinical practice, the tabulated values are of general

interest. The presence of air bubbles immediately below the surface of a Thiokol impression cured at mouth temperature will result in a distinct sinking of the impression surface on cooling to room temperature. This condition is of essential importance in assessing the accuracy of the materials. — The average thermal contraction coefficient for all 11 brands is about $150 \cdot 10^{-6}$, i.e. a contraction of 0.225 per cent through 15 C° from mouth to room temperature.

ELASTICITY

The contraction measurements showed that the Thiokol pastes are not completely cured at the time they are allowed to re-cool to room temperature after staying at 37° C in the period specified by the manufacturers. Their elastic conditions must therefore also be expected to change after an impression is withdrawn from the mouth. As it is only at the moment the material is removed from the mouth that their elastic properties are of special interest, the determination of these properties must be made at a corresponding polymerization stage.

This was done in the following way: a brass ring, 15 mm in diameter and 10 mm in height, was placed on a glass slab. The Thiokol paste was spatulated according the manufacturer's instructions and filled into the brass ring, which was covered with a glass slab, so that the end surfaces of the paste were plane and flush with the rims of the brass ring. The manipulation time of the pastes was determined for each test and was approximately as stated in Table 4 (normal proportioning = 1 portion accelerator). After manipulation, the paste, ring, and glass slabs were immersed in water at 37° in the number of minutes the material was to remain in the mouth according to the directions. Immediately afterwards, the top slab was removed from the paste, and no later than 15 seconds after removal from the thermostat a steel ball (diam. 4 mm) was pressed quickly down in the middle of the plane surface to a depth of 5 mm (50 percent), after which the pressure on the ball was removed at once. The ball was mounted at the end of the movable rod of a dial gauge so adjusted that the maximum penetration of the ball into the impression material was 5 mm. Fifteen minutes after the test the rubber

Table 9

Brand No.	1	2	3	4	5	6	7	8	9	10	11
Plastic	30	122	63	10	90	60	14	273	80	33	170
deformation	34	133	65	12	95	65	15	250	83	34	181
in 1/100 mm	31	128	67	13	88	64	14	261	78	31	176
Average	32	128	65	12	91	63	15	261	80	33	176

surface was covered with a quick-setting dental stone. When the stone had set the height of the more or less hemispherical bulge in the — otherwise plane — stone surface was measured. The measurements were carried out by means of a dial gauge by a method that was accurate to within ± 0.01 mm. The size of the bulge is an expression of the plastic part of the aforementioned total deformation of 5 mm. The more elastic the material, the smaller the bulge. The results of the measurements appear from Table 9.

From Table 9 is seen that the elastic properties vary to a large

Table 10

Brand No.	Time in thermostat. Minutes				
	3	5	7	10	15
1	32	16	14	14	13
3	65	38	28	16	11

extent with the different Thiokol products. It is doubtful whether the materials with the highest values are sufficient in regard to precision. Deformations of 50 per cent, which forms the basis for the measurements, can hardly be regarded as improbable in the clinical use of these materials.

A prolongation of the curing time, caused by a reduction in the relative humidity, will further deteriorate the elastic properties of the Thiokol pastes at the time they are removed from the mouth after manipulation as specified in the instructions. The paste from one of the most moisture-sensitive brands (No. 10)

still had a doughy consistency when removed from the thermostat after a week's storage at 45—50 per cent humidity.

For a few brands the experimental procedure was varied by maintaining the plastic deformation of 50 per cent for 5 seconds. This increased the plastic deformation considerably: No. 1 from 32 to 83, and No. 3 from 65 to 203. — Consequently, the Thiokol impressions should be removed with a jerk, not with a slow pull.

Finally, the time in which the materials were kept in the thermostat was varied. The change in plastic deformation for two brands appears from Table 10.

Table 10 shows that an essential improvement of the elastic properties is obtained by leaving the impression in the mouth for a short time (e.g. 2 minutes) beyond that recommended by the manufacturers.

HARDNESS

The hardness was measured at the same polymerization stage as in the elasticity measurements described above. The test specimens were placed in cylindrical brass moulds with a diameter

Table 11

Brand No.	1	2	3	4	5	6	7	8	9	10	11
Impression	235	575	425	85	525	410	210	640	470	370	590

of 15 mm and a depth of 10 mm, and had plane end surfaces. The loading was as follows: ball diameter 4.0 mm, pressure 500 g, time of pressure 15 seconds. The penetration of the ball was measured in 1/100 mm with an accuracy of $\pm$ 0.05 mm. All the test pieces showed more or less distinct flow in the course of 15 seconds, least for the hardest brands. The findings appear from Table 11. The values are averages of three measurements.

A comparison between Tables 9 and 11 shows that the most elastic (i.e. least plastic) materials have the highest hardness (i.e. lowest value for the impression depth in Table 11). The proportionality is not mathematically perfect, however.

WATER ABSORPTION

It is generally known from the rubber industry that not only natural, but also synthetic rubber products absorb small quantities of water with expansion as a result. As such an absorption may be of importance in evaluating the precision of the Thiokol impression materials, the linear changes were measured for some of the brands when they were covered with water after 24 hours' polymerization at room temperature. The apparatus and test specimens described in the section on linear changes during polymerization were also used in this case. The test specimens were covered with water at room temperature, and their linear changes measured in the course of the following hour. The results in Table 12 represent the average of three measurements for each brand.

Table 12

Brand No.	1	2	4	5	6	7	9	10
Expansion per cent	0.00	0.00	0.02	0.05	0.04	0.05	0.00	0.02

SUMMARY

According to the present investigation the new group of impression materials, based on the synthetic rubber Thiokol, seems to be suited for dental purposes. Their properties may be characterized as follows:

(1) Some of the brands give pastes of insufficient homogeneity, so that it is not possible to obtain a uniform mixing proportion of Thiokol and PbO_2.

(2) The consistency of the spatulated pastes varies considerably with the different brands. The most viscous pastes are probably best suited for impressions of prepared teeth, since they will more easily tear air bubbles off the tooth surface; the most viscous brands are No. 1, 2, 3, 4, and 8. Table 1. As the viscosity increases after the mix is completed, it will obviously be expedient to insert the impression material into the mouth as late as possible.

(3) The manipulation time and polymerization rate of the mixes depend to a considerable degree on their water content, which varies with the relative humidity of the atmosphere. This condition may cause great inconvenience in clinical work. It is suggested that the manufacturers consider whether a standardization of the products can be obtained in this respect by special transport and storage measures. According to the experimental results the most stable brands are Nos. 1 and 3.

(4) The curing rate can be controlled by the worker by addition of one or a few drops of water (accelerator) or oleic acid (retarder) before spatulation.

(5) The Thiokol pastes develop heat during polymerization, but very likely to such a small degree as to be without clinical interest.

(6) Thiokol pastes shrink during polymerization and continue to do so after they have been removed from the mouth. The total contraction varies considerably (from 0.13 to 0.39 per cent) with the various brands. Nos. 1, 4, 5 and 7 showed least contraction. The impressions should therefore be cast as soon as possible after removal from the mouth. This is essential, at least for brands with a relatively strong tendency to shrink.

(7) The thermal contraction of the materials is rather great, from about 0.20 to 0.25 per cent, on cooling from mouth to room temperature. The materials should be manipulated in such a way that incorporation of air is reduced to a minimum. Large air bubbles immediately below the surface of an impression will produce distinct depressions in the surface on cooling from mouth to room temperature.

(8) At the time they are withdrawn from the mouth the Thiokol impressions possess both elastic and plastic properties. The more predominant are the elastic properties, the more accurate will be the fit of the materials.

With regard to these properties the tested materials showed great differences. Listed in order of quality (beginning with the best) the sequence was found to be the following: Nos. 4, 7, 1, 10, 6, 3, 9, 5, 2, 11, 8. The elastic properties of the materials are considerably improved by allowing the impressions to remain

in the mouth for a few minutes beyond the time stated by the manufacturers. The impressions should always be removed from the impression area with a jerk.

(9) The hardness of the materials increases with their elasticity.

(10) A few commercial brands expand slightly in water, probably on account of water absorption.

RÉSUMÉ

THIOKOL, UN NOUVEAU GROUPE DE MATÉRIAUX POUR EMPREINTE

Il paraît que le nouveau groupe de matériaux pour empreinte à base de la gomme synthétique de Thiokol est, conformément aux recherches ci-dessus, utilisable à des fins dentales. Voici comment on peut évaluer leurs qualités:

1) L'homogénéité des pâtes est pour certains produits insuffisante, de façon qu'il n'est pas possible d'atteindre un mélange constamment homogène de Thiokol et de PbO_2.

2) A l'égard des différents produits la consistance des pâtes mélangées diffère considérablement. Il paraît probable, que les pâtes les plus visqueuses s'appliquent le mieux au moulage de dents préparées, puisqu'elles pourront plus facilement arracher les bulles d'air des surfaces des dents; les produits les plus visqueux sont les nos 1, 2, 3, 4 et 8. — Au sujet de la viscosité il conviendra évidemment le mieux d'introduire dans la bouche les matériaux de moulage aussi tard que possible, puisque leur viscosité s'accroît après la fin du délayement.

3) La durée du travail comme la vitesse de la polymérisation des mélanges de pâtes dépendent sensiblement de leur teneur en eau, qui varie avec le degré d'humidité de l'atmosphére. Cet état des choses peut entrainer des inconvénients importants à leur application dans la clinique. Les fabricants doivent peut-être examiner la possibilité d'une standardisation des produits sur ce point par des dispositions particulières pour le transport et l'emmagasinage. — A en juger par les données d'expériences présentes les produits les plus stables sont les numéros 1 et 3.

4) Le consommateur peut ajuster la vitesse de polymérisation en versant une ou peu de gouttes d'eau (pour pousser) ou d'acide oléique (pour retarder) avant le mélange.

5) Les pâtes Thiokol produisent de la chaleur pendant la polymérisation, mais apparemment dans de si petites proportions, que c'est sans intérêt clinique.

6) Les pâtes Thiokol se resserrent pendant la polymérisation et continuent de le faire, après qu'on les a enlevées de la bouche. La contraction totale varie sensiblement (de 0,13 justqu'à 0,39 %) pour les différents produits. Les produits des nos 1, 4, 5, et 7 ont montré le moins de contraction. Par conséquent, on doit couler les moulages aussi vite que possible, aprés qu'on les a enlevés de la bouche, ceci est important du moins pour les produits d'une contraction relativement forte.

7) La contraction thermique des matériaux est assez grande, environ 0,20 à 0,25 % à l'abaissement de la température de la bouche à celle du laboratoire. On doit traiter les matériaux de telle façon, que le minimum d'air s'y incorpore; des bulles d'air importantes, près de la surface du moulage causeront des creux apparents là-dedans à l'abaissement de la température de la bouche à celle du laboratoire.

8) Les matériaux de moulage à base de Thiokol possèdent au moment où l'on les enlève de la bouche, d'une part des qualités élastiques, et aussi des qualités plastiques. Les matériaux sont d'autant plus précis que dominent les qualités élastiques. A l'égard de ces qualités les produits examinés diffèrent beaucoup les uns des autres, et au point de vue de la qualité on peut les ranger dans l'ordre suivant: no 4, 7, 1, 10, 6, 3, 9, 5, 2, 11, 8. Les qualités élastiques des matériaux l'améliorent essentiellement, si l'on garde le moulage dans la bouche peu de minutes plus longtemps que ne l'indiquent les fabricants. En tout cas on doit enlever les moulages de la zone de moulage avec une secousse.

9) La dureté des matériaux s'accroît avec leur élasticité.

10) Un petit nombre de produits se détendent légèrement dans l'eau, vraisemblablement à cause d'absorbtion d'eau.

ZUSAMMENFASSUNG

THIOKOL ALS DENTALES ABDRUCKMATERIAL

Eine neue Gruppe von Abdruckmaterialien, die auf dem synthetischen Gummi Thiokol basiert ist, scheint nach der vorliegenden Untersuchung für die Zahnheilkunde brauchbar zu sein. Ihre Eigenschaften können folgendermassen bewertet werden:

1. Die Homogenität der Pasten einiger Fabrikate ist unzureichend, so dass es nicht möglich ist, ein völlig gleichartiges Mischungsverhältnis zwischen Thiokol und PbO_2 herzustellen.

2. Die Konsistenz der ausgerührten Pasten der verschiedenen Fabrikate weicht stark voneinander ab. Am geeignetsten für den Abdruck präparierter Zähne scheinen die stark viskösen Pasten zu sein, da diese leichter in der Lage sind Luftblasen von den Zahnoberflächen fortzureissen; die Fabrikate mit den Nummern 1, 2, 3, 4 und 8, sind die, die am stärksten viskös sind. Da die Viskosität nach abgeschlossenem Zusammenrühren zunimmt, scheint es am zweckmässigsten zu sein, mit dem Einführen des Abdruckmateriales so lange wie möglich zu warten.

3. Die Arbeitszeit und die Polymerisationsgeschwindigkeit der Pastenmischungen sind in hohem Grade abhängig von ihrem Wassergehalt, welcher mit dem Feuchtigkeitsgrad der Luft schwankt. Dieser Umstand kann zu wesentlichen Unannehmlichkeiten bei der Verarbeitung in der Praxis führen. Die Hersteller sollten in Erwägung ziehen, ob die Produkte mit Hilfe von besonderen Versand- und Aufbewahrungseinrichtungen in dieser Beziehung stabilisiert werden können. Nach den vorliegenden Untersuchungsresultaten sind die stabilsten Fabrikate Nummer 1 und 3.

4. Die Polymerisationsgeschwindigkeit kann vom Verbraucher vor dem Mischen reguliert werden durch Hinzusetzen von einigen wenigen Tropfen Wasser (Akzeleration) oder Ölsäure (Retardation).

5. Die Thiokolpasten entwickeln während der Polymerisation Wärme, aber anscheinend in so geringen Mengen, dass diese ohne klinisches Interesse ist.

6. Die Thiokolpasten schrumpfen während der Polymerisation und setzen hiermit auch nach der Entfernung aus dem Munde

fort. Die totale Kontraktion der einzelnen Fabrikate ist stark schwankend von 0,13 bis 0,39 Prozent. Die geringste Kontraktion wiesen die Fabrikate 1, 4, 5 und 7. Aus diesem Grunde sollte man so schnell wie möglich die Abdrücke nach der Entfernung aus dem Munde ausgiessen; dies ist sehr wesentlich zumindestens für die relativ stark kontrahierenden Präparate.

7. Die thermische Kontraktion der Materialien ist ziemlich gross, ca. 0,20 bis 0,25 Prozent bei Abkühlung von Mund- auf Zimmertemperatur. Die Materialien sollten so behandelt werden, dass so wenig wie möglich Luft in sie hineingemischt wird; grössere Luftblasen dicht unter der Oberfläche in einem Abdruck führen zu deutlichen Einsenkungen in der Abdruckoberfläche beim Abkühlen von Mund- auf Zimmertemperatur.

8. Die Thiokolabdruckmaterialien besitzen in dem Augenblick, in dem sie aus dem Munde entfernt werden, teils elastische, teils plastische Eigenschaften. Die Genauigkeit der Materialien ist am grössten, je mehr die elastischen Eigenschaften dominieren. Die untersuchten Fabrikate sind mit Hinblick auf diese Eigenschaften sehr verschiedenartig und können qualitätsmässig in dieser Reihenfolge aufgestellt werden (die besten sind zuerst genannt): 4, 7, 1, 10, 6, 3, 9, 5, 2, 11, 8. Die elastischen Eigenschaften der Materialien werden wesentlich verbessert, wenn der Abdruck einige Minuten länger als vom Hersteller angegeben im Munde behalten wird. Die Abdrücke sollten unter allen Umständen mit einem Ruck von ihrer Unterlage entfernt werden.

9. Die Härte der Materialien wächst mit ihrer Elastizität.

10. Einige Fabrikate expandieren schwach in Wasser, wahrscheinlich auf Grund von Wasserabsorbtion.

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