

## DETERIORATION OF PHOSPHATE-BONDED INVESTMENT ON EXPOSURE TO 100% RELATIVE HUMIDITY ATMOSPHERE

BY

Toshiyuki MIYAJI\*<sup>1</sup>, Kayoko UTSUMI, Ei SUZUKI  
and Yuu SHIMIZU\*<sup>2</sup>

### ABSTRACT

Changes in the powdery composition and setting characteristics of the phosphate-bonded investment (Ceramigold) on exposure to 100% relative humidity atmosphere were investigated by means of Thermogravimetry-Differential Thermal Analysis (TG-DTA) and X-ray diffraction. The following results were obtained.

1. In the powder,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$  contained as the setting agents were converted into  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  through  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ .

2. As compared with the result of the powder stored in the thermo-hygrostatic room (control=not exposed), the setting time of the mixture of the exposed powder with the colloidal silica solution decreased temporarily but increased after 4 days of exposure when the quantity of  $\text{NH}_4\text{H}_2\text{PO}_4$  in the powder became small and couldn't be measured after 10 days of exposure.

3. The compressive strength and diametral tensile strength of the mixture at 2 hours increased slightly but decreased after 4 days or more of exposure and couldn't be measured after 10 days of exposure.

4. The thermal expansion of the mixture at 800°C produced little difference between the control and after 8 days of exposure.

As for the setting agents the process of deterioration is similar to the setting reaction. The quantity of  $\text{NH}_4\text{H}_2\text{PO}_4$  in the powder seems to be related to the setting time and the strength of the set investment. The quantity of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  in the powder may contribute to the extreme delay of the setting reaction.

### INTRODUCTION

Gypsum-bonded investment powders are well known to deteriorate on exposure to high humidity atmospheres. This deterioration results from the reaction of the plaster or stone contained in the investment as a binder. Farmer and Skinner [1] reported that one "model" plaster powder on exposure to 100% relative humidity exhibited, first of all, a progressive increase in the setting rate when

mixed with water but later became "deadened". Buchanan and Wörner [2] claimed that the plasters absorbed water from the moist atmosphere and underwent hydration of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and that the rate of absorption of moisture at any particular humidity appeared to depend mainly on the quantity of the dehydrate already present in the plaster. So, in the Dentist's Desk Reference (ADA [3]), the following notice is written regarding the use of the gypsum-bonded investments: Use only a

\*<sup>1</sup> 宮治俊幸: The First Department of Dental Technology (Chief: Prof. S. NOMOTO), Faculty of Dentistry, Tokyo Medical and Dental University.

\*<sup>2</sup> 内海嘉代子・鈴木 暎・清水 友: Department of Dental Technology (Chief: Prof. T. MIYAJI), School of Dentistry, Showa University.

Received for publication, February 19, 1982.

fresh investment, especially avoid investments which have been stored for a prolonged period in a humid atmosphere. But for the use of phosphate-bonded investments such notice is not written. And despite the presence of the hygroscopic primary phosphates contained in the phosphate-bonded investments as the setting agents, reports of this type have not been published to date.

This study dealt with the changes in the powdery composition by means of Thermogravimetry-Differential Thermal Analysis (TG-DTA) and X-ray diffraction and in the setting characteristics by measuring the setting time, compressive strength, diametral tensile strength and thermal expansion. The purpose of this study was to elucidate the deterioration process of one of the commercial phosphate-bonded investments (Ceramigold) on exposure to 100% relative humidity atmosphere.

#### MATERIALS AND METHODS

The investment used in this study is Ceramigold (Whipmix Corp., Louisville, Ky.). In order to investigate the deterioration of this powder owing to humidity, the following methods of storage were chosen.

- (A) Exposing to 100% relative humidity atmosphere; stored in the hygostat (26 cm in diameter and 30 cm high)
- (B) Exposing to ordinary humidity atmosphere; stored in the uncontrolled room
- (C) Ordinary storage as control (not exposed); stored in the thermo-hygrostatic room (20°C, 50%)

The powder was collected carefully from, at and near each surface and after being collected the remainder was mixed with each other. The result in the case of (C) above was plotted at day 0.

The collected powder was used as a very

fine powder by grinding it in the mortar made of agate in the TG-DTA measurement (No. 8076, Rigaku Denki Co., Ltd., Japan) and in the X-ray diffraction (CN 2028, Rigaku Denki Co., Ltd., Japan). In the TG-DTA measurement, the sample was  $30.00 \pm 0.05$  mg in weight and carried out from the room temperature to about 110°C at a heating rate of 5°C/min. The weight loss was calculated from the initial weight at room temperature and the final weight after the temperature was decreased. X-ray diffraction was carried out on the sample at room temperature. Cu target and Ni filter were used.

As to the setting characteristics, the powder was mixed with a colloidal silica solution at a L/P ratio of 0.16 for 30 seconds by using the VAC-U-VESTOR (Whipmix Corp., Louisville, Ky.) and poured into each teflon mold. And finally the rod-like samples (10 mm in diameter and 20 mm long) were prepared, and the compressive strength (Universal Testing Instrument, Model 1125, Instron Corp., USA) and the diametral tensile strength (Universal Testing Instrument, Model 1125, Instron Corp., USA) were measured after 2 hours. Finally the rod-like samples (7 mm in diameter and 14 mm long) were prepared, and the thermal expansion (High temperature type, Cat. No. 8096, Rigaku Denki Co., Ltd., Japan) at 800°C was measured after 24 hours.

#### RESULTS

Fig. 1 shows the weight loss of the Ceramigold powder due to heating up to about 110°C. The weight loss was very little on day 0 (control), and little more than 2.5% at 60 days of exposure to the ordinary humidity atmosphere but about 10% at 25 days of exposure to 100% relative humidity atmosphere. Fig. 2 shows

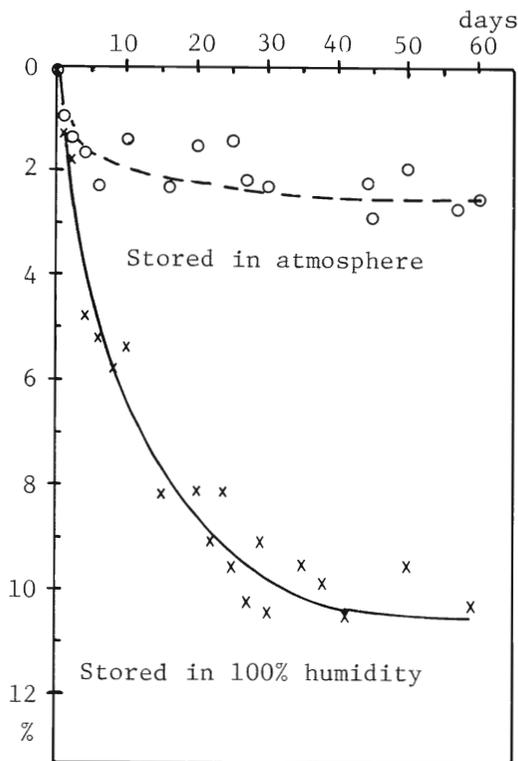


Fig. 1. Variation in weight loss of Ceramigold powder on exposure to 100% relative humidity atmosphere (crosses), or ordinary humidity atmosphere (open circles).

how the powdery composition changed on exposure of the Ceramigold powder to 100% relative (left-hand and center columns) and ordinary (right-hand column) humidity atmospheres by means of X-ray diffraction. In this range of diffraction angles ( $2\theta=4$  to  $28^\circ$ ) the peaks of  $\alpha$ -quartz and  $\alpha$ -cristobalite, which represented q and C in the bottom row (control), were detected in all cases. The peaks of MgO are not detected in this range. In the left-hand and center columns in Fig. 2, the peaks of  $\text{NH}_4\text{H}_2\text{PO}_4$  became weak at 4 days of exposure and were difficult to be detected at 6 days of exposure. The peaks of  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  were detected even at 1 day of

exposure and the former was difficult to be detected at 27 days of exposure. In the right-hand column in Fig. 2, the patterns showed little variation from 6 to 60 days of exposure and were similar to the pattern at 1 day of exposure in the left-hand column. Fig. 3 shows how the curves of DTA (middle), TG (upper) and D-TG (lower) changed on exposure of Ceramigold powder to 100% relative (left-hand and center columns) and ordinary (right-hand column) humidity atmospheres. As shown in the bottom row (control) there was little variation in these curves. But in the other cases, the endothermic peaks detected in the DTA curves were accompanied by a weight loss. Each shape detected in the left-hand and center columns in Fig. 3 showed a single peak at 1 day of exposure but double peaks from 2 to 15 days of exposure. Each temperature of the endothermic peaks at the extrapolated onset was measured in the order of 63, 67, 71 and  $73^\circ\text{C}$ . The shape detected at 27 days of exposure was that of a single peak and the temperature of the endothermic peak at the extrapolated onset was  $82^\circ\text{C}$ . So the peak detected at 27 days of exposure corresponds to that detected at a higher temperature in the case of a double peak. By weighing each area of the peaks separated from each double endothermic peak, the following results were obtained; the area detected at a lower temperature became gradually larger till the 6th day of exposure, showed little variation from 6 to 15 days of exposure and became gradually smaller after 15 days of exposure; that detected at a higher temperature showed little variation till the 4th day of exposure, became gradually larger at 4 to 6 days of exposure, showed little variation at 6 to 8 days of exposure and gradually became larger after 8 days of exposure. In the

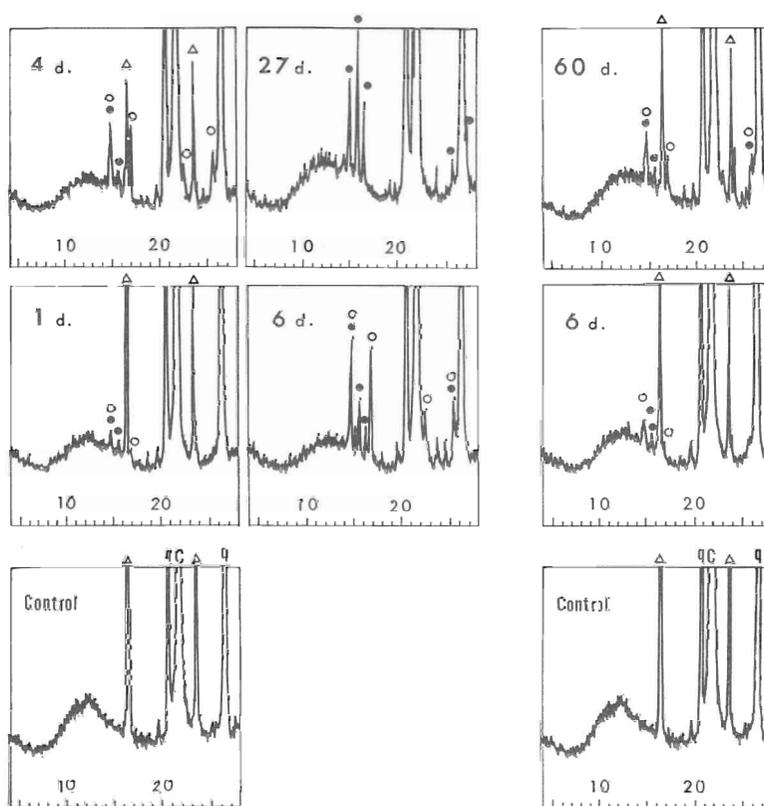


Fig. 2. Variation in the X-ray diffraction patterns on exposure of Cerami-gold powder to 100% relative humidity atmosphere (left-hand and center columns) and ordinary humidity atmosphere (right-hand column). Control=not exposed, open triangles= $\text{NH}_4\text{H}_2\text{PO}_4$ , open circles= $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , solid circles= $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , d.=day or days of exposure

right-hand column in Fig. 3, there was little variation as the exposure time was prolonged. The patterns were similar to the pattern at 2 days of exposure in the left-hand column in Fig. 3.

As shown in Fig. 4, the setting time decreased temporarily but increased after 4 days of exposure as compared with that of the control and couldn't be measured at 10 days of exposure to 100% relative humidity atmosphere. The compressive strength and the diametral tensile strength at 2 hours are shown in Fig. 5. The tendency obtained in Fig. 5 was almost the

reverse of that obtained in Fig. 4. The thermal expansion curves are shown in Fig. 6. In the range of 200 to 250°C the shrinkage was detected clearly at 8 days of exposure to 100% relative humidity atmosphere, slightly at 27 days of exposure to the ordinary humidity atmosphere but not detected at day 0 (control). The thermal expansion at 800°C, however, was about 1.2% in each case.

In order to clear the conversion detected in the setting agents owing to the humidity, the mixed powder of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$  at a ratio of 1:1 (molecular weight)

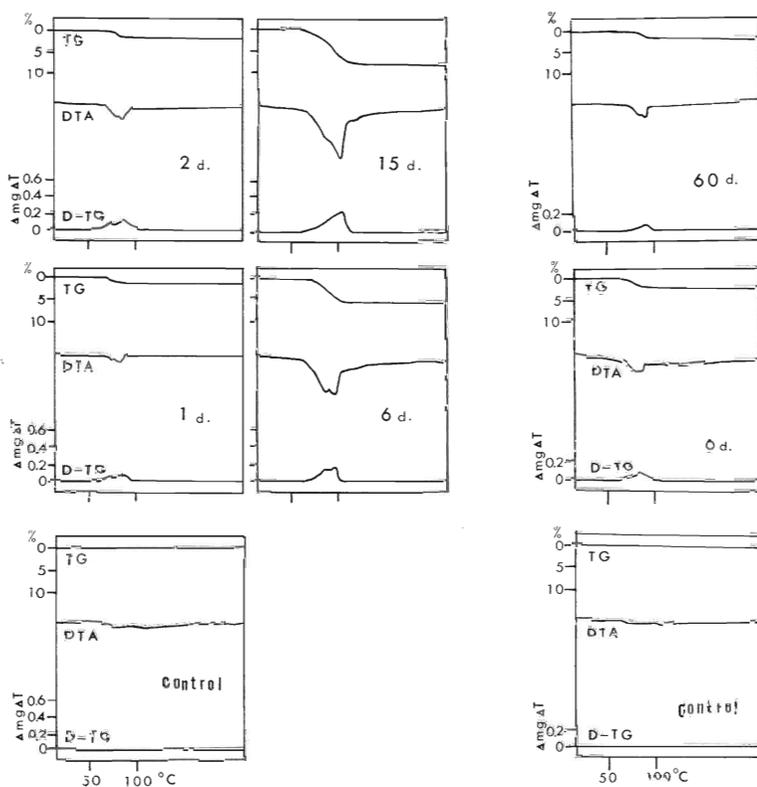


Fig. 3. Variation in curves of DTA (middle), TG (upper) and D-TG (lower) on exposure of Ceramigold powder to 100% relative humidity atmosphere (left-hand and center columns) and ordinary humidity atmosphere (right-hand column). d.=day or days of exposure

was exposed to 100% relative humidity atmosphere. In Fig. 7 and the left-hand column in Fig. 8, the X-ray diffraction patterns and the curves of TG and DTA are shown in the same manner as in Figs. 2 and 3. The conversion detected in the setting agents was similar to that detected in the Ceramigold powder. As the peaks of  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  were stronger, a double endothermic peak was detected in the DTA curve. The weight loss was about 45% at 28 days of exposure. The right-hand column in Fig. 8 shows the variation in the X-ray diffraction patterns, whose range of diffraction angles was from  $36^\circ$  to  $46^\circ$ . The peak of MgO was detected in this range. As the exposure was prolonged,

the peak of MgO was weaker and the peaks of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  were stronger.

#### DISCUSSION

Ceramigold powder is composed predominantly of  $\alpha$ -quartz and  $\alpha$ -cristobalite (75 to 85%) and the remainder are the setting agents. In the Ceramigold powder used in this study,  $\text{NH}_4\text{H}_2\text{PO}_4$  and MgO were added as the setting agents. Owing to the humidity, the Ceramigold powder contained chemically combined water because of the reaction of the setting agents as well as of the hygroscopic or physically absorbed water. Both the weight loss of this powder, detected in the TG curve, and the endothermic peaks, detected in the DTA

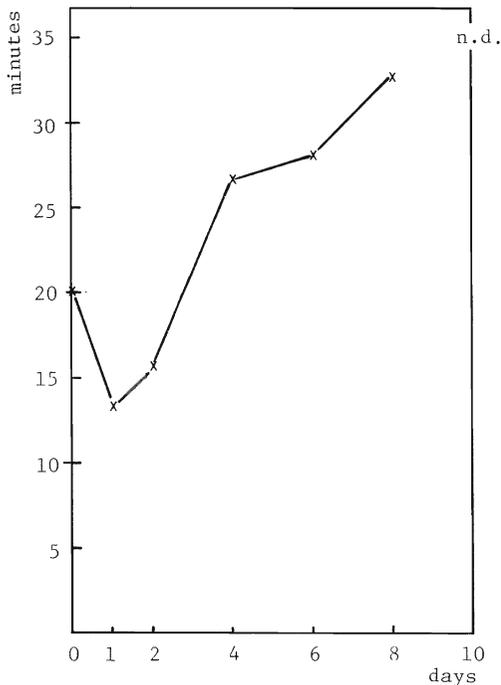


Fig. 4. Variation in setting time measured by the use of Ceramigold powder on exposure to 100% relative humidity atmosphere. n.d.=not done

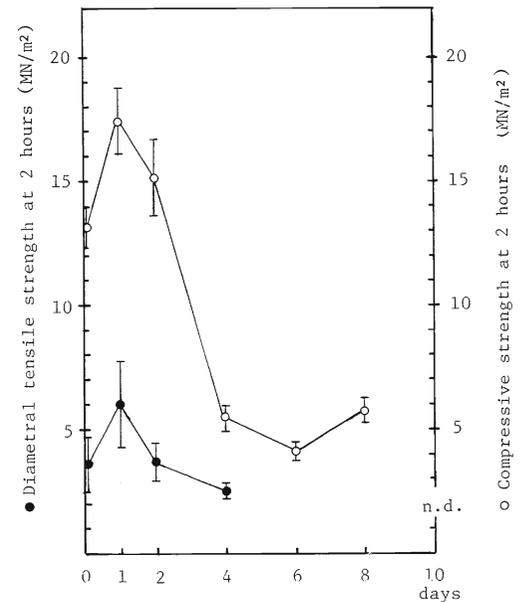
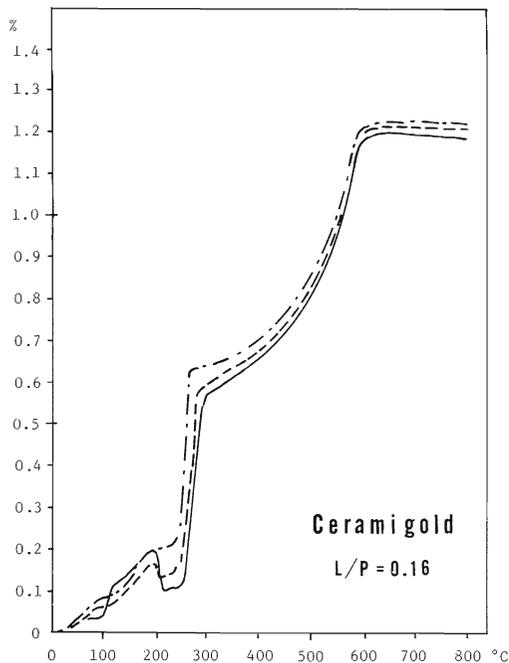


Fig. 5. Variation in compressive strength and diametral tensile strength at 2 hours, measured by the use of Ceramigold powder on exposure to 100% relative humidity atmosphere. Each plotted point is the average of 10 measurements. Standard deviation ( $s = \sqrt{\sum x^2 - n\bar{x}^2 / n - 1}$ ) n.d.=not done

Fig. 6. Thermal expansion curves

Solid line=The powder on exposure to 100% relative humidity atmosphere for 8 days was used.

Dotted line=The powder on exposure to ordinary humidity atmosphere for 27 days was used.

Chain line=The powder stored in a thermo-hygrostatic room (not exposed) was used as control.

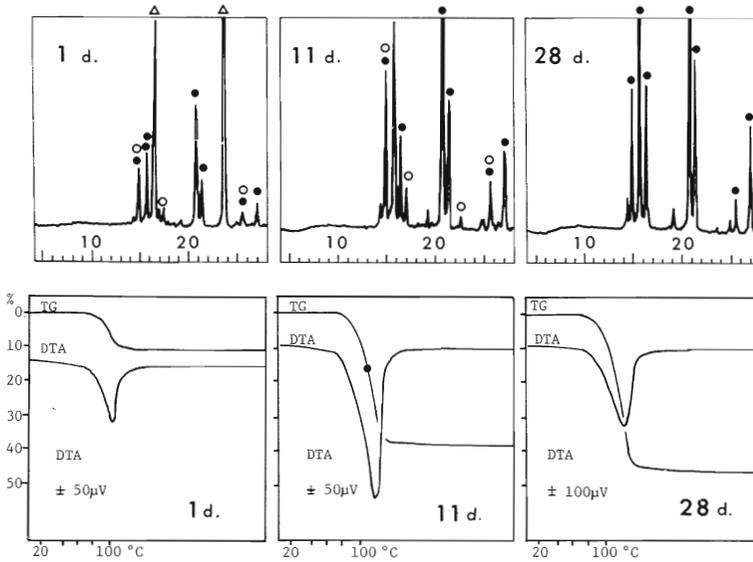


Fig. 7. Variation in the X-ray diffraction patterns (top row) and the curves of DTA and TG (bottom row) of the mixed powder of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$  in the ratio of 1:1 (molecular weight) on exposure to 100% relative humidity atmosphere. d.=day or days of exposure

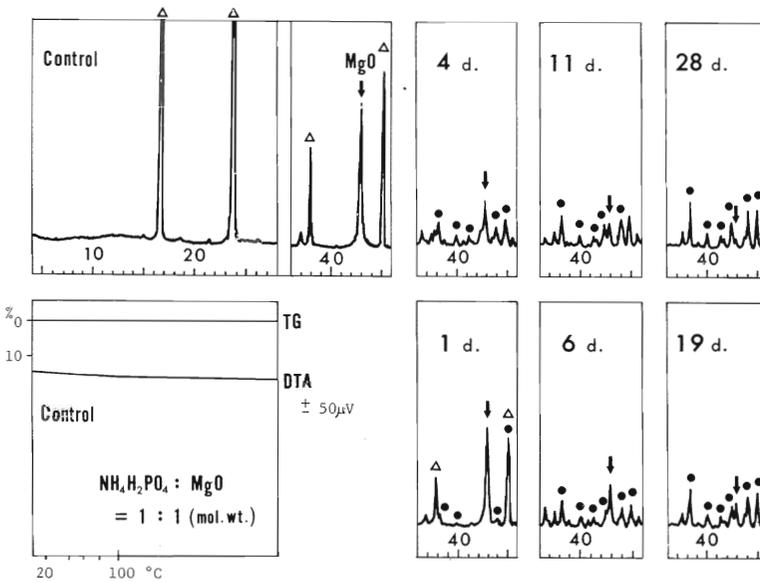
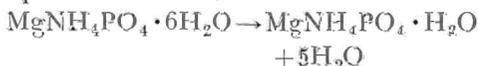


Fig. 8. Left-hand column; the X-ray diffraction pattern (top row) and DTA and TG curves (bottom row) of the mixed powder of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$  at the ratio of 1:1 (molecular weight) collected immediately after mixing.

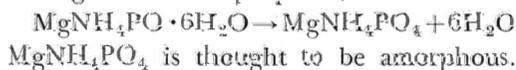
Right-hand column: Variation in the X-ray diffraction patterns of that on exposure to 100% relative humidity atmosphere.

Open triangles= $\text{NH}_4\text{H}_2\text{PO}_4$ , solid circles= $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ , arrows= $\text{MgO}$ , d.=day or days of exposure

curve, resulted from the evaporation of water. In the DTA curve the area of the peak corresponds to the quantity of the reaction accompanying the heat change. Jones [4] reported that the mixture of phosphate-bonded investment powder with water had a double endothermic peak at about 85 to 110°C in the DTA curve. And Takeda et al. [5] reported that the mixture of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$  with water also had a double endothermic peak. Jones [4] claimed that the double peak was due to the overlapping of the two reactions: (1) the volatilization of free and absorbed water and (2) the partial dehydration of the chemically combined water of magnesium ammonium phosphate. Takeda et al. [5] gave support to this claim. But in this study (1) was negligible because the quantity of free and absorbed water in the powder exposed to the humidity atmosphere was very small. The reason is as follows. In Fig. 7 the weight loss was about 45% at 28 days of exposure when the powder consisted mainly of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . It is well known that  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  forms an intermediate hydrate  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  at about 50°C (Kiehl and Hardt [6]; Utsumi, Suzuki, Shimizu and Miyaji [7]). That reaction is proposed as follows;

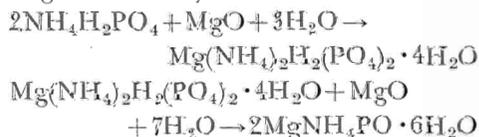


The weight loss is theoretically about 37%. In our previous study by means of the X-ray diffraction (Utsumi et al. [7]),  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  remained at 100°C and was difficult to be detected at about 200°C in the atmosphere, but in the vacuum state  $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$  could not be detected at any temperature. In the vacuum state the following reaction is proposed;

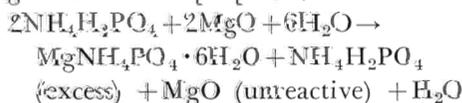


The weight loss is theoretically about 44%. When the powder of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{MgO}$ , which had been exposed for 4 days to 100% relative humidity atmosphere, was heated from room temperature to about 110°C, the variation in the X-ray diffraction patterns was measured. The peaks of  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  were difficult to be detected at a lower temperature, and secondly those of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  were also difficult. Both of them became amorphous at temperature below 100°C. So the latter reaction was likely to occur.

A double endothermic peak is thought to be due to (2). The excessive or unreactive  $\text{MgO}$  remains even at 700°C (Suzuki, Utsumi and Miyaji [8]). The excessive  $\text{NH}_4\text{H}_2\text{PO}_4$  remains at 100°C (Takeda et al. [5]). A double peak detected in the DTA curve is likely to correspond as follows; the first peak occurs from the conversion of  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and the second peak occurs from that of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The result of the Ceramigold powder on exposure to 100% relative humidity atmosphere in the DTA curves (Fig. 3) by weighing each area of the peaks and that in the X-ray diffraction patterns (Fig. 2) by measuring each height of the peaks agree almost quantitatively. The following reactions are proposed during the deterioration of the Ceramigold powder owing to humidity:



According to Allan and Asgar [9], at room temperature during the mixing of the phosphate-bonded investment the following reaction was proposed;



According to Sawada [10] and Kato et al. [11, 12], accompanying the setting of the phosphate-bonded investment  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  was initially produced and finally converted into  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The setting reaction seems to be similar to the process of the deterioration as for the setting agents.

As for the fluidity of the setting as well as the strength of the set investment, the results at 4 days of exposure to 100% relative humidity atmosphere were inferior to those with a shorter exposure. At 4 days of exposure the quantity of  $\text{NH}_4\text{H}_2\text{PO}_4$  was extremely smaller. According to Marbie [13], the microscopic work on the phosphate-bonded investment (Synchro-X) revealed that  $\text{NH}_4\text{H}_2\text{PO}_4$  was readily dissolved when the investment powder was mixed with the liquid, and the gel-like bond enveloped many of the particles on the setting. The matrix between the quartz and the cristobalite grains consists of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  (excess),  $\text{MgO}$  (unreactive), and  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and so on. If the quantity of  $\text{NH}_4\text{H}_2\text{PO}_4$  in the investment powder is small, the setting of the phosphate bond is expected to be slow and the strength of the set investment is expected to decrease. At 6 days of exposure to 100% relative humidity atmosphere, the peak at  $23.7^\circ$  corresponding to  $\text{NH}_4\text{H}_2\text{PO}_4$  was difficult to be detected although the peak at  $23.9^\circ$  remained. At 10 days of exposure to 100% relative humidity atmosphere the setting was extremely slow and the strength of the set investment at 2 hours was impossible to be measured. Because the quantity of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  tended to be larger after 10 days of exposure, that may contribute to the delay of setting.

In thermal expansion the shrinkage was detected at 8 days of exposure to 100%

relative humidity atmosphere. But in the range of 200 to  $250^\circ\text{C}$ , the heat change was difficult to be detected in the DTA curve and the change was also difficult to be detected in the X-ray diffraction patterns. So this shrinkage was likely to result from the physical change. The quantity of  $\text{Mg}(\text{NH}_4)_2\text{H}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  in the investment powder may contribute to the shrinkage because the quantity of the matrix on the setting in the case of 8 days of exposure to 100% relative humidity atmosphere is larger than that in the case of the control.

#### ACKNOWLEDGEMENT

The authors express their sincere appreciation to Professor Sunao Nomoto for his kind guidance and encouragement throughout the course of this study.

#### REFERENCES

- 1) Farmer, C. J. and Skinner, E. W.: Effect of relative humidity on the setting time of plaster of Paris. *Northwestern University Bull.*, 43: 12, 1942. Cit. by Buchanan, A. S., and Worner, H. K., in *Changes in the composition and setting characteristics of plaster of Paris on exposure to high humidity atmospheres*. *J. Dent. Res.*, 24: 65-75, 1945.
- 2) Buchanan, A. S., and Worner, H. K.: *Changes in the composition and setting characteristics of plaster of Paris on exposure to high humidity atmospheres*. *J. Dent. Res.*, 24: 65-75, 1945.
- 3) *Dentist's Desk Reference*, American Dental Association, Chicago, 1981, pp. 201-205.
- 4) Jones, D. W.: Thermal analysis and stability of refractory investments. *J. Prost. Dent.*, 18: 234-241, 1967.
- 5) Takeda, S., Kawabara, H., Nakamura, M., Sogawa, K., Maehara, S., Mori, H., Yokoyama, M., Takahashi, H., and Yata, A.: A study of the thermal changes of the binder in phosphate-bonded investment (in Japanese, English abstract). *J. Osaka odont. Soc.*, 42: 429-436, 1979.
- 6) Kiehl, S. J., and Hardt, H. B.: The dissociation pressures of magnesium ammonium phosphate hexahydrate and some related substances. *VII. J. Amer. Chem. Soc.*, 55: 605-618, 1933.

- 7) Utsumi, K., Suzuki, E., Shimizu, Y., and Miyaji, T.: Study on thermal physical properties of phosphate-bonded investments in vacuum as well as in atmosphere used by X-ray diffraction (in Japanese, English abstract). *J. Jpn. Res. Soc. Dent. Mat. & Appl.*, 37: 370-379, 1981.
- 8) Suzuki, E., Utsumi, K., and Miyaji, T.: Study on X-ray diffraction of phosphate-bonded investments at various temperatures (in Japanese, English abstract). *Ibid.*, 36: 535-548, 1980.
- 9) Allan, F. C., and Asgar, K.: Reaction of cobalt-chromium casting alloy with investment. *J. Dent. Res.*, 45: 1516-1528, 1966.
- 10) Sawada, T.: On setting mechanism and hygroscopic expansion of phosphate-bonded investment mixed with colloidal silica solution (in Japanese, English abstract). *J. Jpn. Res. Soc. Dent. Mat. & Appl.*, 32: 6-16, 1975.
- 11) Kato, K., Shiba, M., Nakamura, M., and Ariyoshi, T.: Study on phosphate-bonded investment. On setting mechanism, composition and particle size of raw material and physical properties (in Japanese, English abstract). *Rep. Inst. Med. & Dent. Eng., Tokyo Med. Dent. Univ.*, 10: 45-61, 1976.
- 12) Kato, K., Shiba, M., Aono, H., and Tsutsumi, Y.: The study on phosphate-bonded investment (II). On effect to physical properties by reaction during kneading (in Japanese, English abstract). *Ibid.*, 13: 1-12, 1979.
- 13) Mabie, C. P.: Petrographic study of the refractory performance of high-fusing dental alloy investments. I. High-fired, phosphate-bonded investments. *J. Dent. Res.*, 52: 96-110, 1973.