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Thermal Change of Magnesium Highpolyphosphate Coacervates[1)]

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The thermal change of magnesium highpolyphosphate coacervates with various sodium contents was studied by means of DTA, TGA and high temperature X-ray diffraction technique. Most of the highpolyphosphates in the coacervates were degraded into hydrated orthophosphates up to about 100 °C, the pyrophosphates and tetrametaphosphates being formed at 200—300 °C and 300—500 °C, respectively. The formation temperature of "X" (a mixture of $Mg_2P_2O_7$ and $MgNa_2P_4O_{12}$) was lowered with an increase of sodium content in the coacervate samples. $Mg(H_2PO_4)_2 \cdot 2H_2O$, $Mg(H_2PO_4)_2$, $MgH_2P_2O_7$, "X" and $Mg_2P_4O_{12}$ were determined in the crystalline substances obtained by the isothermal heat treatment of coacervates at various temperatures.

Kingery[2)] found that various metal oxides react with phosphoric acid to form stable refractory compounds. Some commercial aluminum phosphates are used as binders for castable refractories.[3)] Bonding of basic refractories with sodium polyphosphates was studied by Lyon, Fox and Lyon.[4)] Some phosphate-bonded magnesite refractories of high hot modulus strengths were obtained by Foessel and Treffner.[5)]

In previous works, magnesium highpolyphosphate coacervates (MPC) were examined as potential binders,[6)] and their thermomechanical properties were described at temperatures from −120 to 100 °C.[7,8)] However, there seems to be no detailed report on the thermal change of magnesium highpolyphosphates, although the degradation of some highpolyphosphates in aqueous solutions was studied by Thilo and Wieker[9,10)] and Gill and Riaz.[11)]

This paper deals with the relationship between the sodium content of MPC and its thermal change. MPC always contains sodium, the presence of which in the coacervate is necessary for the formation of "X".[12,13)] We have studied the thermal change of the MPC containing various amounts of sodium by means of DTA, TGA and high temperature X-ray diffraction, in order to clarify the phosphate bonding formation.

Experimental

Preparation of Magnesium Highpolyphosphate Coacervates with Various Sodium Contents. The MPC samples were obtained from mixtures of the aqueous solutions of sodium metaphosphate and magnesium chloride by addition of ethyl alcohol. The sodium contents in the MPC samples are determined by those in sodium metaphosphate solutions. In order to prepare the coacervates of low sodium contents, the sodium metaphosphate solutions were passed through the ion exchange resin (Amberlite IR-120H) twice or more before being mixed with the chloride solutions. The sodium metaphosphate solutions were kept at −5—0 °C during the course of ion exchange to avoid the hydrolytic degradation of the highpolyphosphates. The chemical compositions of the MPC samples are given in Table 1.

Chemical Analysis of the Coacervates. The analytical methods for magnesium, sodium and phosphorus were described previously.[8)] Paper chromatography of the polyphosphate ions in the coacervate solutions was carried out according to the method by Kolloff.[14)]

Determination of the Average Chain Length of Coacervates. The end group titration[15)] was carried out in order to determine the average number of phosphorus atoms per chain in the polyphosphates of the coacervates. Solutions of the coacervate (*ca.* 1%) were titrated with 0.1 M sodium hydroxide with a pH meter (Denki Kagaku Keiki Model HG-2). Small amounts of 0.1 M sodium hydroxide were successively added to the coacervate solutions and the pH values of the solutions were recorded after each addition until the pH became 10.

In ^{31}P NMR spectra of polyphosphate, the chemical shifts of 9.5—12 ppm and of 20—27 ppm show the presence of terminal PO_4 and middle PO_4, respectively. Each integrated intensity represents the quantity of each PO_4 group in the phosphate chain.[16)] The chain length of the polyphosphates was also determined from the ratio of the integrated intensities for the two chemical shifts. All the NMR spectra were recorded on a Nichiden-Varian NMR Spectrometer Model NV-14 operating at 24.3 MHz at room temperature, using a dilute H_3PO_4 solution as an external reference of ^{31}P.

IR Absorption Spectra. The IR absorption spectra of the coacervates were recorded on a Hitachi IR spectrometer Model EPI-G2 in order to examine the presence of the P–O–P bonds.

Thermal Analysis of the Coacervates. DTA curves were recorded on a Shinku Riko AGNE Differential Thermal Analyzer DT-1500 up to 1100 °C at a heating rate of 5 °C/min. The coacervate samples were dried at 100 °C before DTA measurements in order to avoid swelling and foaming of the samples on abrupt dehydration in a platinum cell.

TGA was carried out by measuring the weight decrement of the coacervates with a quartz spring balance, heating rate being 5 °C/min.

X-Ray Analysis. X-Ray powder diffraction patterns were obtained with a Rigaku Denki Diffractometer Model D-3F, to which a device for high temperature measurements of some coacervates was attached.

Results

Average Chain Length of Highpolyphosphates in the Coacervates. The average chain length of highpolyphosphates in the MPC samples was calculated to be 19—23 from the titration curves, assuming that no sample contains cyclic phosphate ions.

The spectra of ^{31}P MNR for the coacervate solutions (Fig. 1) were almost the same as those of polyphosphates reported by Crutchfield *et al.*[16)] The two peaks in these spectra show the presence of the end PO_4 and the middle PO_4. Table 1 shows the average chain length calculated from the ratios of the integrated intensities of the two peaks. The values from the end group measurement coincide with those from the NMR spectra.

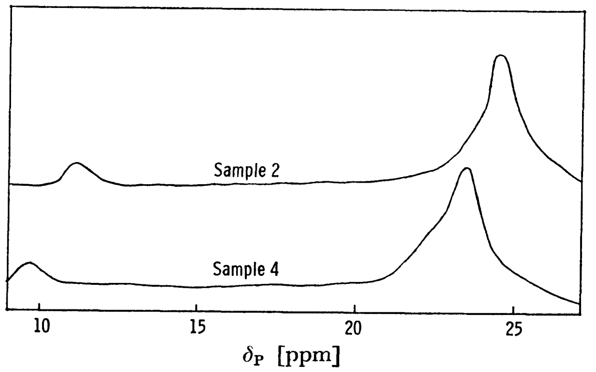

Fig. 1. ^{31}P NMR spectra of coacervates in aqueous solutions.

Table 1. Chemical composition of magnesium highpolyphosphate coacervates

No. of coacervate sample	Contents (%) NaO	MgO	P_2O_5	H_2O	Average chain length
1	1.07	11.8	39.2	53.0	
2	1.50	10.7	38.7	44.5	23
3	2.17	13.0	41.3	53.5	
4	3.46	6.65	34.6	61.1	22
5	7.46	5.60	29.0	58.0	

DTA and TGA of Magnesium Highpolyphosphate Coacervates. From the results of paper chromatography and IR, we see that most of the highpolyphosphates in the coacervates turn to hydrated orthophosphates after being heated at 100 °C. As shown in DTA and TGA curves (Fig. 2), two or more endothermic peaks at 100—200 °C suggest the occurrence of dehydration with various types. The endothermic peaks in the range 800—1000 °C appear due to the melting of some of the dehydrated coacervate samples, these melting temperatures being lowered with an increase in sodium content.

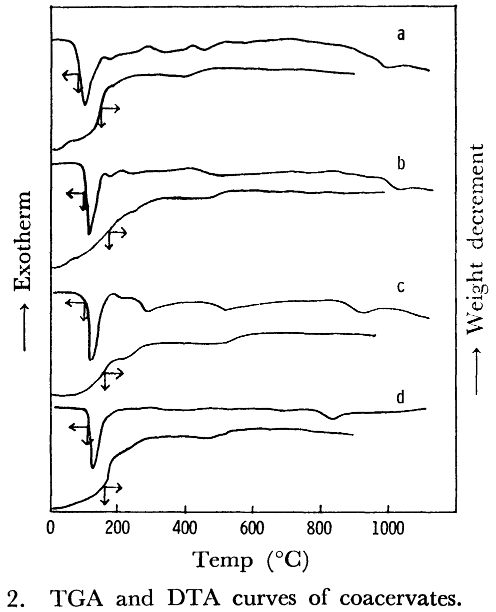

Fig. 2. TGA and DTA curves of coacervates.
a: Sample 1, b: sample 2, c: sample 3, d: sample 4.

Table 2. Products of the isothermal heat treatment of coacervates at various temperatures

No. of coacervate samples	Products[a)]
1	A(~100 °C), $Mg(H_2PO_4)\cdot 2H_2O$(120 °C), $Mg(H_2PO_4)_2$(130 °C), $MgH_2P_2O_7$(300 °C), X(400 °C), MTP(450 °C).
2	A(~100 °C), U(100—400 °C), X(460 °C), MTP(460 °C).
3	A(~100 °C), U(100—300 °C), X(350 °C), MTP(460 °C).
4	A(~100 °C), U(100—300 °C), X(320 °C).
5	A(~120 °C), U(120—300 °C), X(300 °C).

X[18]: a mixture of $Mg_2P_2O_7$ and $MgNa_2P_4O_{12}$, A: amorphous orthophosphates, U: a mixture of unknown crystalline substances, MTP: $Mg_2P_4O_{12}$.
a) Temperatures in parentheses represent those of formation of the products.

X-Ray Analysis of the Products Obtained by the Isothermal Heat Treatment. Taking the above results of DTA and TGA into account, the coacervates were isothermally dehydrated and heated at various temperatures. Table 2 shows the products obtained by the isothermal heat treatment of the coacervates.

After all the coacervates had been heated at 100 °C, orthophosphate ion was detected by paper chromatography and IR spectroscopy. No crystalline phosphate or ortho or pyro form other than $Mg(H_2PO_4)_2\cdot 2H_2O$, $Mg(H_2PO_4)_2$, and $MgH_2P_2O_7$ was found by X-ray diffraction analysis. It seems that the crystallization of magnesium ortho- and pyrophosphates was difficult in the coacervates rich in sodium.

By heat treatment at 300—400 °C most mixtures of the degraded phosphates turned into crystalline $Mg_2P_4O_{12}$ and "X", a new compound,[12,13] only "X" being found in Samples 4 and 5. The temperature for the formation of "X" was lowered with an increase of sodium content in the coacervate samples.

Discussion

The coacervate undergoes degradation, dehydration and condensation on heating as follows:[12,13]

$$\text{Coacervate} \xrightarrow{100^\circ\text{C}} \text{Amorphous orthophosphates} \xrightarrow{120^\circ\text{C}}$$
$$Mg(H_2PO_4)_2\cdot 2H_2O \xrightarrow{150-190^\circ\text{C}} Mg(H_2PO_4)_2 \xrightarrow{210-290^\circ\text{C}}$$
$$MgH_2P_2O_7 \xrightarrow{350^\circ\text{C}} Mg_2P_4O_{12} \text{ and "X"} \xrightarrow{990^\circ\text{C}}$$
$$\text{Partial melting}$$

The thermal change of the coacervates with various sodium contents seems to be as follows:

$$\text{Sample 1} \xrightarrow{100^\circ\text{C}} \text{Amorphous orthophosphates} \xrightarrow{120^\circ\text{C}}$$
$$Mg(H_2PO_4)_2\cdot 2H_2O \xrightarrow{130^\circ\text{C}} Mg(H_2PO_4)_2 \xrightarrow{300^\circ\text{C}}$$
$$MgH_2P_2O_7 \xrightarrow{400^\circ\text{C}} MgH_2P_2O_7 \text{ and "X"} \xrightarrow{450^\circ\text{C}}$$
$$Mg_2P_4O_{12} \text{ and "X"} \xrightarrow{990^\circ\text{C}} \text{Partial melting}$$

Sample 3 $\xrightarrow{100°\mathrm{C}}$ Amorphous orthophosphates $\xrightarrow{150—200°\mathrm{C}}$
Unknown crystalline substances $\xrightarrow{350°\mathrm{C}}$ "X" $\xrightarrow{460°\mathrm{C}}$
$Mg_2P_4O_{12}$ and "X" $\xrightarrow{950\,°\mathrm{C}}$ Partial melting

Sample 5 $\xrightarrow{120°\mathrm{C}}$ Amorphous orthophosphates $\xrightarrow{150°\mathrm{C}}$
Unknown crystalline substances $\xrightarrow{300°\mathrm{C}}$ "X" $\xrightarrow{910°\mathrm{C}}$
Partial melting

The temperature of formation of crystalline "X" is a little lower than that for the appearance of $Mg_2P_4O_{12}$. When the coacervates such as Samples 4 and 5 contain a large amount of sodium, no other crystalline substance than "X" is obtained by isothermal heat treatment. The formation of "X" is closely related to the presence of sodium ion.

The X-ray diffraction patterns of $MagN_2P_4O_{12}$[17] and "X" (Table 3) almost overlap each other. However, some peaks (d=3.0223, 2.9799 and 2.9107 Å), assigned to "X", disappear after the treatment of "X" with aqua regia.[18] Concerning the diffraction pattern of $MgNa_2P_4O_{12}$ there is no peak corresponding to the three peaks of "X". The highest and the next highest peaks of $Mg_2P_2O_7$ (d=3.015 and 2.976 Å) appear in the vicinity of the three peaks of "X" (ASTM X-Ray Powder Data File 8—38). This suggests that "X" is not a single compound but a mixture of $Mg_2P_2O_7$ and $MgNa_2P_4O_{12}$.

$MgNa_2P_4O_{12}$ is insoluble in acidic or alkaline solutions as well as $Mg_2P_4O_{12}$. If magnesium high-polyphosphates are used as binders, the principal bonding phase is expected to consist of chemically inert magnesium tetrametaphosphates.

Table 3. X-Ray powder diffraction data of "X"[12]

d(Å)	I/I_0	d(Å)	I/I_0
13.1	3	2.2553	8
6.43	12	2.2228	3
5.06	21	2.2004	9
4.76	9	2.1276	3
4.52	1	2.0993	1
4.29	4	2.0809	1
4.150	1	2.0368	4
3.695	4	2.0157	8
3.817	76	1.9733	1
3.572	100	1.9572	2
3.477	7	1.9324	6
3.281	5	1.9049	3
3.1114	7	1.8728	2
3.0223	9	1.8567	3
2.9799	5	1.8260	3
2.9107	12	1.8103	7
2.8536	5	1.7811	7
2.7790	4	1.7035	8
2.7493	3	1.6573	4
2.7281	2	1.6211	3
2.6473	3	1.6142	5
2.5974	3	1.5946	4
2.5230	25	1.5878	4
2.4242	2	1.5370	5
2.3131	5	1.4550	6

Conclusion

1) The thermal change is considered to take place in the following order:

a. degradation of polyphosphates into hydrated orthophosphates (≈100 °C).

b. dehydration of the hydrated orthophosphates (100—200 °C).

c. formation of pyrophosphates (200—300 °C).

d. formation of "X" and $Mg_2P_4O_{12}$ (300—500 °C).

e. melting of some phosphates obtained on heat treatment of the coacervate samples (800—950 °C).

2) The crystalline substances obtained by the progress of the thermal change of the coacervates are $Mg(H_2PO_4)_2\cdot 2H_2O$, $Mg(H_2PO_4)_2$, $MgH_2P_2O_7$, "X" and $Mg_2P_4O_{12}$.

3) The formation temperature of "X" is lowered with an increase of sodium content in the coacervate samples.

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References

1) Presented at the 26th National Spring Meeting of the Chemical Society of Japan, Hiratsuka, April, 1972. Some data were cited from Ref. 6.

2) W. D. Kingery, *J. Am. Ceram. Soc.*, **33**, 239 (1950).

3) A. D. F. Toy, "Comprehensive Inorganic Chemistry," Vol. 2, ed. by J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, New York, N. Y. (1973), p. 501.

4) J. E. Lyon, T. U. Fox, and J. W. Lyon, *Am. Ceram. Soc. Bull.*, **45**, 1078 (1966).

5) A. H. Foessel and W. S. Treffner, *Am. Ceram. Soc. Bull.*, **49**, 652 (1970).

6) T. Kanazawa, T. Umegaki, and H. Kawazoe, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, **21**, 81 (1972).

7) T. Umegaki and T. Kanazawa, *Bull. Chem. Soc. Jpn.*, **46**, 3587 (1973).

8) T. Umegaki and T. Kanazawa, *Bull. Chem. Soc. Jpn.*, **48**, 1452 (1975).

9) E. Thilo and W. Wieker, *J. Polym. Soc.*, **53**, 55 (1961).

10) E. Thilo and W. Wieker, *Z. Anorg. Allgen. Chem.*, **291**, 164 (1957).

11) J. B. Gill and S. A. Riaz, *J. Chem. Soc., A*, **1969**, 1803.

12) T. Kanazawa, H. Kawazoe, and T. Matsubara, *Kogyo Kagaku Zasshi*, **74**, 1784 (1971).

13) T. Kanazawa, H. Kawazoe, Y. Nogami, and T. Kawashima, *Nippon Kagaku Kaishi*, **1973**, 2084.

14) R. H. Kolloff, *Anal. Chem.*, **33**, 373 (1961).

15) J. R. van Wazer, E. J. Griffith, and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954).

16) M. M. Crutchfield, C. F. Callis, R. R. Irani, and G. C. Roth, *Inorg. Chem.*, **1**, 813 (1962).

17) B. Thonnerieux, J. C. Grenier, A. Drif, and C. Martin, *Compt. Rend.*, **267**, 968 (1968).

18) T. Kanazawa, H. Kawazoe, T. Umegaki, and K. Isozaki, Abstracts of the Annual Meeting of the Ceramic Society of Japan, C7 (1975), p. 27.