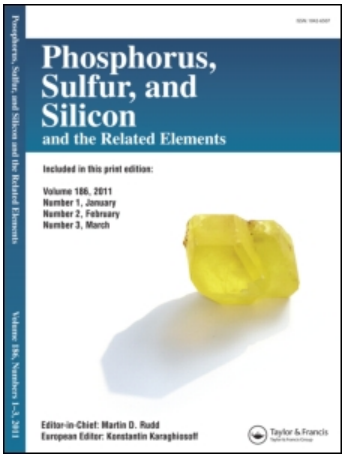

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Phase Transition of APP Form I to II and Synthesis of APP Form II from the System of Ammonium Orthophosphate-Urea

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Phase transition of ammonium polyphosphate (APP) form I to II was examined and 100% transformation of form I to II was achieved by heating form I at 280 to 290 °C under alternate gas flow of wet ammonia and dry air. Direct preparation of APP form II was made by heating a mixture of ammonium hydrogenorthophosphate and urea under wet ammonia at 280 to 300°C for 3 to 4 h. By adding APP form II as a seed crystal, APP form II was prepared by heatng a mixture of ammonium hydrogenorthophosphate and urea under wet ammonia at 280 to 305 °C for 1 h.

Keywords: ammonium polyphosphate; phase transformation

INTRODUCTION

Long-chain ammonium polyphosphates (APP) have been used as flame retardants for orgamic polymer naterials. When a flame retarding agent is used for organic materials, no chemical interaction between an organic material and a flame retatdant and no bleeding of a flame retardant are very inportant to prevent drowing down of a material power. APP has six crystal forms of I to VI[1,2]. Among the crystal forms, APP form I is easily prepared by heating a mixture of ammonium orthophosphate and urea. APP form II is made by heating a mixture of ammonium orthophosphate, phosphorus pentaoxide, and urea or by heating APP

form I at 200 to 375 °C in a well-covered container for more than 60 h^{-1}. APP forms III to VI are difficult to produce and the preparation needs sophisticated techniques. Accordingly, APP forms I and II are usually used as a flame retardant. APP form I is soluble in water and bleeds easily when an organic polymer material containing APP form I is exposed to humid air. APP form II has a high crystallinity and is slightly soluble in water. Therefore, APP form II is more suitable chemicals for a flame retardant than APP form I. As mentioned above, phosphorus pentaoxide must be used for the preparation of APP form II. Phosphorus pentaoxide is very active chemicals and harmful for a human body. When it is used on a factory scale, careful treatment is required. The preparation of APP form II from APP form I is not easy on a large scale, because the process needs a well-covered container. This paper describes a new easy transformation process of APP form I to II and direct preparation processes of APP form II without using phosphorus pentaoxide.

EXPERIMENTAL PROCEDURE

APP form I was made by heating an equimolar mixture of ammonium dihydrogen-orthophosphate and urea at 250 °C for about 1 h. The effect of experimental conditions (heating temperature, heating time, and atmosphere) on the phase transition of APP form I to II was studied. About 1 g of APP form I was used for the examination. Atmosphere in a reaction glass-tube was controlled by sending air, dry air, dry ammonia, and wet ammonia. Dry ammonia was prepared by passing ammonia through a glass tube filled with potassium hydroxide tablets. Wet ammonia was made by passing air through 1 to 29% ammonia water. The flow rate of any atmospheric gas was 40 dm^3/h. A direct preparation of APP form II from the systems of ammonium orthophosphate-urea and ammonium orthophosphate-urea-APP form II under wet ammonia was studied. In the second system, APP form II was used as a seed crystal. The effect of experimental conditions (mixing ratio, heating temperature, heating time, and atmosphere) was examined. The crystal form of the product was studied X-ray diffractometrically.

RESULTS AND DISCUSSION

The result of the phase transition of APP form I to II under dry air, dry ammonia, and wet ammonia are listed in Table 1. Reaction time was 3 h in all reaction systems. Under dry air, about 65% of APP form I transformed to APP form II at 260 °C. A sample melted at a temperature higher than 260 °C. Under dry ammonia, only a small amount (about 15%) of APP form I transformed to form

II even at 300 °C. Under wet ammonia which was made by passing air through 5% ammonia water, about 86% of APP form I transformed to form II at 300 °C. Under usual air, a sample melted even at 250 °C.

TABLE 1 Phase transition of APP form I to II

Atmosphere	Reaction temp. (°C)	Content (%) of APP form II
Dry air	250	62
	260	65
Dry ammonia	250 ~ 290	11 ~ 12
	300	15
Wet ammonia (5% ammonia water)	250 ~ 270	13 ~ 18
	280	32
	290	50
	300	86

Under all atmospheric conditions, it seemed that it was impossible to convert completely APP form I to II. It gave a fairly good transformation result under dry air and wet ammonia, so the transformation under alternate gas flow of dry air and wet ammonia was examined. The experimental condition listed in Table 2 gave a good result.

TABLE 2 Summary of preferable phase-transition condition of APP form I to II

Heating temperature: 280 ~ 290 C
Concentration of ammonia water: 3 ~ 5 %
Gas flow condition (min): alternate gas flow of wet ammonia and dry air
6 → 14 → 6 → 14 → 6 → 14 → 6 (66)
9 → 21 → 9 → 21 → 9 → 21 → 9 (99)

It is said that the preparation of APP form II is impossible from the system of ammonium orthophosphate-urea and phosphorus pentaoxide is required. According to the result obtained above, APP form I easily transformed to APP

form II under alternate gas flow of wet ammonia and dry air. The direct preparation of APP form II from the system of ammonium orthophosphate-urea was examined and it was found that APP form II can be prepared from the system under the reaction condition shown in Table 3.

TABLE 3 Summary of preferable reaction condition for the preparation of APP form II form the system of diammonium hydrogenorthophosphate-urea

Mixing molar ratio: $(NH_4)_2HPO_4$:$CO(NH_2)_2$=1:3 ~ 1:4
Heating temperature: 280 ~ 300 C
Reaction time: 3 ~ 4 h (for 1 g of raw material)
Atmosphere: wet ammonia obtained by passing air through 3 ~ 5% ammonia water with a flow rate of 40 dm^3/h

According to the result obtained above, APP form II can be prepared from the system of ammonium orthophosphate-urea. The reaction system takes 3 to 4 h of reaction time to obtain a good result. The reaction time is too long for a practical preparation. To short reaction time, the preparation pf APP form II was carried out with the system of ammonium orthophosphate-urea using APP form II as a seed crystal. The preferable reaction condition is shown in Table 4.

TABLE 4 Summary of preferable reaction condition for the preparation of APP form II from the system of $(NH_4)_2HPO_4$-$CO(NH_2)_2$-APP form II

Mixing molar tatio: $(NH_4)_2HPO_4$:$CO(NH_2)_2$=1:3 ~ 1:4
Mixing weight ratio of APP form II to raw material: smaller than 1:15
Heating temperature: 280 ~ 305 C
Heating time: longer than 0.5 h (for 1g of raw material)
Concentration of ammonia water: 1 ~ 8%

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