

## Thermal behaviour of ammonium polyphosphate–inorganic compound mixtures. Part 1. Talc

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### Abstract

The chemical interaction between ammonium polyphosphate (APP) and talc was studied under dynamic or isothermal heating conditions. The products of interaction were identified by X-ray methods or separated by thin layer chromatography and analysed. It was shown that APP decomposes above 280°C and starts to interact with talc above 300°C, giving binary ammonium silicon tetrapolyphosphate and ammonium magnesium polyphosphate or cyclophosphate depending on the initial APP/talc ratio in the mixture. The formation of magnesium cyclotetraphosphate, magnesium ultraphosphate, silicon oxymonophosphate and silicon diphosphate is observed after further heating at 400–800°C. A glass of magnesium silicon phosphate is formed at 1000°C.

The schemes of chemical reactions occurring at different temperatures are proposed for various APP/talc ratios.

### INTRODUCTION

Ammonium polyphosphate (APP) added with some organic compounds is widely used as an intumescent fire retardant for commercial polymers [1]. This type of fire retardant produces on the surface of the burning polymer an intumescent charred layer which provides thermal insulation to the polymer from the heat evolved in combustion, and hinders both access of oxygen to the polymer surface and diffusion of gaseous products of degradation to the flame [2–4].

Recently it was shown [5–8] that the addition of inorganic fillers to polymers in which these fire retardants are used either improves or impairs the protective properties of the intumescent layer depending on the type of filler. Our preliminary experiments showed that many inorganic compounds (metals, metal oxides, hydroxides, carbonates, etc.) which are widely used as fillers for commercial polymers [9] interact with APP at high temperatures.

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We therefore began a mechanistic study of the chemical interaction at high temperature between APP and some important inorganic fillers. This first part of our work deals with the mechanism of chemical interaction between APP and talc at temperatures up to 1000°C.

## EXPERIMENTAL

Ammonium polyphosphate Exolit 422 (Hoechst  $(\text{NH}_4\text{PO}_3)_n$ ,  $n \approx 700$ ) and talc for personal care ( $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ , the X-ray pattern of which was identical to that of the specimen described in ref. 10) were used. Thermal analysis of APP/talc mixtures (2:1; 3.6:1 and 6:1 weight ratio) was carried out using a Mettler TA 3000 thermal analyser (heating rate  $10^\circ\text{C min}^{-1}$ ; argon flow rate  $100 \text{ cm}^3 \text{ min}^{-1}$ ).

Products of chemical interaction between APP and talc were collected after isothermal heating of the mixtures for 10–12 h under air at 300, 400, 500, 600, 800 and 1000°C. The crystalline products were identified by X-ray analysis using a Zeiss HZG-4/A diffractometer (Carl Zeiss Jena; range of angles  $2\theta = 5\text{--}50^\circ$  Cu  $\text{K}\alpha$  radiation). In the water soluble fraction of the products, cations were identified by chemical analysis [11], and anions were analysed [12] after separation by thin layer chromatography (TLC).

## RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric (TG) curves of thermal decomposition of talc and APP. Talc (curve b) undergoes practically no weight loss up to 600°C, whereas at higher temperature (600–900°C) a small weight loss (3%) is observed (probably due to elimination of  $\text{H}_2\text{O}$ ).

It is known from the literature [13] that APP melts at 180–185°C. Apart from the removal of absorbed water between 100 and 220°C, the onset of weight loss due to APP degradation is observed at  $\approx 280^\circ\text{C}$  (Fig. 1, curve a). Above this temperature and up to 600°C, mostly the evolution of ammonia and water was detected [14]. The composition of the condensed phase ( $\text{P}_2\text{O}_5 \cdot 2m\text{NH}_3 \cdot p\text{H}_2\text{O}$ ,  $m < 1$  and  $p < 1$ ) changes with a decrease in both  $m$  and  $p$ ; however, the ratio  $p/m$  increases with increasing temperature. At 400–500°C,  $m \rightarrow 0$  and the composition of the residue effectively corresponds to the composition of polyphosphoric acid,  $\text{HPO}_3$ . In addition, ultraphosphate fragments are already detectable at 500°C [13] and their content increases with increasing temperature.

With further increase of temperature ( $T > 500^\circ\text{C}$ ),  $p \rightarrow 0.68$ , which corresponds to the azeotropic mixture of various polyphosphoric acids [15]. The polyphosphoric acids start to volatilize at 350–400°C [16]; however, maximum volatilization is observed at 560–630°C (Fig. 1, curve a).

Figure 2 shows experimental and calculated TG curves for 2:1; 3.6:1 and 6:1 APP/talc mixtures. The calculated curves (a', b' and c') are linear

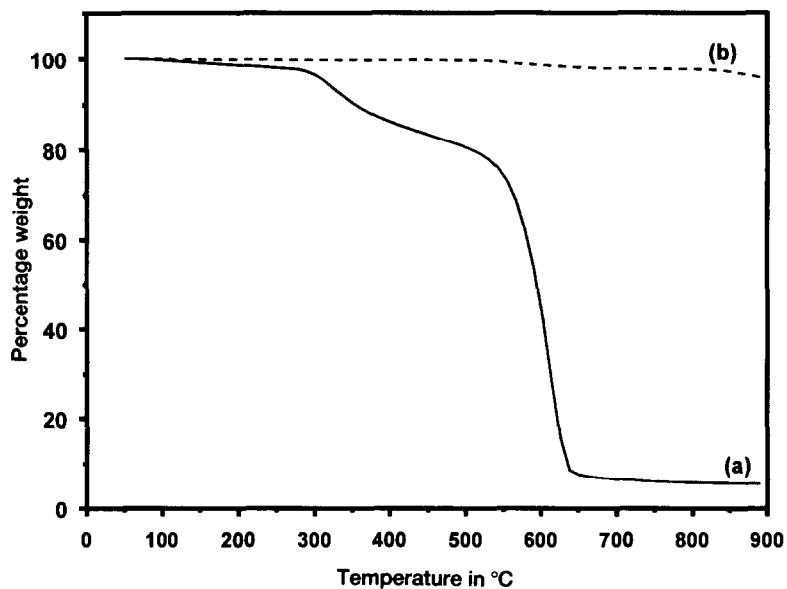


Fig. 1. TG curves of (a) APP and (b) talc. Heating rate  $10^{\circ}\text{C min}^{-1}$ , argon flow rate  $100\text{ cm}^3\text{ min}^{-1}$ .

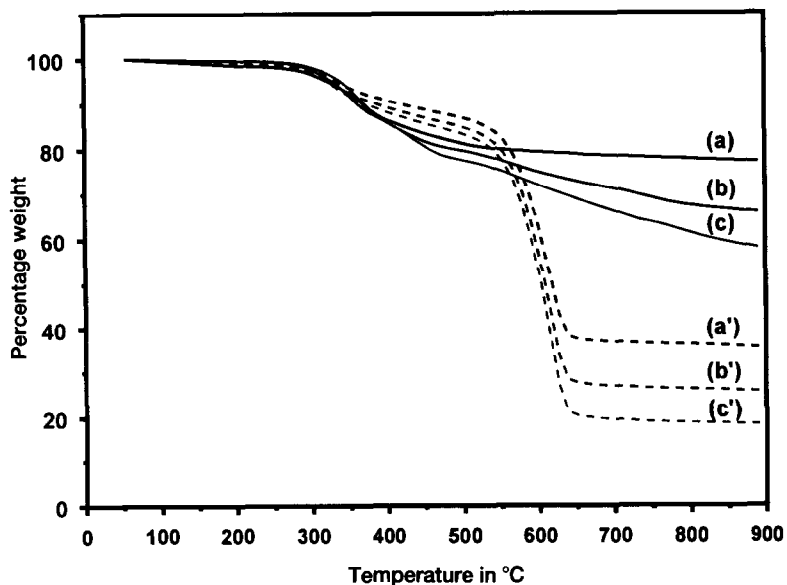


Fig. 2. Experimental (solid lines) and calculated (broken lines) TG curves of APP/talc mixtures: (a, a') 2:1; (b, b') 3.6:1; (c, c') 6:1. Experimental conditions as in Fig. 1.

combinations of the TG curves of APP and talc (Fig. 1) with coefficients depending on the ratio of APP to talc. The ratio 3.6:1 corresponds to an equivalent content of APP and talc, assuming the equivalence between  $\text{NH}_4^+$

and ( $\text{Mg}^{2+} + \text{Si}^{4+}$ ). The ratio 6:1 is an example of a mixture with APP in excess, whereas the ratio 2:1 is an example of a mixture with talc in excess.

There is practically no difference between the calculated and experimental curves up to 360°C (Fig. 2). Minor differences are observed at 360–560°C, where APP loses mainly  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , whereas at 650°C, after volatilization of polyphosphoric acids from APP, the differences are  $\approx 50\%$  for the ratio 6:1,  $\approx 45\%$  for the ratio 3.6:1 and  $\approx 40\%$  for the ratio 2:1. Thus, it becomes evident that talc interacts with APP at high temperature, giving products which are stable up to 900°C.

Figure 3 shows X-ray diffractograms of the products of interaction between APP and talc (ratio 2:1) after isothermal heating at different temperatures. There is no crystalline phase of APP after heating at 300°C (diffractogram a). The major products of interaction at this temperature are binary ammonium magnesium polyphosphate  $\text{MgNH}_4(\text{PO}_3)_3$  [17] and ammonium silicon tetrapolyphosphate  $\text{Si}(\text{NH}_4)_2\text{P}_4\text{O}_{13}$  [18]. The excess of

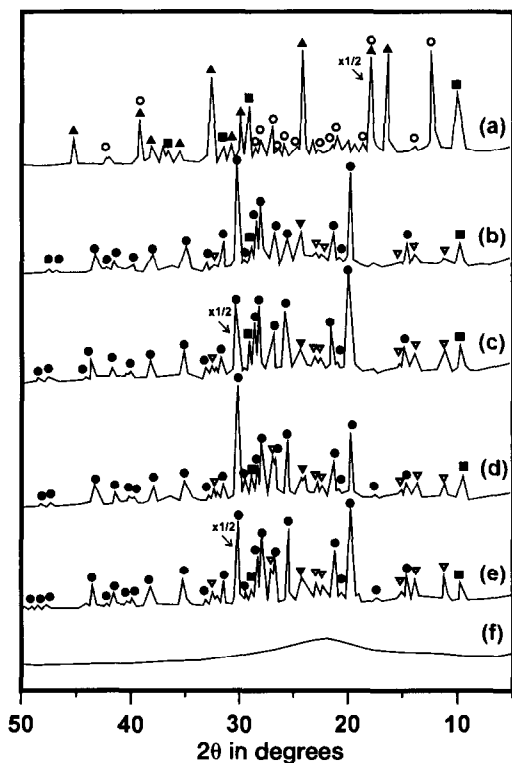
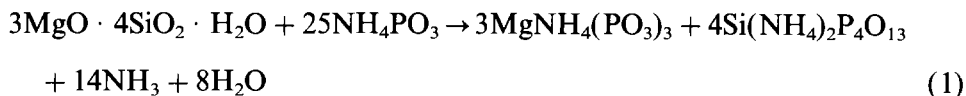


Fig. 3. X-ray diffractograms of products of interaction in the mixture APP/talc 2:1 at: (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C, (e) 800°C and (f) 1000°C. Diffraction peaks attributions:  $\blacktriangle$ ,  $\text{MgNH}_4(\text{PO}_3)_3$ ;  $\triangle$ ,  $\text{MgNH}_4\text{P}_3\text{O}_9$ ;  $\circ$ ,  $\text{Si}(\text{NH}_4)_2\text{P}_4\text{O}_{13}$ ;  $\bullet$ ,  $\text{Mg}_2\text{P}_4\text{O}_{12}$ ;  $\diamond$ ,  $\text{MgP}_4\text{O}_{11}$ ;  $\nabla$ ,  $\text{Si}_5\text{O}(\text{PO}_4)_6$ ;  $\blacktriangledown$ ,  $\text{SiP}_2\text{O}_7$  of pseudotetragonal crystalline form;  $\square$ ,  $\text{SiP}_2\text{O}_7$  of cubic crystalline form;  $\blacksquare$ , talc.

unreacted talc is detected at this temperature. The following scheme corresponds to the reaction between talc and APP at a temperature of 300°C:



Chemical analysis of the water soluble fraction of the amorphous part of the residue at 300°C showed the presence of  $\text{Mg}^{2+}$  and  $\text{NH}_4^+$ , and TLC revealed the presence of polyphosphate anions with different degrees of condensation (mainly with  $n > 4$ ).

Further transformations were observed in the mixture at 400°C (Fig. 3, diffractogram b). A set of diffraction peaks corresponding to a mixture of magnesium cyclotetraphosphate  $\text{Mg}_2\text{P}_4\text{O}_{12}$  [19] and silicon oxymonophosphate  $\text{Si}_5\text{O}(\text{PO}_4)_6$  [19, 20] appears. Traces of silicon pyrophosphate  $\text{SiP}_2\text{O}_7$  in pseudotetragonal crystalline form [21], for which only the most intense peak is detected, and of unreacted talc are also found. Thus, at this temperature the binary polyphosphates  $\text{MgNH}_4(\text{PO}_3)_3$  and  $\text{Si}(\text{NH}_4)_2\text{P}_4\text{O}_{13}$  lose all their ammonia and interact with excess of talc.

Further heating at 500, 600 and 800°C (Fig. 3, diffractograms c, d and e) does not change the composition of the residue. At 1000°C all components of the mixture melt and give a magnesium silicon phosphate glass on cooling (Fig. 3, diffractogram f).

The products of interaction in the 3.6:1 APP/talc mixture at 300°C are the same as in the 2:1 mixture (compare Figs. 3 and 4, diffractograms a). However, talc exhibits here less intense diffraction peaks, probably because of its more complete transformation. TLC shows an increase in the content of polyphosphate anions soluble in water. In general, scheme (1) may be operative in this case also.

The major products of interaction at 400°C (Fig. 4, diffractogram b) are  $\text{Mg}_2\text{P}_4\text{O}_{12}$  and  $\text{SiP}_2\text{O}_7$ . There are also weak diffraction peaks of talc. Further heating at 500°C leads to the appearance of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and of magnesium ultraphosphate  $\text{MgP}_4\text{O}_{11}$  [22] (Fig. 4, diffractogram c). The last-named product probably originates from cation exchange between  $\text{Mg}_2\text{P}_4\text{O}_{12}$  and ultraphosphoric moieties, which were detected at this temperature in the products of thermal decomposition of APP [13]. At 600°C the content of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  increases, whereas that of  $\text{MgP}_4\text{O}_{11}$  decreases (Fig. 4, diffractogram d).

On heating to 800°C, the intensity of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  diffraction peaks decreases, whereas that of the  $\text{SiP}_2\text{O}_7$  peaks increases (Fig. 4, diffractogram e). These data are in agreement with the literature [20], where preferential crystallization of  $\text{SiP}_2\text{O}_7$  instead of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  from the melt of mixtures of silicates and phosphates was observed in the same temperature interval.

The  $\text{MgP}_4\text{O}_{11}$  formed at 500°C starts to decompose at 600°C and completely decomposes at 800°C, whereas the intensity of diffraction peaks

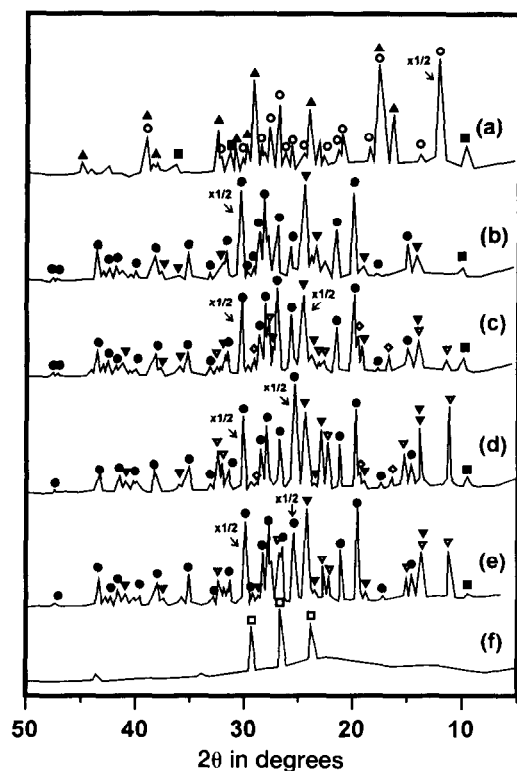


Fig. 4. X-ray diffractograms of crystalline products of interaction in the mixture APP/talc 3.6:1. Curves and peak attributions as in Fig. 3.

of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  increases slightly at  $800^\circ\text{C}$  (Fig. 4, diffractogram e). It is known from the literature [23] that  $\text{MgP}_4\text{O}_{11}$  becomes unstable at  $600^\circ\text{C}$  and decomposes to the more stable  $\text{Mg}_2\text{P}_4\text{O}_{12}$ :



The major products of interaction at  $1000^\circ\text{C}$  are a glass of magnesium silicon phosphate and crystals of  $\text{SiP}_2\text{O}_7$  of cubic crystalline form [24] (Fig. 4, diffractogram f).

The 6:1 APP/talc mixture contains an excess of APP, therefore talc is completely consumed by interaction with APP at  $300^\circ\text{C}$  (Fig. 5, diffractogram a). The major crystalline products at this temperature are  $\text{Si}(\text{NH}_4)_2\text{-P}_4\text{O}_{13}$  and binary ammonium magnesium cyclophosphate  $\text{MgNH}_4\text{P}_3\text{O}_9$  [25]. The latter was not detected in the mixtures with higher content of talc. A large amount of amorphous product, probably polyphosphoric acid, is detected at  $300^\circ\text{C}$ . The aqueous extract contains various polyphosphate anions and  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$  cations. The concentration of  $\text{NH}_4^+$  is much higher than the concentrations of  $\text{Mg}^{2+}$  and  $\text{Si}^{4+}$ .

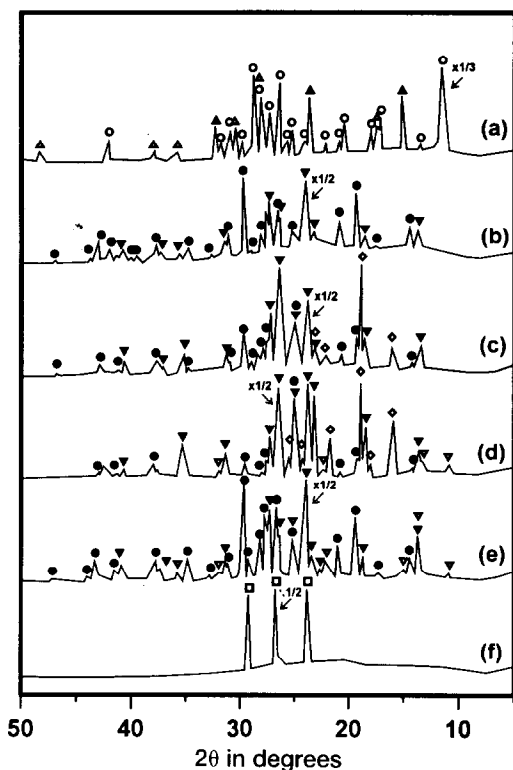


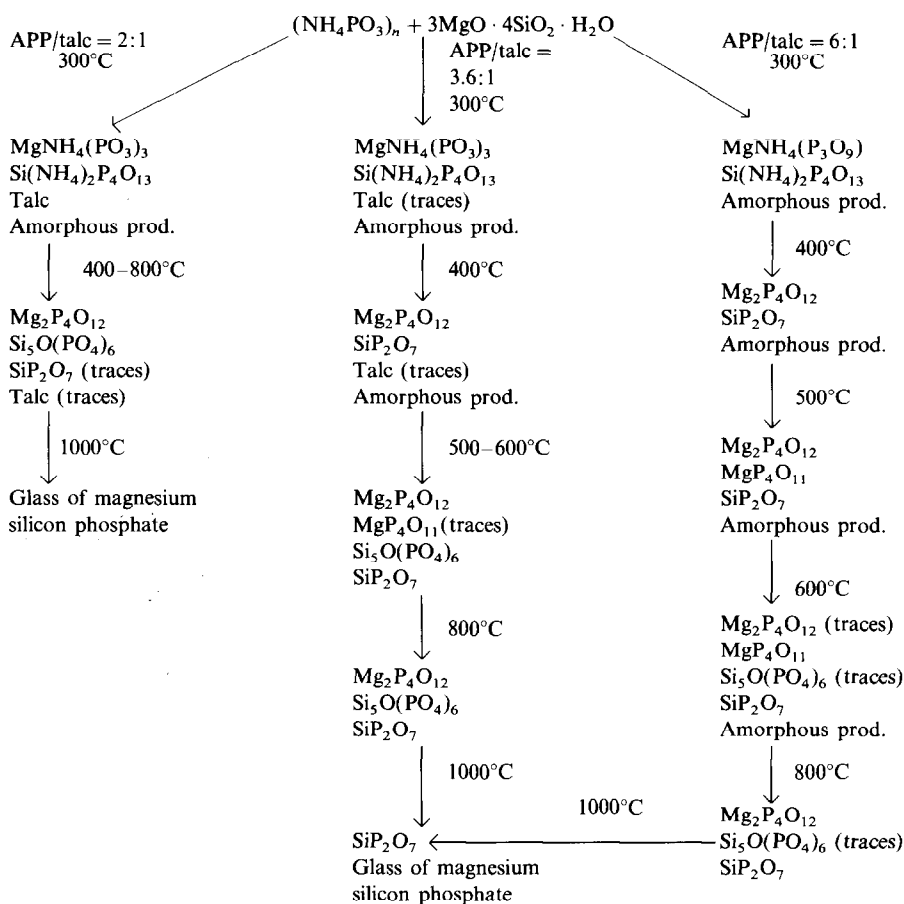
Fig. 5. X-ray diffractograms of crystalline products of interaction in the mixture APP/talc 6:1. Curves and peak attributions as in Fig. 3.

The mixture of products at 400°C contains crystalline  $\text{Mg}_2\text{P}_4\text{O}_{12}$  and  $\text{SiP}_2\text{O}_7$  (Fig. 5, diffractogram b);  $\text{Si}_5\text{O}(\text{PO}_4)_6$  is not formed here, probably because the excess of polyphosphoric acid formed from APP suppresses its crystallization. Further heating at 500°C (Fig. 5, diffractogram c) leads to the transformation of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  into  $\text{MgP}_4\text{O}_{11}$ , which proceeds at 600°C (Fig. 5, diffractogram d). At this temperature only traces of  $\text{Mg}_2\text{P}_4\text{O}_{12}$  are observed.

Weak diffraction peaks of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  appear at 600°C, probably because the excess of polyphosphoric acid evaporates at this temperature and therefore competition between the crystallization of  $\text{SiP}_2\text{O}_7$  and  $\text{Si}_5\text{O}(\text{PO}_4)_6$  shifts in favour of the latter. At 800°C  $\text{MgP}_4\text{O}_{11}$  decomposes in accordance with reaction (2). That is why its peaks disappear, whereas the intensity of the  $\text{Mg}_2\text{P}_4\text{O}_{12}$  peaks increases (Fig. 5, diffractogram e).

The products of interaction for the 6:1 APP/talc mixture at 1000°C (Fig. 5, diffractogram f) are the same as for the 3.6:1 mixture.

Taking into account the above considerations, the following scheme is proposed for the chemical interactions observed at high temperatures in the APP/talc mixtures:



This scheme shows that the products of interaction of APP with talc depend on the ratio of components in the initial mixture. An increase in the content of APP in the blends results in increased amounts of amorphous products, which comprise mostly polyphosphoric acid. The excess of polyphosphoric acid is detectable after heating the 6:1 APP/talc mixture at 600°C, whereas in the 3.6:1 mixture it interacts completely with talc at 500°C and in the 2:1 mixture at 400°C. Polyphosphoric acid suppresses the formation of  $\text{Si}_5\text{O}(\text{PO}_4)_6$  and promotes the formation of  $\text{MgP}_4\text{O}_{11}$  in the 3.6:1 mixture and, even more so, in the 6:1 mixture.

Chemical and physico-mechanical properties of the various phosphates formed by interaction of APP with talc are probably important in determining the protective ability of the intumescent layer formed on the surface of burning polymers. These aspects, as well as the mechanism of thermal decomposition of polymers added with APP/talc mixtures, are the objectives of our further study which is now in progress.



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