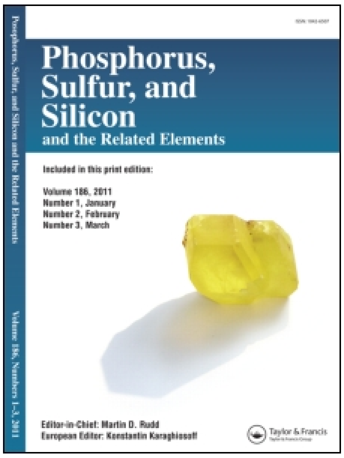

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Ammonium Polyphosphate and Red Phosphorus Two Well-Known Flame Retardants

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AMMONIUM POLYPHOSPHATE AND RED PHOSPHORUS TWO WELL-KNOWN FLAME RETARDANTS

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Abstract Improvements of application properties and application examples of ammonium polyphosphate and red phosphorus are discussed.

AMMONIUM POLYPHOSPHATE (APP)

About 40 years after the first manufacturing processes for APP were described[1], Hoechst succeeded in 1980 in developing a process for the manufacture of pure form-II-APP[2], one of five known crystal forms[3].

Table I
Properties of ammonium polyphosphate–commercial products

Producer	1) Crystal form			2) Water soluble parts	3) pH	4) Acid number	Sieve analysis (%)	
	I	II	V	at 25 °C		mg KOH/g	<45µm	<25µm
Monsanto - USA -	XXX	X	X	18 %	6,0	7,6	90	43
Hoechst - FRG -		XXX		3,6 %	5,9	0,3	>99	92

1) C.Y. Shen et al., J. Amer. Chem. Soc. 91, 62 (1969)
2) Monsanto-method: 10g sample in 100ml water, 20 min. stirring
3) Measurement in 1% aqueous suspension
4) Measurement in 5% aqueous suspension

This product distinguishes itself from competitive commercial products by its extreme fine particle size, low water solubility and a very low acid number.

Microencapsulation of APP

Although form-II-APP has comparatively favourable properties, there are some areas for improvement. They include flowability and water solubility at higher temperatures. These problems have been solved by microencapsulation with synthetic resins[4].

Table II Improvement of application properties of ammonium polyphosphate by microencapsulation with synthetic resins

Product	1) Water soluble parts		2) Flowability	Sieve analysis (%)		
	at 25° C	at 60° C	cot φ	<75µm	<45µm	<25µm
Form II-APP	3,6 %	42 %	< 0,7	>99	>99	92
Form II-APP *	0,1 %	0,6 %	1,8	>99	>99	90
Form II-APP **	0,3 %	1,6 %	1,3	>99	50	10

1) Monsanto-method: 10g sample in 100ml water, 20 min. stirring
2) Flowability according to Pfrengle (DIN 53916)
* Microencapsulated with melamine / formaldehyde resin
** Microencapsulated with epoxy resin

The values given in Table II indicate a 91 - 97 % decrease in water-soluble parts at 25 °C and a reduction by 97 - 99 % at 60 °C. The data demonstrate how a product with excellent flowability can be made from a non free-flowing material. It is remarkable that the fine particle size was not affected through microencapsulation with melamine/formaldehyde resins.

Application of APP

APP is used in various fields as a flame retardant. Patents granted to Monsanto[5] and Scott Paper[6] disclose the use in polyester-based rigid and flexible polyurethane foam. A self-extinguishing foam is obtained with about 10 - 15 parts APP per 100 parts of polyol.

Another field of application is the flame retardation of thermoplastics. The desired effects are achieved by the combination of APP with an organic nitrogen compound[7].

The third important application area for APP is intumescent coatings. Figure 1 gives an impression of the efficiency of intumescent coatings covering steel. The

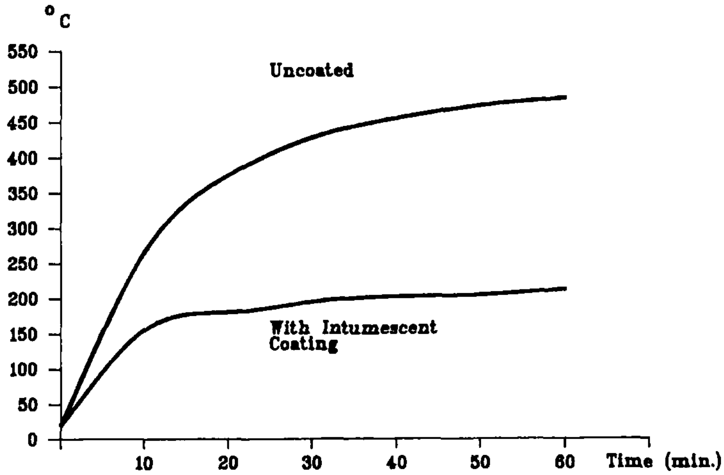

Figure 1 Test plate temperature in "Screening Test"

curves are the result of a "screening test" developed in our laboratories. It can be seen, that the temperature of the uncoated test plate rises to about 500 °C, while the coated test plate is protected and the temperature levels off at about 210 °C.

RED PHOSPHORUS

In the flame retardation of organic polymers red phosphorus plays a role similar to that of APP.

Without further treatment powdered red phosphorus tends towards the evolution of phosphine in the presence of moisture and air. Along with the dust problem, this disadvantage is an obstacle to greater use as a flame retardant. By developing processes for stabilisation and microencapsulation of red phosphorus, Hoechst overcame these problems in the mid 1970s[8]. The data in Table III show a very remarkable reduction of phosphine generation and formation of phosphoric acid as well.

Table III
Improvement of oxidation resistance of red phosphorus

Stabilizer	Concentration (%)	PH_3 - Generation 1) mg PH_3 /g	PH_3 - Generation 1) variation 2)	Formation of phosphoric acid 1) (%)	Formation of phosphoric acid 1) variation 2)
$Al(OH)_3$	1,18	2,30	-85%	8,2	-45%
Melamine/formaldehyde resin	4,20	0,48	-97%	4,2	-73%
Epoxy resin + $Al(OH)_3$	0,92 0,67	<0,02	-99%	0.05	-99%
unstabilized		15,1		>15	

1) Determination: Indian Standard "Specification of Red Phosphorus" (IS 2012-1961)
2) Compared to untreated red phosphorus

Application of red phosphorus

From the patent literature it becomes apparent, that red phosphorus is particularly suitable for oxygen-containing polymers like polyamide, saturated polyesters and epoxy resins. For example, glass fiber reinforced polyamide 6.6 and epoxy resins can be made flame retardant with 5 % respectively 8 - 10 % of red phosphorus[9,10].

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