Phosphorus: from urine to fire

Part 5: Phosphates in fire retardants

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Putting out fires

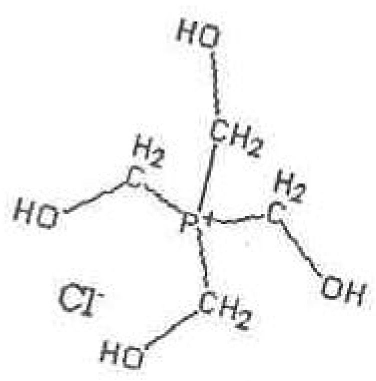
Phosphorus was discovered by its spectacular reaction with air - white phosphorus catches fire spontaneously (see part 1, CinA!, #60, Spring 2000). Sadly phosphorus has been used in incendiary bombs and burning phosphorus is difficult to put out. However, once oxidised to phosphates (O.S. +5), the most stable oxidation state for phosphorus, the compounds cannot be oxidised further and are thus fire-resistant. Phosphates are important additives to confer fire-resistance to otherwise flammable materials such as wood, paper and textiles.

Ammonium dihydrogenphosphate ($NH_4H_2PO_4$) is used to make paper and fabrics fire-resistant and is made by neutralising phosphoric acid with ammonia. More ammonia will give ammonium hydrogenphosphate ($(NH_4)_2HPO_4$) but this decomposes on heating losing ammonia and reverting to the dihydrogenphosphate. Ammonium phosphate ($(NH_4)_3PO_4$) is even more unstable to heat. (Ammonium phosphates are also used in fertilisers and in dyeing textiles.) The use of ammonium phosphates as fire retardants was first proposed by Gay-Lussac in 1891. Acids slow down the combustion of cellulose by producing carbonaceous char, rather than flammable gases, which prevents further combustion, although acids can also damage the fibres but the ammonium hydrogenphosphates decompose on heating, losing ammonia, and producing phosphoric acid which then slows down the combustion of cellulose.

To flameproof cloth or paper, they are sprayed with or dipped in ammonium phosphate solution and then dried, taking up 3-5% by mass of the retardant. Timber and wallboards are also fireproofed in the same way but the fire-proofing is removed by water. Wooden and paper matches are also treated with ammonium phosphate to prevent after-glow when the match is extinguished. This type of fire-proofing is limited to to internal use.

Another important fire-retardant is urea phosphate, a 1:1 adduct of urea (a base) with phosphoric acid. Cotton is fire-proofed by soaking in a solution of urea phosphate, so that there is about a 15% increase of dry mass. The dried fabric is then heated to 160oC, the urea partly decomposes and the phosphate is bound to the cellulose. This treatment does not wash off easily, but fire-proofing is reduced by prolonged washing. The treatment also reduces the strength of the fabrics and their wear resistance. Melamine phosphate can be used to treat wood.

Another phosphorus compound, tetrakis(Hydroxylmethyl)phosphonium chloride, $(HOCH_2)_4PCl$ or THPC, is used as a fire-retardant for nightwear. The phosphorus compounds are bonded covalently to the cellulose chains, without any soluble ions involved, and so they are wash-resistant. This process is expensive and almost doubles the cost of the garment. This process was invented by John D. Guthrie and Wilson A. Reeves in 1953.



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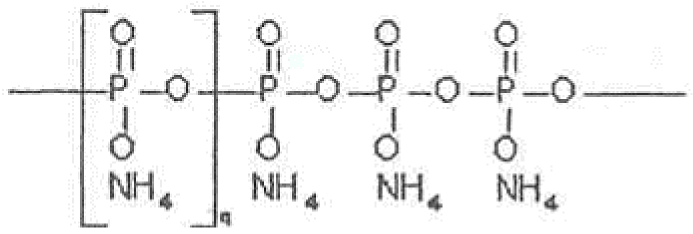

Ammonium polyphosphate is also used, the ammonium salt of polyphosphoric acid. It decomposes on heating to give polyphosphoric acid and ammonia. The organic surface layer is dehydrated to form carbon, giving a charred carbon foam surface layer which resists further burning. The surface swells and foams protesting the underlying material, a process known as intumescence. This process is used to protect structural steel using fire-retardant paint.

Amazingly red phosphorus is also used as a fire-retardant additive for plastics such as polyamides, polyesters and polyurethanes, which are loaded with 2-10% red phosphorus. When burnt the phosphorus abstracts oxygen and water from the polymer to form phosphoric acid and leaving a fire-resistant char behind.

Flame retardant chemicals work in one or more of the following ways:

promotion of char formation

conversion of combustible gases to non-flammable gases

forming a glaze barrier at the surface

forming an intumescent barrier at the surface

free radical termination in the gaseous phase

The chapter on flame retardants in Toy and Walsh describes many other phosphorus-based fire retardants. Borates are also used in fire-proofing.

References:

ch.10 in Arthur D.F. Toy and Edward N. Walsh, Phosphorus Chemistry in Everyday Living, 2mnd. edition,ACS 1987

Some useful websites:

www.fireretard.com

European site for high-fire performance wood products.

www.cefic-efra.com

Website of the European Lame Retardant Association with some useful factsheets on different fire retardant chemicals.

In the next issue: organophosphates