Commercial Developments in Red Phosphorus Performance and Stability for Pyrotechnics

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ABSTRACT

Red phosphorus has become an essential ingredient in the production of modern smoke and obscurant devices. Nearly all multi-spectral developmental projects are being based on the new versions of red phosphorus available from Clariant.

In pyrotechnics and munitions, phosphine liberated by the traditional red phosphorus-based smoke compounds may diffuse through the device and can give rise to corrosion of essential working parts. It is shown in this paper that surface modification treatment of red phosphorus can dramatically reduce the formation of decomposition products. New developments in coating the surface are presented and the long-term stability of various pretreated red phosphorus powders are discussed.

The best stabilization results are found by using special combinations of precipitated inorganic salts together with special micro encapsulation systems. The use of dust suppression agents is also discussed.

The newly-developed materials reduce the potential hazards that arise during the manufacturing process whilst improving the shelf life of the smoke composition.

Keywords: red phosphorus, stability, smoke microencapsulation

Commercial Production of Red Phosphorus

White phosphorus (also known as yellow phosphorus) is produced in an electric furnace at 1,400–1,500 °C from a sintered mixture of rock phosphate (fluorapatite), coke and silica. The gaseous white phosphorus (P_4) is distilled from the furnace by condensing with water.

Red Phosphorus is commercially produced from white phosphorus by a thermal conversion. The existing process has been used in Knapsack, Germany since 1953. See Figure 1. The conversion of white phosphorus to red phosphorus is performed in multi-ton batches in special sealed reactors. Each reactor consists of a rotary iron furnace resting on two hollow shafts with a drive mechanism and contains milling balls to grind the converted phosphorus to the desired particle size. The thermal conversion takes place at elevated temperatures over a period of several hours. The reactor is then cooled and filled with water, and the red phosphorus is milled to a fine-grained powder.

An aqueous dispersion of red phosphorus is pumped to stirred vessels, where remaining white phosphorus is removed with sodium hydroxide. Technical red phosphorus contains significantly less than 200 ppm white phosphorus. The phosphorus is filtered, washed and dried under nitrogen. Red phosphorus is then packed in anti-static plastic bags, steel drums or other specialized containers.

Table 1. Safety Data of Red Phosphorus (source: Clariant's Investigations).

Parameter	Value
Red phosphorus purity	>99%
White phosphorus (P_4) content	<0.02%
Acute oral toxicity LD50 (rat)	>15,000 mg/kg
Fish toxicity LC50 (brachidanio rerio) Method: 92/69/EEC, C.1	>10 mg/l, 96 h exposure
Bacteria toxicity EC50 (activated sludge) Method: OECD 209	>1,000 mg/l, 3 h exposure

Applications for Red Phosphorus

Red Phosphorus is commercially used in a wide variety of industrial applications (see Figure 2), with the classical ones being, safety matches, chemical catalyst, phosphides and pyrotechnics.

In most applications, the red allotrope is favored over the white allotrope because of its greater stability in air and its easier handling characteristics. Red phosphorus is not considered problematic with regard to environmental and occupational health issues. It is not soluble in water and is considered non-toxic when pure (see Table 1). When the content of white phosphorus is less than 0.02%, the LD50-value is >15,000 mg/kg (rat).

a) Safety Matches

The production of safety matches is still an important market for high-grade, fine-grained red phosphorus. The phosphorus is used on the striking surface of the matchboxes. It is typically applied by using a rotogravure printing process together with binders (e.g., polyvinyl alcohol, PVA) and special fillers (see Tables 2 and 3). The modern printing process requires especially fine-grained red phosphorus to operate efficiently and economically.
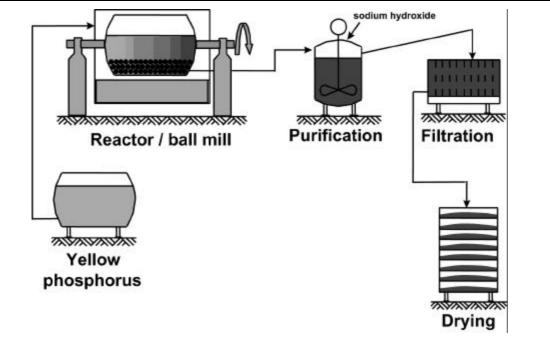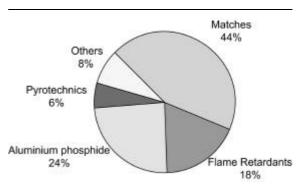

Figure 1. Production of red phosphorus.

Table 2. Traditional Friction Compound Guide Formula for Safety Matches.

Ingredient	% by weight
Red phosphorus grade NF	17–24
Binder (gum Arabic/gelatin type)	10–12
Antimony sulfide	20–24
Filler*	2–6
Water	38–48

Table 3. Rotogravure-Style Friction

Figure 2. Application areas of red phosphorus worldwide 1999.

Compound Guide Formula.

Ingredient	% by weight
Red phosphorus grade NFC	60–80
Binder (water based PVA)	40-20
Friction fillers*	0–2

* fillers are typically mixtures of silicates and metal oxides

Although the match industry is still growing in some regions the total quantity of red phosphorus in match making applications has been declining for some years due to the consolidation of production units, improved processing efficiency and wide spread introduction of rotogravure printing technology.

b) Flame Retardants

Red phosphorus is often used as a flame retardant additive for plastics. It is quite astonishing that red phosphorus, being a flammable powder, can act as one of the most efficient flame-retardants known for plastics. The addi-

tion of red phosphorus is typically in the range of 5–10%. The flame-retarded plastics are used widely in electronics, where it is replacing brominated and chlorinated flame-retardants. Red phosphorus is incorporated in plastics like polyamide, epoxy resins, polyurethanes and rubbers and is now available in a wide range of polymer carriers such as polyolefins, polyamides and special thermoplastic resins. The polymer industry is now able to obtain the red phosphorus as dispersions, pastes, pellets or prills, which eliminates the issues of handling red phosphorus powders.

c) Phosphides

A considerable portion of red phosphorus is converted to aluminium phosphide. This is applied as a fumigant for pest control purposes in grain and tobacco silos, mainly due to its ability to liberate phosphine gas. The aluminium phosphide is formulated with other additives and then pressed in small pellets. The pellets are left to react with atmospheric moisture in the silos to generate phosphine gas; the aluminium is converted into a residual slag of aluminum oxides and hydroxides. The residual phosphine in the silo is then further oxidized to phosphoric acids.

d) Pyrotechnics—Smoke and Obscurants

Red Phosphorus is an essential component in the production of energetic, multi-spectral smoke and obscurant devices in both current and future applications. The red phosphorus is normally mixed with a binder and an initiator (e.g. magnesium) in a solvent. The resulting mixture is then physically processed to the required shape or form. The binder is typically a butyl rubber, fluorinated rubber or epoxy resin. However, some formulations also include magnesium in the composition. It reacts in the slag formed on the pellets to consume the slag and promote complete combustion.

When a smoke grenade is launched, the pellets are ignited and dispersed. The burning red phosphorus produces a dense white smoke, while the binder maintains the integrity of the pellets to promote duration of the smoke screen. The burning red phosphorus produces mainly phosphorus pentoxide in the presence of excess oxygen. Phosphorus trioxide is the major prod-

uct when combustion is oxygen limited.[1] The phosphorus pentoxide hydrolyses to form a series of polyphosphoric acids, which are biologically degradable.

Minimal quantities of red phosphorus within the field of pyrotechnics are also used in the production of toy pistol caps.

Stability of Red Phosphorus

One significant problem with pure red phosphorus powder is that on storage, a gradual release of toxic phosphine gas occurs and various phosphoric acids are produced. This decomposition reaction takes place in the presence of oxygen and water. See Figure 3. The decomposition rate depends directly on the availability of air, moisture and temperature. In pyrotechnics and munitions, the phosphine liberated by standard red phosphorus charges may diffuse through the device and can give rise to corrosion, presumably after subsequent oxidation to phosphoric acids.
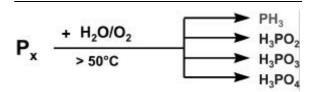

$$P_x \quad \xrightarrow[> 50°C]{+ H_2O/O_2} \quad \begin{matrix} PH_3 \\ H_3PO_2 \\ H_3PO_3 \\ H_3PO_4 \end{matrix}$$

Figure 3. Red phosphorus disproportionates in the presence of moisture at elevated temperatures.

The formation of phosphine gas can be suppressed by:

- ? controlling the availability of moisture and oxygen
- ? store at room temperature
- ? using stabilisers to inhibit phosphine formation
- ? using dust suppressants (oiling)
- ? coating the surface of the red phosphorus (microencapsulation)

The first generation of pyrotechnical red phosphorus basically evolved in the late 1940's and early 1950's when the US military intro-

duced a procurement specification for red phosphorus powder. The result was the initial version of US MIL-P-211. The focus was to try to control the presence of white phosphorus and moisture. These were recognized as being key issues in the processing and stability as the white phosphorus is spontaneously combustible and the moisture specification was used to ensure that dry material was delivered.

In the following years, producers improved the stability of red phosphorus by introducing additives to the powder. Additives can be a mixture of dust suppressing agents, stabilisers or microencapsulating resins. The principle behind these additives is to reduce the sensitivity of red phosphorus to chemical influence and decomposition. It is shown in the following section how these additives reduce phosphine emission from red phosphorus powder. The major improvement was the introduction of new microencapsulation technology, a technique now regarded as being standard in the plastics industry, but not applied until now in pyrotechnic formulations.

Experimental Work

The phosphine emission of red phosphorus powder grades can be measured with Draeger tubes either at 25 °C (room temperature) and 65% humidity (vapor pressure over saturated aqueous ammonium nitrate solution), or at 80 °C and 100% humidity. Data is given in micrograms of phosphine per gram of red phosphorus powder.

a) Dust Suppression

Handling red phosphorus powder can be hazardous due to the potential for dust explo-sions. Dust suppressing[2] or "oiling" prevents dust explosions, improves the handling and increases its stability in air due to the reduction of the active surface of red phosphorus. In dust suppressing, the dust particles are agglomerated to form bigger particles. See Figure 4.
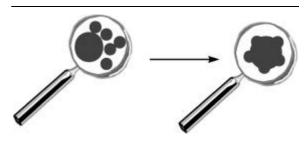

Figure 4. Effects of dust suppressant.

The 1980's saw the introduction of "oiled" red phosphorus, which basically involved the introduction of dust suppressants. In practice the red phosphorus producers "oiled" the material and the red phosphorus customers then used a solvent (e.g., acetone or methylene chloride) to remove the oil before processing. The US MIL-P-211 specifications required 0.8–1.5% dust suppressant.

Typical dust suppressants are liquid organic compounds. The US MIL-P-211 allows the use of commercially available long chain ethoxy-lates rather than the original transformer oils. Table 4 shows the reduction of phosphine emission by the addition of dust suppressant, measured at 25°C and 65% humidity compared to non-dust suppressed red phosphorus. Note that in the first days a decrease in phosphine emission by a factor of seven is observed but after two or four weeks, the reduction is by only half the amount of phosphine observed with the untreated red phosphorus.

Table 4. PH$_3$ Generation at Room Temperature (25 °C) and 65% Humidity. A Comparison of various Red Phosphorus grades.

Red phosphorus grade	PH$_3$ formation (µg/g RP)			
	24 hr	48 hr	14 days	28 days
Non dust suppressed *Clariant grade SF*	150	290	1300	2400
Dust suppressed *Clariant grade HB 250*	18	40	507	980
Stabilized *Clariant grade NF*	3	5	48	81
Stabilized and dust suppressed *Clariant grade NFD*	3	5	32	48
Microencapsulated *Clariant grade HB 700**	2	3	7	8
Microencapsulated *Clariant grade HB 714***	0.8	1.2	3	4

* HB 700: stabilized, dust suppressed and microencapsulated.

** HB 714: stabilized and microencapsulated.

b) Stabilisation

Various metal oxides can be used as stabilizers[3] by precipitating them on the surface of the red phosphorus grains. Typical metal oxides are aluminium and magnesium and they work by buffering acid traces formed on oxidation of red phosphorus. Freshly prepared red phosphorus in an aqueous dispersion gives a nearly neutral pH. After storage, the pH value decreases with time from pH 7 to pH 2. Stabilized red phosphorus keeps the neutral pH value for a longer time (e.g., approximately six months).

In the mid-1980s, the stabilizer technology for red phosphorus was improved further by the matchmaking and plastics industry. The basic idea behind the improvements can be found in the MIL-P-670A dating back to 1948 but this was mostly used for Navy markers and not for general smoke and obscurant applications. The MIL-P-670A included an aluminium stabilizer coupled with a basic particle size distribution requirement but no dust suppressant.

As shown in Table 4 (grade NF), stabilisers suppress the phosphine emission from RP powder (in addition to maintaining a neutral pH.)
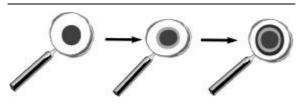
c) Combination of Stabilisers and Dust Suppressants

As expected, the combination of both stabilizing metal oxides and dust suppressing oils on the red phosphorus surface gives further improved effects. See Table 4, grade NFD as an example. Such red phosphorus is used in the match industry as the top quality red phosphorus grades.

d) Microencapsulation

Microencapsulation[4,5] of red phosphorus reduces its active surface. It is a very thin coating on the individual grains. Various resins can be used for microencapsulation with the best results obtained using selected thermoset resins, such as epoxy resins or phenolic resins.

Figure 5. Stabilisation and microencapsulation of red phosphorus grains.

Microencapsulation is normally combined with stabilization and dust suppression to optimize performance. See Figure 5.

The resin content can vary from 1–8% by weight of red phosphorus. Some interesting combustion characteristics can be obtained by changing the microencapsulation system.
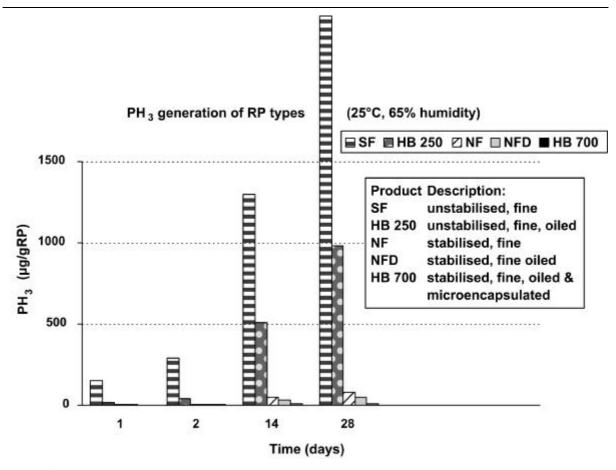
Microencapsulated red phosphorus grades are used extensively in the plastics industry, where approximately 5–8% by weight are added to different polymers as a flame retardant. Such plastics include polyamides, polyurethanes, polyethylene, EVA (ethylene-vinyl-acetate), and epoxy resins. Microencapsulation is currently not included in military specifications.

As shown in Table 4 (grades HB 700 and HB 714), microencapsulated RP red phosphorus grades provide a significant improvement in stability. The use of red phosphorus in the plastic industry would be virtually impossible without applying these techniques.

A graphic overview of the change in phosphine generation is shown in Figure 6.

Conclusion

The reported data shows that the stability of red phosphorus in air and in a humid environment can be improved by a combination of

Figure 6. PH₃ generation of red phosphorus types.

stabilisers and microencapsulation. The newly developed materials reduce the potential hazards in the manufacturing process of smoke compounds and can lead to shelf life improvements in red phosphorus-based obscurants. The development work is continuing, driven by the requirement to further improve the stability of phosphine and to produce flame-retardants with better performance characteristics. The future research and development work will continue to be focused on the technical improvements required to further penetrate the polymer industry with high performance flame-retardants.

The efforts will benefit manufacturing safety and performance of both military and civilian pyrotechnic items in the future.

Literature

1) F. G. Burton, M. L. Clark, R. A. Miller, and R. E. Schirmer, *American Industrial Hygiene Association Journal*, Vol. 43, No. 10 (1982) p 767–772.

2) H. Staendeke, and U. Thuemmler, *EP* 176 836 (1985).

3) H, Staendeke, U. Thuemmler, *EP* 378 803 (1989).

4) H. Staendeke, U. Thuemmler, *EP* 176 834 (1985).

5) H. Staendeke, U. Thuemmler, *EP* 283 759 (1987).