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Improvements in Stability of Red Phosphorus

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Abstract

Red phosphorus has become an essential item in the production of modern smoke and obscurants devices, additionally 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 red phosphorus charge may diffuse through the device and can give rise to corrosion of essential working parts. It is shown in this work that surface modification treatment of red phosphorus reduces dramatically the formation of decomposition products. New developments in coating the surface are presented and the long term stability of different pre-treated red phosphorus powders are discussed.
The best results are found by using special combinations of precipitated inorganic salts with micro encapsulations. The use of dust suppression agents is also discussed.
The new developed materials reduce the hazards in the manufacturing process and should improve the shelf life of smoke compounds.

Introduction

Red Phosphorus is produced from white phosphorus by a thermal conversion. The process has been used in Germany since 1936 in Bitterfeld and since 1953 in Knapsack, where Clariant produces red phosphorus.
Red Phosphorus has a wide variety of industrial applications, for instance in the production of safety matches, production of metal phosphides, as flame retardant additive in some plastics and in pyrotechnics. The red allotrope is favoured over the white allotrope because of its greater stability in air and easier handling characteristics. Red phosphorus is considered to be harmless with regard to environmental and occupational health issues. Red phosphorus is not soluble in water and non toxic. The content of white phosphorus is less than 0.02%, the LD50-value equals > 2000 mg/kg (rat).

Table 1: Safety data of Red Phosphorus

Parameter	Value
Purity	> 99%
P_4-content	< 0.02%
Acute oral toxicity LD50 (rat)	> 15000 mg/kg
Fish toxicity LC50 (brachidanio rerio)	> 100 mg/l, 96 h exposure
Bacteria toxicity EC50 (activated sludge)	> 1000 mg/l, 3 h exposure
R-phrases	11,16
S-phrases	7,43

Red Phosphorus is an essential component in the production of energetic multi spectral white smoke in both current and future applications. The red phosphorus is normally mixed with a binder and an initiator 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.
When a grenade is launched, the pellets are ignited and dispersed. The burning red phosphorus produces a dense white smoke, whereas the binder improves the distribution of the smoke screen. The burning red phosphorus produces mainly phosphorus pentoxide in the presence of excess oxygen. Phosphorus trioxide is the major product when combustion is oxygen limited [1]. The phosphorus pentoxide hydrolyses to form a series of polyphosphoric acids, which are biologically degredable. .

One signifikant problem with standard red phosphorus powder is that on storage, there is a gradual release of toxic phosphine gas and different phosphoric acids. This is a decomposition reaction which takes place in air, the decomposition rate depends directly on the availability of moisture and temperature. In pyrotechnics and munitions, the phosphine liberated by standard red phosphorus charge may diffuse through the device and can give rise to corrosion, presumably after oxidation to phosphoric acids.

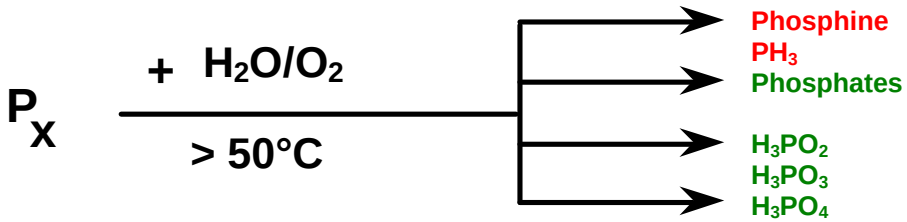

Figure 1: Scheme of the disproportionation of red phosphorus in the presence of moisture at elevated temperatures

The formation of phosphine gas can be suppressed by:

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

Experimental work

Another approach is to deposit additives on the surface of red phosphorus to enhance its stability in air. These additives can be a mixture of dust suppressing agents, stabilisers or microencapsulating resins. The principle idea of these additives is to reduce the sensitivity of red phosphorus to chemical influence and decomposition.

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

1. Dust suppressing [2]

Red Phosphorus dust is dangerous for dust explosions. Dust suppressing or oiling prevents dust explosions, improves the handling and improves the stability in air due to reduction of the active surface of red phosphorus. In dust suppressing, the dust particles are fixed to bigger particles. Typical dust suppressants are liquid organic compounds as described in the military specifications, e.g. US MIL-P-211 and GB 68-96. Table 2 shows the reduction of phosphine emission by addition of dust suppressant, measured at 25°C and 65% humidity. Whereas in the first days a decrease in phosphine emission by a factor of seven is observed, after two or four weeks it is only half the amount of phosphine observed, compared with untreated red phosphorus.

Table 2: PH_3 generation at room temperature (25°C) and 65% humidity
Comparison of dust suppressed and non-dust suppressed phosphorus

RP grade	PH_3 formation / µg/g RP			
	24 h	48 h	14 days	28 days
Non dust suppressed *Clariant grade SF*	150	290	1300	2400
Dust Suppressed *Clariant grade HB 250*	18	40	507	980

2. Stabilisation [3]

Different metal oxides are used as stabilisers for red phosphorus. These oxides buffer acid traces formed upon oxidation of red phosphorus.
Freshly prepared red phosphorus reacts in an aqueous dispersion nearly neutral. After storage, the pH value of red phosphorus, suspended in water, decreases from 7 to 2-3 over some month, depending on the temperature. Stabilised red phosphorus keeps the neutral pH value when dispersed in water for longer time, e.g. approximately six month.
The metal oxides are precipitated on the surface red phosphorus. The military specification US MIL-P-670A describes an aluminiumhydroxide stabilized red phosphorus.
As shown in table 3, stabilizers not only keep the pH values neutral, but suppress also the phosphine emission from RP powder.

Table 3: PH_3 generation at room temperature (25°C) and 65% humidity
Comparison of stabilized and non-stabilized phosphorus

RP grade	PH_3 formation / µg/g RP			
	24 h	48 h	14 days	28 days
Non stabilized *Clariant grade SF*	150	290	1300	2400
Stabilized *Clariant grade NF*	3	5	48	81

3. Combination of stabilisers and dust suppressants

As expected, combinations of stabilising metal oxides and dust suppressing oils added on the RP surface give additional effects. Such RP grades are used in the match industry being the top quality RP grades.

Table 4: PH_3 generation at room temperature (25°C) and 65% humidity
Comparison of stabilised and dust suppressed phosphorus to stabilised or dust suppressed phosphorus

RP grade	PH_3 formation / µg/g RP			
	24 h	48 h	14 days	28 days
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

4. Microencapsulation [4,5]

Microencapsulation of red phosphorus reduces the active surface of the phosphorus. It is a very thin coating of the single grain. Different resins can be used for microencapsulation. We found the best results using thermoset resins, applied from solution and cured directly on the red phosphorus particles.

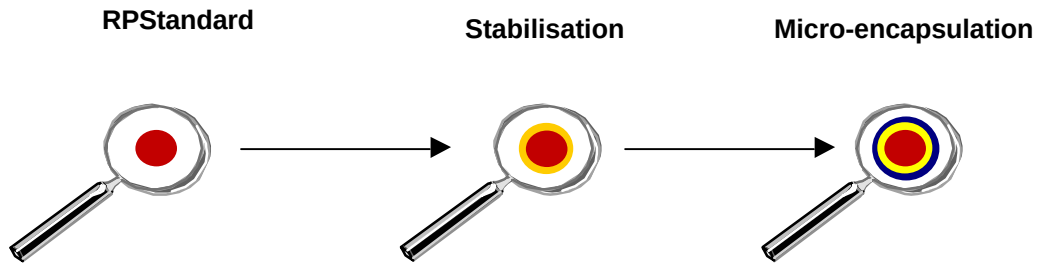

Figure 2: Scheme of stabilisation and microencapsulation of RP grains

Microencapsulation is normally combined with stabilisation and dust suppressing, if required. The resin content varies from 1-8%w/w of RP. The burning characteristics of red phosphorus are not changed by the stabilisers and the resins applied.

Microencapsulated red phosphorus grades are widely used in the plastics industry, where approximately 5-8% w/w are added to different polymers to make them flame retarded. Such plastics include polyamides, polyurethanes, polyethylene, EVA (ethylenevinylacetate) and epoxy resins.

Currently, microencapsulation is **not** included in military specifications.

Table 5: PH_3 generation at room temperature (25°C) and 65% humidity
Comparison of microencapsulated and not encapsulated phosphorus

RP grade	PH_3 formation / µg/g RP			
	24 h	48 h	14 days	28 days
Stabilised 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: stabilised, dust suppressed and microencapsulated
** HB 714: stabilsed and microencapsulated, phosphorus content lower than HB 700

As shown in table 5, microencapsulated RP grades are a big improvement in the stability of red phosphorus. The use of red phosphorus in the plastic industry would be impossible without applying these technique.

5. Overview of Clariant's RP product range

Clariant offers a wide range of RP products with different stabilizers, dust suppressants and microencapsulations. Tailor made concentrates as well as different partcle sizes are also available.

Table 6: Clariant's current range of red phosphorus products for pyrotechnical applications

RP product	**properties**	**features**
SF	-	> 99% phosphorus
OM 3	dust suppressed	GB Def. Standard
HB 100	stabilised, dust suppressed	
HB 250, HB 251	dust suppressed, non-stabilised	US MIL-P-211 E,F
HB 300	stabilised, microencapsulated	
HB 400	stabilised, microencapsulated	
HB 600	stabilised, microencapsulated	
HB 700	stabilised, microencapsulated, with dust suppressant	
HB 710	stabilized	US MIL-P-670A
HB 714	stabilized, microencapsulated	> 91% phosphorus
HB 800	development product	

Conclusion

It is shown in this work that the stability of red phosphorus against air and humidity can be improved by a combination of stabilisers and microencapsulation. The new developed materials reduce the hazards in the manufacturing process of smoke compounds and can lead to shelf life improvements in red phosphorus based obscurants.

Literature

[1] Burton, F.G., Clark, M.L., Miller, R.A., Schirmer, R.E., American Industrial Hygiene Association Journal 43, (10), 767-772, 1982
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[3] Staendeke, H., Thuemmler, U., EP 378 803 (1989)
[4] Staendeke, H., Thuemmler, U., EP 176 834 (1985)
[5] Staendeke, H., Thuemmler, U., EP 283 759 (1987)