Review

Special Materials in Pyrotechnics: V. Military Applications of Phosphorus and its Compounds

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Abstract

This paper reviews the military applications of phosphorus in obscurants, incendiaries, float and smoke signals, friction igniters and decoys. Whereas white phosphorus (WP) is still in use as both incendiary and obscurant ammunition it has been mainly replaced today by red phosphorus (RP). For part VI see Ref. [1].

Keywords: Incendiaries, Obscurants, Red Phosphorus, White Phosphorus

1 Introduction and Scope of Work

Phosphorus is one of the most versatile elements applied in chemical warfare. Among the fuels applied in pyrotechnics the exposed position of phosphorus is mainly related to its low ignition temperature – and even pyrophoricity as in the case of the white phosphorus (WP) – its high reactivity towards oxygen making it thus virtually inextinguishable, its high enthalpy of combustion and the impressive obscuring power not reached by any other material.

Hence, the main military applications for phosphorus and its compounds are igniters, incendiaries, screening smoke ammunition, flame and smoke signals and decoys just to name the most important ones. The combustion chemistry of red phosphorus (RP) and WP as well as hazardous reactions and toxicity of both RP and WP have been discussed by the author recently [2]. From this it is obvious that WP is inadmissible in today's military applications. Nevertheless very weak specifications for the quality of RP on the other hand still feed the 'phosphine (PH_3)-problematic' known since some 50 years now. Thus, it is highly desirable that military users and procurement agencies together with the defence industry define new standards for the quality of RP for further safety of ammunition [3].

In the following the application of phosphorus in a variety of military applications will be discussed.

2 Obscurant Smokes

Obscurants fulfil a prominent role in today's warfare in that they serve for screening, blinding, deception and training. An obscurant smoke is an aerosol cloud brought into the line of sight (LOS) between an observer and a target (Figure 1).

To evaluate the performance of obscurant materials both yield factor Y_f (–) and mass extinction coefficient α_λ ($m^2\ kg^{-1}$) have to be considered as figures of merit.

The yield factor Y_f gives the ratio between the mass of the aerosol m_s and the mass of the pyrotechnic payload m_p. It is dependent on the chemistry of the combustion products and on potential secondary reactions of the aerosol in the atmosphere such as, for example, hydration reactions.

$$Y_f = \frac{m_s}{m_p} \qquad (1)$$

The mass extinction coefficient, α_λ, is given by Lambert Beer's law, Eq. (2).

$$\alpha_\lambda = -\frac{\ln T_{obsc}}{cl} \qquad (2)$$

where c is the concentration of obscurant aerosol in obscurant cloud (kg m^{-3}), l the optical pathlength within the obscurant cloud (m) and T_{obsc} is the dimensionless degree of transmission (–), that is

$$T_{obsc} = \frac{I_t}{I_0} \qquad (3)$$

in this context the absorbance A is defined as

$$A = \ln\frac{I_0}{I_t} \qquad (4)$$

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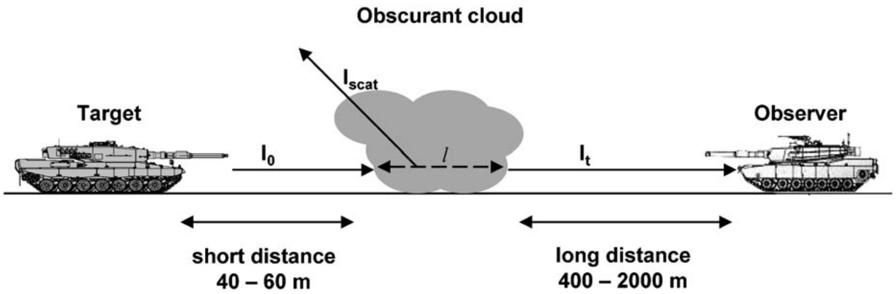

Figure 1. Typical obscuration scenario.

where I_0 is the initial radiant intensity emanating from the target and I_t is the fraction of radiant intensity transmitted after passing the aerosol cloud.

Considering an obscurant aerosol one has to distinguish between hygroscopic and non-hygroscopic aerosols. In contrast to non-hygroscopic smoke materials such as carbonaceous soot and brass particles the performance of hygroscopic aerosols like, for example, $LiCl_{(s)}$ [4], $ZnCl_{2(s)}$ [5] or $P_4O_{10(s)}$ [5] is always dependent on the relative humidity RH (%) in the air which itself is a function of the ambient temperature. Figure 2 gives the maximum water content of the atmosphere as a function of the temperature.

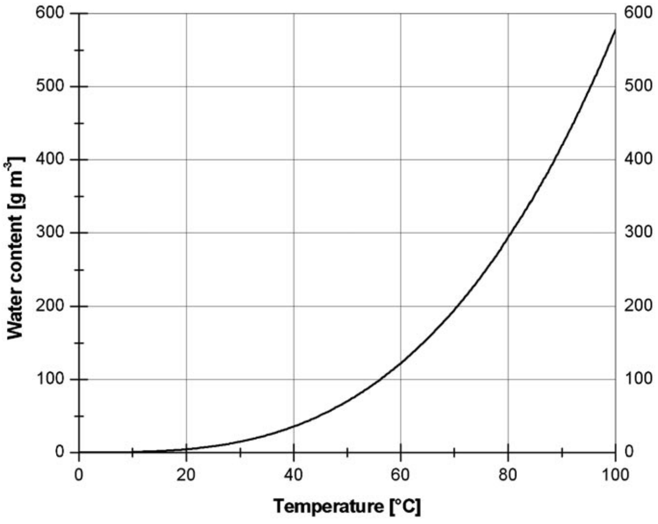

Figure 2. Maximum water content of the atmosphere.

Table 1 displays α_λ and Y_f values for different obscurant materials at different relative humidities at 25 °C taken from Ref. [4, 5].

From Table 1 it becomes obvious that phosphorus pentoxide (P_4O_{10}) is superior to any other smoke material in terms of yield factor.

When it comes to the design of phosphorus-based obscurants for the visual (Vis = 0.36 – 0.76 μm) to near infrared (NIR = 0.76 – 1.3 μm) range the particle size of the aerosol constituents is the major factor that affects the mass extinction coefficient α_λ. The extinction coefficient for – virtually – non-absorbing spherical particles can be calculated on the basis of Mie theory [6]. Figure 3 displays $\alpha(\lambda)$ function for different particle radii with an assumed refractive index $n(0-14\ \mu m) = 1.33$.

It can be seen that for small wavelength that is the UV, Vis and NIR the mass extinction coefficient is very large. Recalling that typical natural clouds contain water droplets having mean radii of ~20 μm [7] this is consistent with our natural perception that these clouds are opaque at least in the Vis. Milham et al. have investigated the infrared optical properties – mass extinction coefficient, real and imaginary parts of complex refractive index (see Section 2.3) of RP-based aerosol at various relative humidities. They found the composition of the smoke droplets to be a function of the relative humidity and hence time [8]. That is at high relative

Table 1. Yield factor and visual mass extinction coefficient for different obscurants at various relative humidities at STP according to Ref. [4, 5].

Parameter	Water Mist	RP	RP/NaNO$_3$/Binder	LiClO$_4$/B	$C_2Cl_6 \cdot ZnO/Al$
	H_2O	P_4O_{10}	P_4O_{10}	LiCl	$ZnCl_2$
Y_f					
20% RH	–	3.73	2.99	n.a.	1.25
50% RH	–	4.32	3.45	n.a.	1.58
80% RH	–	5.77	4.61	n.a.	2.77
$\alpha_{0.4-0.7\ \mu m}$ (m^2kg^{-1})					
20% RH	n.a.	3.5	3.5	0.8	3.5
50% RH	n.a.	4.2	4.2	1.2	3.9
80% RH	n.a.	3.8	3.8	1.6	2.9
100% RH	1.33	n.a.	n.a.	1.8	n.a.

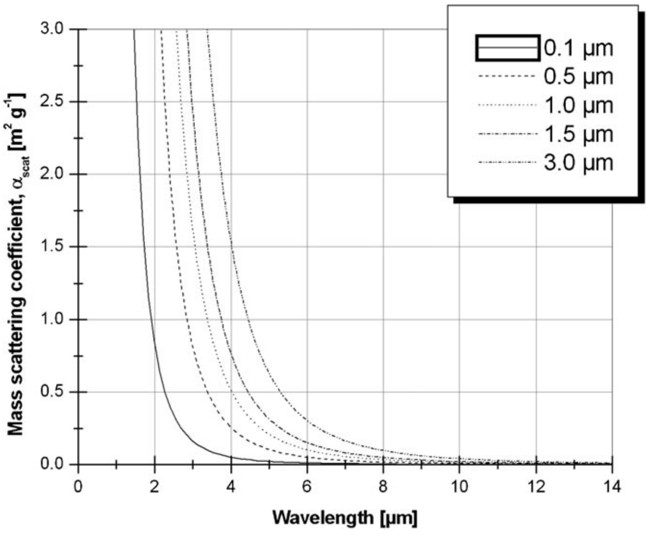

Figure 3. Pure Mie scattering of aerosol having different radii and fixed value of $n(\lambda)$.

humidities $>90\%$ RH the extinction spectrum is close to pure water, whereas at low RH values the extinction spectrum is similar to pure ortho-phosphoric acid. Nevertheless very early after their formation distinct vibration at ~ 8 µm calls for intermediate formation of diphosphoric acid ($H_4P_2O_7$) that successively undergoes hydration to ortho-phosphoric acid.

Appleyard and Davies have calculated the mass extinction coefficients for a series of phosphoric acid droplets from 0.1 to 5 µm diameters [9]. From their calculation it is evident that *o*-phosphoric acid is little better than pure water mist.

2.1 First Generation Smoke Materials Based on Red Phosphorus

The first large-scale military use of phosphorus as an obscurant, then WP, occurred in World War I. Then WP was used as a smoke material by the entente forces since they had access to the large phosphate deposits in Algeria. Smoke grenades were then filled with WP by under water melt-casting operations. The grenades were ruptured by internal explosive charges. Combined smoke and incendiary charges based on WP have been followed even after World War II [10].

The first smoke munitions comprising RP occurred at the end of World War II in Germany [11]. Then RP phlegmatized with about 10% paraffin was used as payload for artillery smoke shells. Other compositions were based on either RP/rubber or latex compositions [12–14], which were fragmented with an inner high explosive charge [15]. In these munitions the shock wave from the detonation of the HE charge travels through the RP-based composition and causes a sudden increase in temperature thus causing direct thermal ignition upon dispersion.

Douda has proposed to subject a filler of RP by a detonation in order to generate WP *in situ*. After the blast the WP instantaneously burns in the open to provide a dense white smoke [16]. The invention was prompted by the observation that conventional thermal ignition of RP-based compositions would not result in a sufficiently fast consumption of the phosphorus. In contrast to that an RP-based charge subjected to a detonation will burn as fast as dispersed WP.

Now there are two explanations for the effect. At first the shock wave acting on RP will result in a temperature rise in the payload. Thus, instantaneous combustion may take place as the system temperature is well above its ignition temperature. In the following this effect will be addressed as 'detonative ignition'. In addition after shock heating of RP sublimation takes place yielding gaseous phosphorus that will resublime out of the gas phase in accordance with the 'Ostwald Vollmer Rule' – that is giving rise to the formation of the allotrope with the lowest density first after cooling – that is WP.

The author made similar observation with RP-based obscurant compositions constituted from ~ 60 wt.-% RP, and energetic filler. Subjecting 800 g of a cylindrical charge (70 × 160 mm) by the detonation of an internal PETN-based detonation cord (~ 1.5 g) will result in the instantaneous combustion of the payload within 1.5 s. Normally such a payload would take ~ 40 s to burn when ignited conventionally. Thus, it is quite likely that the major impact is the shock heating of the entire payload material (detonative ignition) well above its ignition temperature that causes instantaneous combustion.

Ritchie has proposed to use small amounts of WP dissolved in carbon disulphide to alter the performance of titanium tetrachloride ($TiCl_4$) smoke material [17].

2.2 Second Generation Smoke Materials Based on Red Phosphorus

Although the yield factor is at its maximum when pure RP is applied, the combustion efficiency is not at its optimum. Thus screening an object of critical size with payloads based on pure RP may take too long. Hence faster smoke munitions were sought for. These munitions were then based on RP/sodium or potassium nitrate and an organic binder. In these systems the combustion efficiency is significantly enhanced in terms of aerosol mass-release rate. Turetsky and Young describe such composition and give figures of merit for several RP-based visual smoke compositions [18].

A post-war invention from Germany calls for compositions with a very low RP-content [19], which allows for complete combustion of phosphorus. In addition to RP ammonium chloride is present as an aerosol agent.

Composition 1

• RP	10 wt.-%
• Potassium nitrate	30 wt.-%
• Ammonium chloride	60 wt.-%

Webster has proposed to apply calcium sulphate as an oxidiser in smoke generating compositions [20]. The following composition is said to have a burn rate of 3.2 cm s^{-1}.

Composition 2

• RP	50 wt.-%
• Calcium sulphate	37 wt.-%
• Boron	10 wt.-%
• Viton™	3 wt.-%

Combined float – smoke signal compositions based solely on RP and calcium sulphate as sole oxidiser have been described in Ref. [21]. The fact that such an exothermic compound $CaSO_4$ ($\Delta_f H = -1435$ kJ mol^{-1}) can be used as an oxidiser is another proof for the nearly proverbial oxophilicity of phosphorus also known from organic chemistry (vide Wittig reaction).

A former operational composition for DM 35 Vehicle Screening Smoke Grenade is given below [22].

Composition 3

• RP	75 wt.-%
• Copper(II) oxide	10 wt.-%
• Magnesium	11 wt.-%
• Binder	4 wt.-%

2.3 Third Generation Smoke Materials Based on Red Phosphorus

Although visual smoke performance with second generation smoke materials is satisfactory, the increasing use of electro-optical sensors operating in the mid and far infrared has forced the development of obscurant munitions capable of screening the infrared wave band. Hence, the above-described systems no longer fulfilled the requirements.

When looking at RP-based smoke systems, the major constituents of the aerosol in the case of RP/$NaNO_3$ compositions are either cyclotetrametaphosphates ($P_4O_{12}^{4-}$) or dihydrogen diphosphates ($H_2P_2O_7^{2-}$). In the case of RP/$NaNO_3$/Mg compositions the major constituents are hydrogenphosphates (HPO_4^{2-}) and diphosphates ($P_2O_7^{4-}$) [23]. The major vibrational transitions of P–O–H–M compounds are listed in Table 2. Also pure P_4O_{10} displays useful absorption bands at either 7.13, 9.89 or 13.10 µm [24]. Figure 4 displays the mass extinction coefficient of RP aerosol. The extinction coefficients of RP aerosols have been determined in Ref. [25, 26]

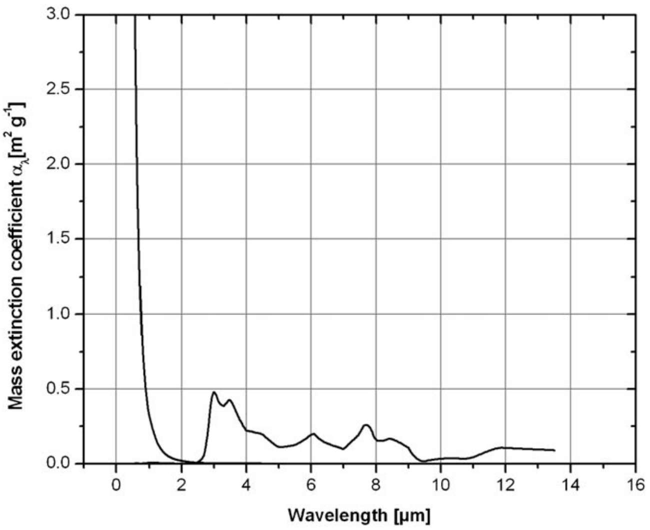

Figure 4. Mass extinction coefficient of RP aerosol.

Despite the actual chemical constitution of the aerosol very often H_3PO_4 is considered as a model substance. The extinction coefficient α_λ of H_3PO_4 is not steady from the visual to the infrared wavebands (0.38 – 14 µm). This stems from the fact that the extinction coefficient α_λ itself is the sum of both contributions from scattering of radiation and absorption of radiation (Eq. 5).

$$\alpha(ext)_\lambda = \alpha(scat)_\lambda + \alpha(abs)_\lambda \tag{5}$$

Whereas the scattering coefficient $\alpha(scat)_\lambda$ is majorly dependent on the size and morphology of the aerosol constituents, the absorption coefficient $\alpha(abs)_\lambda$ is only dependent on the chemical composition of the aerosol constituent. Both coefficients are a function of the complex refractive index $\tilde{n} = n + ik$, where $n(\lambda)$ is the real part of complex refractive index and $k(\lambda)$ is the imaginary part of complex refractive index.

A detailed description of the complex refractive index can be found in the chapter by Schmieder and Walker [27].

On the basis of aforementioned explanation obscurant payloads for the infrared range, that is 3 – 14 µm, require either aerosol particles having large particle diameters compared to wavelength of incident electromagnetic radi-

Table 2. Important vibrational modes of P–H–O–M compounds present in obscurant phosphorus-based aerosols.

Parameter	H_3PO_4 µm	Assignmnt.	$H_2P_2O_7^{2-}$ µm	Assignmnt.	$P_4O_{12}^{4-}$ µm	Assignmnt.	$P_2O_7^{4-}$	Assignmnt.
	3.8	PH	8.1	POH	8.5 – 8.9	PO_2	8.7 – 9.5	PO_3
	7.1	PO_2	8.7	PO_2	13.2 – 13.9	POP	13.3	POP
	9.2	PO_2	9.3	PO_2				
	9.9	PO_2	10.9 – 11.5	POP/POH				
	13.1	POP	14.1	POP				
	17.4	POP						
References	[88]		[28]		[29]		[30]	

ation and/or aerosol particles having distinct vibrational transitions in the same range.

Since there is no superior obscurant agent available compared to RP the only way to increase the extinction in the infrared is to alter the concentration of the aerosol requiring thus that the mass consumption rate, $\dot{m}$ (g s^{-1} cm^{-2}) of mentioned payloads has to be increased. Thus, smoke ammunition for the infrared requires greater amounts of RP combustion products to be released in a shorter time scale in order to provide higher aerosol concentration c (g m^{-3}) as the only factor as to increase the extinction of radiation.

Higher mass consumption rates of RP-based systems require the following steps to be taken:

- Increase the density of composition at atmospheric pressure to allow for better thermal conductivity.
- Increase combustion pressure at low composite densities in order to increase mass consumption rate due to filtration of gaseous combustion products into composite and thus enhancement of rate of reaction. For complete confinement Section 10.
- Increase the thermal conductivity of composite to provide faster rate of reaction.
- Increase the exothermicity of the combustion process.
- Increase the surface area of the composition by using either sheets or fine granules of composition.
- Improve ignition process – vide 'detonative ignition' discussed in Section 2.1.

Whereas increasing the density can be done by increasing the pressure upon pressing pellets, the increase in combustion pressure requires a design which allows for the built-up of pressure inside a combustion chamber with a vent hole area designed as to match with the temporal internal grain surface area.

Increasing the thermal conductivity requires an appropriate percentage of metallic fuels or carbon fibrils to be incorporated in the composite. Nielson and Lester have proposed to increase the burn rate of pyrotechnic compositions by imparting carbon fibres having l/d ratio of >5 with length ranging from 1 to 10 µm [31].

Increasing the exothermicity of the combustion process requires an energetic filler to be added to the RP payload. These can be high energetic composite materials such as

- metal/nitrate
- metal/fluorocarbon
- metal/oxide
- and virtually any homogeneous energetic material.

As mentioned above suitable energetic fillers may also be metal fluorocarbon pyrolants. In these systems Mg/PTFE are applied in stoichiometric proportions to provide maximum heat output. Cudziło has investigated obscurants based on RP/Mg/KNO_3, and compared them with RP/Mg/PTFE [32, 33]. He obtained qualitatively higher aerosol temperatures with the latter system. Cudziło also determined combustion characteristics and obscuration performance of compositions based on Mg-Al alloy/PTFE and RP [34]. As expected from the low thermal conductivity of RP the burn rate decreases linearly within the range of 30–60 wt.-% RP with increase in RP content. However, the performance – that is attenuation of radiation – increases in the same direction. The same author has disclosed mass extinction coefficients of said RP-based obscurant compositions in a patent [35].

Another possibility of increasing the aerosol concentration is by increasing the number of condensation nuclei in the air. This can be achieved by generating ions upon combustion of the smoke material. Such a smoke material is that developed by Weber in 1983 comprising either caesium or rubidium salts as modifiers to conventional obscurant mixtures [36].

A castable RP-based smoke mixture based on Mg/MNO_3 (with M = Na, K) and polyester binder has been disclosed in Ref. [37].

Steinicke et al. have proposed to use potassium peroxodisulphate ($K_2S_2O_8$) as a more fierce oxidiser compared to nitrates in RP-based composites [38]. The use of a sulphur-based oxidiser also gives rise to the release of SO_2, which is known to have strong vibrational transitions at $\lambda = 4.0, 7.4$ and 8.7 µm. On the other hand sulphur compounds are not environmentally acceptable and may also pose harm to humans.

Composition 4 for 'Heavy duty smoke payloads'

• Magnesium	5 wt.-%
• RP	65 wt.-%
• Potassium peroxodisulphate	18 wt.-%
• Polychloroprene binder	12 wt.-%

Two operational Mg-based smoke compositions are given below

Composition 5 designated Z 97 [39]

• Magnesium	7–12 wt.-%
• RP	65–70 wt.-%
• Polytetrafluoroethylene	17 wt.-%
• Polychloroprene binder	6 wt.-%

Composition 6 [87]

• RP	66 wt.-%
• Potassium nitrate	16 wt.-%
• Magnesium	12 wt.-%
• Polyvinylacohol	6 wt.-%

2.3.1 Problems Associated with the Use of Magnesium in RP-based Obscurant Compositions

(a) Although high in caloric energy magnesium generally imparts a series of problems into pyrotechnic payloads. This is even more pronounced with RP-based Mg-containing payloads. Since modern RP-based payloads have substoichiometric oxidiser content, reactions between the phosphorus and the metal fuel are likely. In the case of Mg as fuel this leads to Mg_3P_2 formation.

$$2\,P_{(red)} + 3\,Mg_{(s)} \rightarrow Mg_3P_{2(s)} + 465\ kJ\ mol^{-1} \tag{6}$$

Magnesium phosphide now reacts with atmospheric moisture or acid rain to give the toxins; and toxic phosphane PH_3, which due to contaminations with higher phosphanes such as P_2H_4, is self-inflammable.

$$Mg_3P_2 + 6\,H_2O \rightarrow 3\,Mg(OH)_2 + 2\,PH_3 \uparrow +1037\,kJ\,mol^{-1} \quad (7)$$

Hence, the use of Mg-based RP payloads has been restricted by many training grounds.

(b) Processing RP in water moist condition may lead to entrapment of water and thus enables catastrophic payload degradation due to magnesium oxidation and hydrogen formation in accordance to (Eq. 8)

$$Mg + 2\,H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow +359\,kJ\,mol^{-1} \quad (8)$$

2.3.2 Payloads Based on Titanium and Zirconium

In view of the problems encountered using magnesium as a fuel in RP-based obscurant compositions the author has developed a series of payloads based on zirconium and titanium as fuels [40]. Although both zirconium and titanium react with phosphorus to give phosphides, TiP, ZrP, the latter does not react with either water or even dilute acids but behave inert. Thus phosphine formation does not take place with these fuels [41]. This is due to the strong covalent bonds between both Ti-P and Zr-P. These payloads further comprise additional amounts of both boron and silicon which enhance the screening performance in both the mid and the far infrared as both boron and silicon oxides (B_2O_3, SiO_2) display distinct absorption bands in the 4–5 and 9–10 μm range [40, 42]. A sample composition is given below:

Composition 7 for vehicle discharge grenades

• RP	58.5 wt.-%
• Potassium nitrate	21.1 wt.-%
• Zirconium	4.7 wt.-%
• Silicon	4.7 wt.-%
• Boron	4.7 wt.-%
• Chloroprene	6.3 wt.-%

2.4 Miscellaneous Research with RP-based Obscurants

An exhaustive review on the use of RP in obscurants has been compiled by Davies [43]. The performance of operational obscurant munitions developed by the authors former company [44] has been evaluated by Smit [45]. Smit also evaluated the toxicity of obscurants based on RP-based obscurant payloads [46]. A report on the programmatic life cycle environmental assessment of RP, WP and PWP has been compiled by Yon et al. [47]. The 27th International Pyrotechnics Seminar held in Grand Junction Colorado devoted a complete session with 13 papers to the application of RP in military applications but mainly obscurants [48].

3 Incendiaries

3.1 White Phosphorus

It was Johann Kunckel, the contemporary of the elements discoverer Hennig Brandt, who made the first ever reported proposal in 1678, to use phosphorus, then WP, in warfare as incendiary payload in artillery projectiles [49]. Later Sir Lyon Playfair (sic) proposed to use WP dissolved in carbon disulphide, CS_2, as filler for incendiary projectiles in the Crimea war 1854. This combination with slight modifications was known as 'Fenian Fire', 'Darapski Projectile'. The 'Nikles Mixture' or 'Feu Lorrain' also comprised sulphuryl chloride, SO_2Cl_2. Finally, the 'Gugots mixture' contained sulphuryl bromide, SO_2Br_2, instead of SO_2Cl_2.

In World War I, WP found use in a number of ordnance. It was applied in British and American machine gun ammunition as WP tracer to fight highly inflammable hydrogen filled Zeppelins [50]. In Germany, a 15 cm incendiary shell was in use comprising more than 15 celluloid cylinders filled with WP and sealed with paraffin. A central blackpowder burster scattered the payload.

An 81 mm American shell was still in use in World War II. It had a solid filler of WP and was scattered with a tetryl booster. Whereas WP was mainly used by entente forces in World War I it was also used by the axis forces in World War II.

In World War II German Luftwaffe applied incendiary bombs (Brand C 50 and Brand C 250) filled with either petroleum or gasoline, a polymeric thickener like natural rubber or polystyrene and WP as both fuel and igniter.

A British balloon incendiary measure consisted of glass bottles filled with a ternary phase system ('Brandflaschen'). The upper liquid layer was the actual fuel charge which was separated by a benzene layer (13 g) from the bottom ignition charge.

Fuel charge: 100 g

- 91 wt.-% benzene
- 9 wt.-% natural rubber

Ignition charge: 330 g

- 90 wt.-% WP
- 8 wt.-% sulphur
- 2 wt.-% benzene and minor ingredients

If they ignited at all the burn time was quite short with about 1 min and the incendiary measure was considered a bogyman.

Another also quite ineffective incendiary measure applied by the British Airforce was the 'Aerial Igniter', called 'Visiting cards', the German designation was 'Brandplättchen'. These devices were either sheets of natural rubber or nitrocellulose with a piece of WP fixed in the middle of it. Intentionally the WP was supposed to catch fire in the air and subsequently ignite the rubber/NC which itself should set fire to forest areas. Nevertheless nearly 90% of these devices were reported duds and could be safely removed. The rubber was then collected and used to overcome the short supply for natural rubber in wartime Germany.

From BIOS reports it is evident that [51] a German 105 mm mortar incendiary grenade for use with the 10 cm Nebelwerfer 35 contained:

• Cotton Wool	40 g
• Naphthalene	300 g
• Phosphorus, white	750 g

A similar looking American disclosure teaches the application of mixtures constituted from naphtha, kerosene, wax and WP as filler for infantry ammunition [52].

3.2 Red Phosphorus

Although RP is safer to handle than WP, incendiaries based on it were not developed until some 30 years ago. Even after World War II RP was still regarded not suitable for incendiary purposes since it does not ignite spontaneously and is not soluble in common solvents [53]. Nevertheless, the high heat of combustion of RP as well as the fact that RP upon combustion yields liquified yellow phosphorus that may adhere to different substrates suits it to be applied as incendiary material. In addition RP-based pyrotechnic compositions will once ignited not extinguish, even if submersed in water due to inherent formation of yellow phosphorus – from quenching of primary combustion products with water – which is spontaneously combustible in air. Thus, RP is a safer candidate for incendiary applications.

Incendiary payloads based on RP may be structured into two classes. The first comprising

- only RP and optional binder,
- the second class comprising RP and a reactive partner, that may be either
  - coruscative in nature as, for example, sulphur or magnesium or
  - oxidative in nature such as nitrates and perchlorates (vide infra).

It is obvious that coruscative systems are more potent incendiaries in that the metallic component provides much higher combustion temperature as with RP alone and provides more hot melt liquid slag that can adhere to a target. Hence, modern incendiaries from the 1960s to 1980s – although now often banned in several armed forces – typically comprise magnesium as reductive partner and often sulphur as a complementary fuel [54].

3.2.1 Compositions for Bulk Use

Koch and Licht give RP-based incendiary compositions [54].

Composition 8 designated B 299

• Magnesium	25 wt.-%
• RP	75 wt.-%.

Composition 9 designated B 300

• Magnesium	13.5 wt.-%
• RP	42.5 wt.-%
• Potassium nitrate	11.0 wt.-%
• Gasoline/benzene(50:50)	31.0 wt.-%
• Polystyrene	2.0 wt.-%.

Krien has investigated thermochemistry of B 299 and solvent-free B 300 [22].

A major drawback of the composition B 299 is the intermittent combustion caused by slug formation. In addition the incendiary composition is a powder and thus will not adhere to walls and inclined planes. Thus, Assmann has developed a composition comprising an additional amount of aluminium granules coated with aluminium stearate [55]. Upon combustion the aluminium stearate eventually vaporises and bursts the slag and thus impedes occlusion of unburnt phosphorus.

A similar composition has been used in the formerly used Blend-Brandhandgranate (Combined 'Stun-Incendiary grenade'). This device consists of a frangible plastic shell of unplasticised polystyrene and a loose granulated payload from RP/Mg/polychloroprene which was ignited indirectly by means of a heating charge pressed in a sealed brass cylinder. The powder charge adjacent to the heating cylinder will be heated up to ignition point and catch fire.

A single shot flamethrower formerly used with the German Army was the Handflammpatrone DM 24A1B1 later succeeded by DM 34. This device consisted of a plastic barrel filled with an RP-based payload which is fired up to distances of ~ 90 m. Upon impact or after a certain delay the payload was ignited and disseminated with a bursting charge [56]. The composition of the payload according to Ref. [56] is given in the following:

Composition 10 for 'Handflammpatrone' DM 34

• Magnesium	17.85 wt.-%
• RP	62.50 wt.-%
• Iron oxide	10.72 wt.-%
• Chloroparaffine, liquid	5.36 wt.-%
• Chloroparaffine, solid	3.57 wt.-%.

Incendiary compositions based on RP causing simultaneous corrosive effect to optic materials have been investigated and developed by Keller and Schneider [57, 58].

Composition 11 for corrosive incendiary payloads

• Antimony(III) fluoride	50 wt.-%
• Collodium	25 wt.-%
• Phosphorus, red	25 wt.-%

Nourdin [59] has come up with a series of complex incendiaries comprising hydrocarbons, metals, oxidisers and RP for use in larger projectiles like, for example, mortar shells. Sample compositions are given below. It is interesting to note that Nourdin proposes RP/perchlorate and even chlorate mixtures. Combinations that otherwise would not be considered safe to handle.

Composition 12

Magnesium	10 wt.-%
RP	10 wt.-%
Aluminium	15 wt.-%
Naphthalene	35 wt.-%
Sodium nitrate	10 wt.-%
Ammonium perchlorate	15 wt.-%
Chloroprene	5 wt.-%

3.2.2 Compositions for Use in Bullets

Bullets may contain fluorinated polymers
Composition 13 designated BS 4

Zirconium	40 wt.-%
RP	50 wt.-%
Polytetrafluoroethylene	10 wt.-%

Several American incendiary mixtures for use in bullets have been reported [60].
Composition 14 designated IM 139

Magnesium/aluminium alloy (50:50)	10 wt.-%
RP	40 wt.-%
Barium nitrate	47 wt.-%
Aluminium stearate	35 wt.-%

Composition 15 designated IM 144

RP	50 wt.-%
Barium nitrate	50 wt.-%

The Russian AK 47 incendiary ammunition has been reported to be filled with aluminium/RP compositions.

A German patent teaches the use of apatite $(Ca_5(PO_4)_3$ (OH, F, Cl) as an oxidiser in aluminium-based incendiary ammunition to suppress firefighting operations since Ca_3P_2-based slug will evolve spontaneous highly toxic and self-inflammable phosphanes [61].

4 Decoys

Decoys are countermeasures that serve the imitation of the electromagnetic signature of a target in a certain electromagnetic band of interest.

4.1 Aerial Infrared Decoys

Pyrotechnic aerial infrared decoy flares have been reviewed by the author recently [62, 63]. It has been reported that pure RP yields relatively cool flames of $T < 1000\,^\circ C$. Thus, burning RP has already appropriate temperature for spectral applications. Thus, further addition of endergonic additives to RP-like silica, SiO_2 or alkali halides further reduces combustion temperature and thus helps to achieve the appropriate α/β ratio. For this purpose the wet RP is mixed with mentioned additives and water-soluble binders like, for example, polyvinyl alcohols to give a paste-like mixture. The paste is then applied to thin polyimide foils [64]. These sheets after drying and cutting are then compiled to staples and filled into cartridges. Explosive dissemination causes instant burning clouds. Although spectral adaptation of RP-based flares is better than with MTV-based systems, static behaviour of the sheets which will not move along with the aircraft to be protected leads to discrimination by advanced infrared seekers using kinematic IRCCM.

4.2 Naval Decoys

Likewise as with aerial infrared decoy flares, RP-based sheet-type flares are in use as infrared countermeasure against heat IR guided anti-ship-missiles. Although effective against older generation seekers, unrealistic high radiation contributions in the 1.8–2.5 μm range, that is the α-band, lead to discrimination of these flares. In addition it has been reported that these flares when drifting back to the ship may cause fire on board.

In view of the operational shortcomings with above-mentioned ammunition the author has developed a dark and comparatively cool IR countermeasure based on the on-site neutralisation of phosphoric acid with alkaline solutions [65] see Eq. 9. In contrast to burning RP no emission in the visible or near infrared takes place; thus discrimination by two colour seekers is avoided. Naturally this type of countermeasure poses no danger of fire.

$$3\,LiOH + H_3PD_4 \rightarrow Li_3PO_4 + 3\,H_2O + 219\,kJ\,mol^{-1} \qquad (9)$$

5 Primers and Igniters

As has been discussed above, RP is very sensitive towards friction and impact (vide infra). This property has been used in both friction igniter (vide or safety matches) and stab primer applications.

5.1 Friction Igniters

In general these devices apply the same stimulus as is done in every day product safety match. Baker et al. have invented a high altitude friction igniter based on RP [66]. This igniter is still applied in pyrotechnic infrared decoy flares of 36 mm type such as MJU 8A/B. Figure 5 displays a drawing of that igniter taken from the above disclosure. Item 1 designates the scratch wire coated with a mixture of RP and varnish (resin). Upon ejection of the flare pellet from its housing the pusher plate eventually stops at the end of the cartridge due to reduction in calibre. Thus, the flare pellet together with the igniter move through the scratch-wire, causing ignition of the ignition charge 2 consisting of potassium chlorate and varnish and subsequent ignition of the igniter composition, 3, based on boron and lead dioxide. Due to accidents with this type of friction igniter and successive fires and explosions of flare

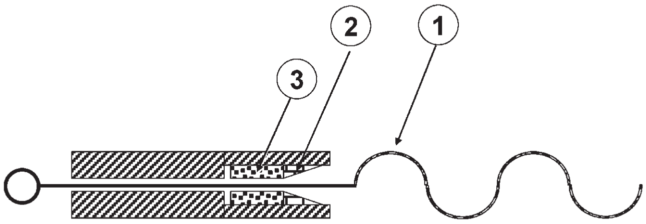

Figure 5. Pull wire igniter, picture in accordance to Ref. [61].

ammunition this type of igniter is now obsolete and has become substituted by bore-rider safety mechanism such as described in Ref. [67]. In addition to aerial infrared decoy flares friction igniters find application in numerous signalling pyrotechnics such as signal smoke and illuminating devices and also as simple scratch igniter in flash bang report devices for simulation purposes.

5.2 Stab Primers

In the 1940s, the use of RP as a fuel in stab priming compositions has been proposed by Pritham et al. [68]. A typical composition **16** that may also include a small amount of glue or binder is given in Table 3.

As the RP oxidised under the catalytic influence of typical cup primer materials such as brass and copper it was proposed by Silverstein to cover these items with small layers of aluminium, zinc or tin, in order to prevent any further oxidation [69].

To overcome the above-mentioned patents and to further the performance of priming compositions, Woodring and McAdams [70] proposed to apply composition similar to those mentioned above but that would comprise additional amounts of both primary explosives such as lead styphnate and a highly sensitive secondary explosive such as PETN. Typical example compositions with (**17**) or without primary explosives (**18**) are given in Table 3.

Nevertheless it was found that the RP available that time based on 'archaic' MIL-P-211 was too impure and thus unstable to be applied in any long-term stable ammunition – a fact that caused perpetual worries with any RP-based ammunition introduced in the USA before the adopted use of stabilised RP most recently. In view of the improved stability of RP available today Busky et al. proposed to use stab priming compositions based on RP similar to those proposed above [71]. Busky et al. reported about the performance of such compositions in Ref. [72]. A typical example composition **19** is given in Table 3. The composition may include additional amounts of binder.

Table 3. RP-based stab priming compositions.

Composition	wt.-%	**16**	**17**	**18**	**19**
RP		25	17	25	25
Metal nitrate		58[a)]	53[a)]	70[a)]	65[b)]
Metallic fuel		17[c)]	–	–	5[d)]
Secondary explosive		–	5[e)]	5[e)]	5[e)]
Primary explosive		–	25[f)]	–	–

a) Barium nitrate; b) Potassium nitrate;c) Antimony sulphide; d) Aluminium; e) Pentaerythrite tetranitrate; f) Lead styphnate.

6 Signalling: Floating – Smoke Devices

RP not only yields a thick smoke upon combustion in the open, but also yields an intense yellow – orange flame, which is principally the result of continuum emission [73]. This effect has been exploited in combined float and smoke signals for applications such as marine location markers. Ellern [74] and Gilliam and Johnson [75] give composition for such a signal-based magnesium, manganese dioxide, phosphorus, linseed oil and zinc oxide.

Composition 20

● RP	51 wt.-%
● Magnesium	8 wt.-%
● Manganese dioxide	35 wt.-%
● Zinc oxide	3 wt.-%
● Linseed oil	3 wt.-%.

Operational compositions for combined float and smoke signals have been given by Liberman [76]

Composition 21

● Magnesium	7.2 wt.-%
● RP	51.5 wt.-%
● Manganese dioxide	35.1 wt.-%
● Zinc oxide	3.1 wt.-%
● Linseed oil	3.1 wt.-%

Composition 22

● Magnesium	5 wt.-%
● RP	68 wt.-%
● Ammonium nitrate	20 wt.-%
● Calcium carbonate	3 wt.-%
● Chloroprene	4 wt.-%

Composition 23

● Aluminium flakes	8 wt.-%
● RP	71 wt.-%
● Sodium nitrate	15 wt.-%
● Calcium carbonate	1 wt.-%
● Titanium isopropoxide	1 wt.-%
● Cured HTPB	4 wt.-%

Vine and Fletcher have given composition and investigated failure causes of float and smoke signals [77].

Composition 24 designated SR414

● Calcium silicide	6 wt.-%
● RP	60 wt.-%
● Manganese dioxide	28 wt.-%
● Magnesium	6 wt.-%

Glyde et al. investigated composition for float – smoke signals based on RP and sulphates as oxdisers or on RP and heating compositions (based on magnesium or calcium

Table 4. Operational RP-Based Ammunition.

Designation	Calibre	Payload	Application	NEW g	Introduced	NSN
76 SSMG	76 mm	RP/nitrate/metal	Vehicle Protection IR-Smoke	870	AU	1330-12-359-1548
MK7	n.a.	RP/nitrate/metal	Floating Smoke Pot	8000	USA	1365-01-487-2843
PIRATE IR seduction round	130 mm	RP	Naval IR-Protection		UK	1377-99-421-8927
DM 69 A1	2 × 1 inch	RP	Aerial Decoy	180	DE	1370-12-336-6251

silicide and manganese dioxide) that allow for sublimation of RP [21]. They found that anhydrous calcium sulphate provides the best performance when compared with potassium barium and strontium sulphate.

7 Red Phosphorus-Based Explosives

Hahma et al. have investigated the effect of RP as an additive to isopropyl nitrate in classical binary thermobaric charges [78]. The results he obtained with these mixtures were not very promising. In contrast compositions made from nitramines and RP display an increase in blast pressure by more than 35% compared to aluminised composition A3 (Hexal) in confined spaces as has been found by the author [79, 80].

8 Phosphorus Compounds

Golding and coworkers have reported about the investigation of polyphosphazenes substituted with nitrate ester groups and/or azidoalkyl groups and/or perfluoroalkyl groups as binders in pyrotechnic flare and smoke compositions based on RP [81 – 84]. The polyphosphazenes have the general make up (P=N)(*O*-alkylidene nitrate ester/azide)(*O*-perfluoroalkyl). The materials generally have interesting densities ranging from 1.5 to 1.6 g cm^{-3}.

Klapötke et al. have reported about the successful structural characterisation of an azide substituted cyclo-phosphazene, P_3N_{21} [85] known since some decades [86].

9 Operational Red phosphorus-based Ammunition

Table 4 gives information on RP-based ammunition introduced with either German, British or US forces.

10 A Word on Safety: Unexpected Explosion of Red Phosphorus-Based Ammunition

RP and its sub-stoichiometric compositions – avoiding critical oxidisers such as chlorates and peroxides [2] – upon thermal ignition in the open that is at $dp = 0$ generally undergo slow successive combustion process with combustion rates in the few millimetre per second range.

Nevertheless combustion in confined space that is $dV = 0$ or under sufficient internal tampering of the loose composition itself will dramatically accelerate and may eventually shock-up to slow order detonation as has been experienced by the author in the course of different experiments. Thus, utmost care has to be taken when designing RP-based ammunition and conducting experiments with RP-based ammunition.

In contrast to WP, which can be melt-cast under water, RP is a powdery substance that has to be mixed with aqueous or organic binders to give mostly pressable and seldomly castable compositions. The inadvertent ignition of RP-based payloads by set-back forces upon firing from mortars and howitzers is most often due to inappropriate structural integrity of the RP grain having cracks and dislocations. In case of complete confinement of the combustion zone ($dV = 0$) this can lead to explosion and DDT.

11 Conclusion

Phosphorus is an indispensable fuel for military pyrotechnics. Within the last few decades the focus has changed from WP to RP. With the advent of high energy materials-like P_3N_{21} and polymer phosphazenes having azide and nitrato-substituents molecular explosive applications of phosphorus come closer.

12 References

[1] E.-C. Koch, D. Clement, Special Materials in Pyrotechnics: VI. Silicon – An Old Fuel with New Perspectives, *Propellants, Explos. Pyrotech.* **2007**, *32*, 205.

[2] E.-C. Koch, Special Materials in Pyrotechnics: IV. The Chemistry of Phosphorus and its Compounds, *J. Pyrotech.* **2005**, *21*, 39.

[3] At the time of proof reading a draft specification for Red Phosphorus titled STANAG 4679 is in discussion with SG-1 of NATO AC 326, May **2008**.

[4] G. A. Lane, W. A. Smith, E. M. Jankowiak, Novel Pyrotechnic Compositions for Screening Smokes, *1st International Pyrotechnics Seminar*, Estes Park, Colorado, USA, August 12 – 17, **1968**, p. 263.

[5] N. Sordoni, W. Heard, W. Rouse, *Pyrotechnic Smoke Analysis*, Vol. 1, ERDEC-TR-129, Edegewood Research Development and Engineering Center, Aberdeen Proving Ground, Maryland, USA, **1993**, p. 25.

[6] C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York **1983**, p. 82.

[7] E. J. McCartney, *Optics of the Atmosphere – Scattering by Molecules and Particles*, John Wiley & Sons, New York **1976**, p. 225.

[8] M. E. Milham, D. H. Anderson, R. H. Frickel, Infrared Optical Properties of Phosphorus-Derived Smoke, *Appl. Opt.* **1982**, *21*, 2501.

[9] P. G. Appleyard, N. Davies, The Estimation of Extinction Properties of Obscurant Clouds by Modelling the Fundamental Electromagnetic Scattering Properties of Individual Particles, *29th International Pyrotechnic Seminar*, Westminster Colorado, USA, **2002**, p. 509.

[10] M. M. Woyski, E. A. Ford, *Smoke Producing Composition*, US Patent 2,798,799, **1957**, USA.

[11] H. J. Eppig, *The Chemical Compositions of German Pyrotechnic Smoke Signals*, CIOS Target Nos. 3A/172, 7/224 and 17/41, June –August **1945**, London.

[12] J. P. Clay, H. B. Elkins, *Smoke Agent*, US Patent 2,574,466, **1951**, USA.

[13] J. P. Clay, H. B. Elkins, *Smoke Agent*, US Patent 2,658,874, **1953**, USA.

[14] R. R. Fry, Jr., *Method for Preparing a Smoke Agent*, US Patent 4,151,233, **1979**, USA, US Army.

[15] G. M. Simpson, *Pyrotechnic Composition for Radiation Blocking Screen*, US Patent 4,728,375, **1988**, Haley & Weller Ltd., UK.

[16] B. E. Douda, R. D. Dwiggins, *Device for Producing White Phosphorus by Imploding Red Phosphorus*, US Patent 3,625,155, **1971**, USA, US Navy.

[17] A. J. Ritchie, *Synthetic Fog or Smoke*, US Patent 2,407,384, **1946**, Electric Boat Co., USA.

[18] A. L. Turetsky, G. P. Young, Advances in Pyrotechnically Based Visual Smoke Systems, *13th International Pyrotechnics Seminar*, Grand Junction, Colorado, USA, July 11 – 16, **1988**, p. 805.

[19] H. Buck, L. Scheichl, *Smoke Agents*, US Patent 3,193,422, **1965**, USA.

[20] D. M. Johnson, H. A. Webster III, *Smoke Generating Composition*, US Patent 4,129,465, **1978**, USA, US Navy.

[21] E. D. Glyde, G. Lewis, J. Robertson, Smoke and Flame Compositions Based on Amorphous Phosphorus, *9th International Pyrotechnic Seminar*, Colorado Springs, Colorado, USA, August 6 – 10, **1984**, p. 819.

[22] G. Krien, *Thermoanalytische Ergebnisse der Untersuchung von pyrotechnischen Sätzen*, Bericht Az.: 3.0-3/5446/81, BICT, Swisttal-Heimerzheim, **1981**.

[23] L. Klusáček, P. Navrátil, The Use and Application of Red-Phosphorus Pyrotechnic Composition for Camouflage in the Infrared Region of Radiation, *Propellants, Explos., Pyrotech.* **1992**, *22*, 74.

[24] R. J. M. Konings, E. H. P. Cordfunke, A. S. Booij, The Infrared Spectra of Gaseous P_4O_{10}, As_4O_6 and As_4O_{10}, *J. Mol. Spectrosc.* **1992**, *152*, 29.

[25] M. E. Milham, *A Catalogue of Optical Extinction Data for Various Aerosols and Smokes*, AD-A034 500, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, USA, June **1976**, available at http://handle.dtic.mil/100.2/ADA034500.

[26] H. R. Carlon, D. H. Anderson, M. E. Milham, T. L. Tarnove, R. H. Frickel, *Infrared Extinction Spectra of Some Common Liquid Aerosols*, AD-A034 669, Edgewood Arsenal, Aberdeen Proving Ground, Maryland, USA, December **1976**, available at http://handle.dtic.mil/100.2/ADA034669.

[27] D. E. Schmieder, G. W.Walker, Camouflage, Suppression, and Screening Systems, in: J. S. Accetta, D. L. Shumaker, (Eds.), *The Infrared and Electro-Optical Systems Handbook*, Vol. 7, (*Countermeasure Systems* edited by D. Pollock, 2nd revised edition), SPIE Optical Engineering Press, Bellingham, USA, **1996**, p. 186.

[28] E. Steger, C. Fischer-Bartelk, Das Schwingungsspektrum des Dihydrogen-Diphosphat-Anions, *Z. Anorg. Allg. Chem.* **1965**, *338*, 15.

[29] N. Santha, V. U. Nayar, Vibrational Spectra of $SrNa_2P_4O_{12} \cdot 6$ $H_2O$and $CaNa_2P_4O_{12} \cdot 5.5$ H_2O, *J. Raman Spectrosc.* **1990**, *21*, 517.

[30] K Brouzi, A. Ennaciri, M. Harcharras, F. Capitelli, Structure and Vibrational Spectra of a New Trihydrate Diphosphate, $MnNH_4NaP_2O_7 \cdot 3$ H_2O, *J. Raman Spectrosc.* **2004**, *35*, 41.

[31] D. B. Nielson, D. M. Lester, *Use of Carbon Fibrils to Enhance Burn Rate of Pyrotechnics and Gas Generants*, WO Patent 95/11207, **1995**, Thiokol Corporation, USA.

[32] S. Cudziło, Studies of IR-Screening Smoke Clouds, *27th International Pyrotechnics Seminar*, Grand Junction Colorado, USA, July 16 – 21, **2000**, p. 223.

[33] S. Cudziło, Studies of IR-Screening Smoke Clouds, *Propellants, Explos. Pyrotech.* **2001**, *26*, 12.

[34] S. Cudziło, Combustion Characteristics and screening Capability of red Phosphorus based Mixtures, *32nd Int. Annual ICT Conference*, Karlsruhe, Germany, July 3 – 6, **2001**, p. V42.

[35] E. Włodarczyk, A. Papliński, S. Cudziło, *Mieszaniny Aerozolotworcze Oparte na Czerwonym Fosforze, ich Granulat i Sposob Jego Wytwarzania*, PL Patent 183882, **1996**, Warzawa, Wojskowa Akad. Tech., Poland.

[36] M. Weber, *Pyrotechnische Nebelsätze*, DE Patent 32,38,444, **1986**, Pyrotechnische Fabrik F. Feistel GmbH, Germany.

[37] G. D. Artz, *Red Phosphorus Castable Smoke Producing Composition*, US Patent 3,650,856, **1972**, North American Rockwell Corporation, USA.

[38] W. Steinicke, G. Skorns, A. Schiessl, H. Büsel, W. Badura, *Hochbelastbarer Nebelformkörper mit Breitbandtarnwirkung*, DE Patent 3,028,933, **1989**, Buck Chemisch Technische Werke, Germany.

[39] L.-E. Norman, *Final Qualification of RP Smoke Composition*, Report Z 97, FGT R91: 125, Swedish Ordnance, **1991**.

[40] E.-C. Koch, J. Schneider, Reactions in Phosphorus based IR-Screening Smoke – An Investigation of the Underlying Phenomena, *Proceedings of 20th Smoke and Obscurants Symposium*, Aberdeen Proving Ground, Maryland, USA, April **1998**, p. 3.

[41] G. Brauer, (Ed.), *Handbuch der Präparativen Anorganischen Chemie*, Vol. 2, Ferdinand Enke Verlag, Stuttgart, **1978**, p. 1382.

[42] E.-C. Koch, A. Dochnahl, *Pyrotechnic Active Mass for Producing an Aerosol Highly Emissive in the Infrared Spectrum and Impenetrable in the Visible Spectrum*, US Patent 6,581,520, **1999**, Pepete GmbH, Germany.

[43] N. Davies, *Red Phosphorus for Use in Screening Smoke Compositions*, Report prepared under Contract No. NBSA5B/2701 Task 8, Royal Military College of Science Cranfield University Shrivenham, February **1999**.

[44] E.-C. Koch, J. Schneider, T. Kothe, *Nebelwurfkörper*, EP Patent 1,514,072, **2005**, Diehl BGT Defence, Germany.

[45] K. Smit, Smoke Obscurants for Leopard MBT and ASLAV Protection, *Proceedings of the Land Warfare Conference*, Melbourne, Victoria, September **2004**, p. 501.

[46] K. Smit, Safety Related Aspects of Red Phosphorus Based Smoke Munitions, *Proceedings of the 6th Australian Explosives Ordnance Symposium* (PARARI 2003), Canberra, ACT, October **2003**.

[47] R. L. Yon, R. S. Wentsel, J. M. Bane, *Programmatic Life Cycle Environmental Assessment for Smoke/Obscurants, Vol. 2 Red, White and Plasticized White Phosphorus*, AD-A135 910, US Army Armament, Munitions and Chemical Command, Aberdeen Proving Ground, Maryland, USA, July **1983**, available at http://handle.dtic.mil/100.2/ADA135910.

[48] *27th International Pyrotechnics Seminar*, Grand Junction, Colorado, USA, July 16 – 21, **2000**, p. 191.

[49] [49] Gmelins Handbuch der Anorganischen Chemie, *Phosphor*, Teil A, System-Nr. 16, 8. Aufl. Verlag Chemie, Weinheim/Bergstrasse, **1974**, p. 46.

[50] R. Wizinger, *Chemische Plaudereien*, 6. Aufl. Verlag der Buchgemeinde Bonn **1942**, p. 207.

[51] F. Lisowski, P. Milholland, *German Pyrotechnic Factories*, BIOS Trip No. 1815, January – February **1946**.

[52] A. Lachs, *Method Comprising Mixing a Wax, Kerosene or Naphtha and Phosphorus*, US Patent 3,314,836, **1967**, USA.

[53] A. Stettbacher, *Spreng- und Schießstoffe*, Rascher Verlag, Zürich **1948**, p. 126.

[54] H. W. Koch, H. H. Licht, *Compositions, Munitions et Effets Incendiaries*, Rapport CO 34/74, ISL, Saint Louis, France, **1974**.

[55] B. Assmann, *Brandmasse für Brand- und Nebelgranaten, Handwurfkörper u. dgl. auf der Basis von Rotem Phosphor und Magnesiumpulver*, AT Patent 339,800, **1974**, Österreich.

[56] A. Schießl, H. Krone, *Incendiary Projectile and Manual Launcher*, US Patent 4,015,355, **1975**, Buck KG, Germany.

[57] F. Keller, *2. Zwischenbericht zur Studie Sichtbehinderung gepanzerter Fahrzeuge III*, BWB-Auftr.-Nr. T/R724/B00019/02756, Buck Neue Technologien 08.07, **1982**.

[58] F. Keller, J. Schneider, Ätz-Brand-Wirkmasse für Panzerabwehrwaffen, DE Patent 3,823,613, **1991**, Buck Werke GmbH, Germany.

[59] E. Nourdin, Composition Incendiaire et Projectile Incendiaire Dispersant une telle Composition, EP Patent 0,663,376, **1994**, Giat Industries, France.

[60] *Engineering Design Handbook Military Pyrotechnics Series Part One Theory and Application*, AMC Pamphlet, AMCP 706 – 185, April 1967, p. 5ff, ARDEC Picatinny Arsenal, NJ, USA.

[61] E. Ritter von Herz, *Aluminothermische Brandwirkmasse mit Doppelter Wirkung*, DE Patent 1,114,419, **1962**, Germany.

[62] E.-C. Koch, Review on Pyrotechnic Aerial Infrared Decoy Flares, *Propellants, Explos. Pyrotech.* **2001**, *26*, 3.

[63] E.-C. Koch, Pyrotechnic Countermeasures: II. Advanced Aerial Infrared Countermeasures, *Propellants, Explos. Pyrotech.* **2006**, *31*, 3.

[64] *DEA 1671 Meeting*, Neuenburg, Germany, 7 July **2005**.

[65] E.-C. Koch, *Verfahren und Vorrichtung zur Erzeugung eines Infrarot-Flächenstrahlers*, EP Patent 1,588,996, **2005**, Diehl BGT Defence, Germany.

[66] C. A. Baker, B. F. Harkness, A. W. Norris, *High Altitude Friction Igniter*, US Patent 3,942,445, **1976**, USA.

[67] D. W. Herbage, S. H. Smith, *Decoy Flare with Sequencer Ignition*, US Patent 5,561,259, **1996**, Alliant Techsystems Inc., USA.

[68] C. H. Pritham, E. R. Rechel, T. Stevenson, *Noncorrosive Priming Composition*, US Patent 2,194,480, **1940**, USA.

[69] M. S. Silverstein, *Primer*, US Patent 2,649,047, **1953**, USA.

[70] W. B. Woodring, H. T. McAdams, *Priming Composition*, US Patent 2,970,900, **1961**, Olin Mathieson, USA.

[71] R. T. Busky, T. R. Botcher, J. Sandstrom, J. Erickson, *Nontoxic, Noncorrosive Phosphorus Based Primer Composition, a Percussion Cap Primer Comprising the Same and Ordnance Including the Same*, EP Patent 1,829,849, **2007**, Alliant Techsystems, USA.

[72] R. T. Busky,T. R. Botcher, J. Sandstrom, R. Blau, P_4RIMER^{TM}; Red Phosphorus Fueled Non-Toxic, Heavy Metal Free Primer for Small Arms Cartridges, *Proceedings of the 9eme Congres International de Pyrotechnie*, Beaune, France, October 8 – 11, **2007**, p. 479.

[73] R. Mavrodineanu, H. Boiteux, *Flame Spectroscopy*, JohnWiley & Sons Inc., New York, London, Sydney **1965**, p. 485.

[74] H. Ellern, *Military and Civilian Pyrotechnics*, Chemical Publishing Company Inc., New York **1968**, p. 359.

[75] C. W. Gilliam, D. M. Johnson, Pollution Abatement – Reclamation of Red Phosphorus Smoke Compositions, *4th International Pyrotechnics Seminar*, Steamboat Village, Colorado, USA, July 22 – 26, **1974**, p. 25.

[76] T. Liberman, *Smoke Composition and Method of Making Same*, GB Patent 2,206,343, **1988**, UK, Secretary of State for Defence, UK, Canada.

[77] T. A. Vine, W. Fletcher, An Investigation of Failures to Function of a Red Phosphorus Marine Marker, *29th International Pyrotechnics Seminar*, Westminster, Colorado, USA, July 14 – 19, **2002**, p. 477.

[78] A. Hahma, K. Palovuori, Y. Solomon, TNT-Equivalency of Thermobaric Explosives, *36th Int. Annual Conference of ICT, Karlsruhe*, Germany, June 28 – July 1, **2005**, p. V10.

[79] E.-C. Koch, *Blastladung auf Basis Roter Phosphor*, DE Patent 2006,10,030,678, **2006**, Diehl BGT Defence, Germany.

[80] D. Clement, B. Eigenmann, K. P. Rudolf, E.-C. Koch, Investigation of Explosives with Tailored Blast Effects, *Proceedings of DEA 1671 Meeting*, Picatinny, NJ, October, **2006**.

[81] P. Golding, A. J. Bellamy, P. Bolton, J. D. Callaway, A. E. Contini, N. Davies, M. K. Till, J. N. Towning, S. J. Trussell, Energetic Polyphosphazenes –A New Category of Binders for Pyrotechnic Formulations, *36th Int. Annual Conference of ICT*, Karlsruhe, Germany, June 28 – July 1, **2005**, p. V2.

[82] A. J. Bellamy, A. E. Contini, P. Golding, S. J. Trussel, Bomb Calorimetric Study of a Series of Energetic Linear Polyphosphazenes, *NDIA Meeting*, San Francisco, November 15 – 17, **2004**.

[83] P. R. Bolton, P. Golding, C. B. Murray, M. K. Till, S. J. Trussell, Enhanced Energetic Polyphosphazenes, *Proceedings of the Insensitive Munitions and Energetic Materials Technical Symposium*, (IMEMTS 2006), Bristol, April **2006**.

[84] P. Golding, S. J. Trussel, Novel Energetic Polyphosphazenes, WO Patent 2006/032882, **2006**, UK, Secretary of State for Defence.

[85] T. M. Klapötke, K. Karaghiosoff, M. Göbel, The First Structural Characterization of a Binary P-N- Molecule: The Highly Energetic Compound P3N21, *Angew. Chem., Int. Ed.* **2006**, *45*, 6037.

[86] N. Wiberg, *Holleman-Wiberg: Lehrbuch der Anorganischen Chemie*, 101. verbesserte und stark erweiterte Auflage, Walter de Gruyter, Berlin **1995**, p. 790.

[87] K. Raupp, W. Brand, H. Lang, W. Kukla, *Ammunition for Smoke Generation*, US Patent 6,612,242, Buck Neue Technologien GmbH, **2003**, Germany.

[88] J. Weidlein, U. Müller, A. Dehnicke, *Schwingungsferquenzen I. Hauptgruppenelemente*, Georg Thieme Verlage, Stuttgart, **1981**.