Red Phosphorus

for Use in

Screening Smoke Compositions

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Contents

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Abstract

It has been known for many years that red phosphorus reacts with moist air to produce phosphorus oxyacids and phosphine. The detailed mechanism remains unknown. This problem is of great concern to MoD and to pyrotechnics manufacturers because of the present and likely future importance of red phosphorus as the major constituent of compositions for visual and infrared screening, and because of the concern about the toxicity of phosphine and the possible consequent degradation of the performance of stores containing red phosphorus.

Because red phosphorus is used extensively in the plastics industry much work has been published in the patents literature on ways of reducing the rate of evolution of phosphine. The scientific basis for the various claims is not well understood.

This report comments on the pyrotechnic problems of using red phosphorus, and surveys the literature (largely patents) to accumulate the wide range of materials which have been claimed to be affective as phosphine and acidity suppressers.

Recommendations are made for future research work to clarify the reaction mechanisms, for collaboration between red phosphorus and pyrotechnics manufacturers work to improve the ingredients supply and processing of red phosphorus pyrotechnic compositions for the development of non-destructive test methods for the stability of powdered and compacted composition, and for the quantification of toxic and environmental hazards arising from the use of red phosphorus.

If red phosphorus is to continue as an acceptable ingredient for screening smoke compositions, the following problems must be addressed:

- The production of phosphine from compositions must be reliably suppressed by a mechanism effective over the planned life of the store (one should now be considering 30 years).
- The production of hydrogen by reactions involving ingredients must similarly be suppressed.
- The formation of white phosphorus under different conditions (on extinguishing in water, when choked by carbonaceous residues etc.,) must be quantified and minimised.
- The toxicity of combustion products of compositions must be assessed, and optimum selection of ingredients and formulations devised to minimise it.
- Environmentally and economically acceptable methods of demilitarising, reusing and destroying red phosphorus compositions and components (particularly plastics contaminated with it) must be devised.

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1. Introduction

Red phosphorus is an important ingredient for the manufacture of pyrotechnic smokes and is likely to be in service for many years. However, it readily reacts with moist air to form acidic, highly hygroscopic oxides, and phosphine which is a toxic, chemically reactive gas. The gas could pressurise unacceptably a sealed store containing red phosphorus compositions, and it reacts with certain metals and plastics causing significant changes in their properties. The moisture usually present on red phosphorus can react with other ingredients of a pyrotechnic composition, specifically with metal powders, to generate significant quantities of hydrogen.

The original red phosphorus screening smoke compositions for use by the land services consisted of nothing more than red phosphorus in a matrix such as butyl rubber to allow it to be formed into a payload for smoke grenades. About 12% rubber gave a mixture that could be incorporated, granulated for convenient handling and pressed with an acceptably low probability of a fire. Such a simple formulation gave the maximum quantity of red phosphorus in the mixture, and therefore, it was expected, the maximum quantity of smoke. It became obvious, however, that under certain conditions, the red phosphorus did not necessarily burn to completion. Not only was this inefficient as far as smoke production was concerned, but residues were considered to form an unpredictable incendiary hazard. Concern was also expressed about the possibility that the residues could be contaminated with highly toxic white phosphorus formed by condensation of unburned phosphorus vapour.

A further disadvantage of the simple formulation was that the burning time of the payload was governed almost solely by the size of the lumps formed on dispersal. The burning rate of the composition could be adjusted only within narrow limits by varying the particle size of the phosphorus and its concentration in the mixture. This was not seen as a great problem for grenades such as the L8 where a rapid build up of fairly long duration visual screening smoke was adequately achieved largely by vigorous fragmentation of the pressed pellet whereby the finest resulting particles burned very rapidly in the air and the larger particles fell burning to the ground.

Such compositions, however, proved inadequate for more sophisticated applications of screening compositions. An artillery shell, for example, can deploy smoke compositions either in smoke pots or as pressed pellets which are released from the carrier shell at some optimum altitude. The simple compositions do not burn in smoke pots. Aerodynamic considerations require good control over the size and shape of deployed pellets, so the pyrotechnic designer must vary the rate of burning of his composition by other means to achieve the required duration and opacity of the screen.

Subsequently, compositions were developed which contained mixtures of metal powders and inorganic oxidants to provide a good source of pyrotechnic heat to allow better control over the burning rate of the composition and, burning anaerobically themselves, ensure that the red phosphorus combustion continued more readily to completion. This method gave the designer much greater flexibility to vary the rate at which smoke was produced from any particular size of pellet. These compositions had two disadvantages in particular. The extra components reduced the amount of phosphorus in a payload, and hence the amount of smoke; the metal powder was prone to corrosion and hydrogen was produced as well as the phosphine from the phosphorus.

1

Other types of composition should be mentioned which have been used in Naval service for many years as signalling smokes from smoke pot type devices. Excess red phosphorus mixed with calcium sulphate generates heat to vaporise the excess which burns in the air. Manganese dioxide will also react with phosphorus. However, these compositions were not designed to produce smoke at the rate necessary for screening purposes. Phosphine evolution has also been a serious problem with them and prompted their reformulation.

One further inconvenience for pyrotechnics manufacturers is that many of the binders used in modern compositions are soluble only in solvents which are toxic, highly flammable (acetone, MEK etc.,) or are undesirable pollutants (chlorinated hydrocarbons). It would be a great advantage if binders were developed which could use solvents such as alcohols. which, even if flammable, are more acceptable environmentally.

2. Phosphorus

2.1. Introduction

Phosphorus is a chemical element. It shows extensive allotropy, the three main forms being white, red and black (the thermodynamically stable form), each of which is polymorphic. Although white phosphorus is the product of solidifying molten phosphorus or of condensing the vapour, it is thermodynamically unstable with respect to red phosphorus and is converted into it by heating. This transformation takes place extremely slowly under normal conditions, and the commercial manufacture of red phosphorus from white phosphorus takes place at high temperature perhaps in the presence of a catalyst such as iodine, sodium or sulphur. It can also be accelerated by ultraviolet irradiation. When white phosphorus is heated at very high pressure or at lower pressures in the presence of a suitable catalyst crystalline black phosphorus is produced.

The liquid, solid white phosphorus and the vapour below about 800°C consist of tetrahedral P_4 molecules. The bonds are under considerable angular strain (estimated at about 96 kJ/mol), in accord with the known reactivity of the molecule. At higher temperatures the P_4 molecules dissociate into P_2.

The structures of the solids are not well characterised. Crystalline black and red phosphorus have a graphite like structure.

The following variants have been reported.[1]

| Modification	Structure	Density g/cc	
Red I	amorphous	2.16	transformation at 460°C
Red II	hexagonal	2.31	transformation at 520°C
Red III	hexagonal	2.31	transformation at 540°C
Red IV	tetragonal	2.31	
Red V	triclinic	2.31	$T_m = 590$°C
Red VI	?	2.31	
Black	amorphous	2.55	
Black	orthorhombic	2.69	From white phosphorus at 200°C and 120 MPa
Table 1. Some Polymorphs of Phosphorus			

Only two allotropes, white phosphorus (also called yellow) and red phosphorus (also called amorphous) are of practical importance. As far as military use is concerned, white phosphorus must be considered obsolescent because of its toxicity and the unacceptable injuries that it inflicts when used as an incendiary.

	White phosphorus	Red phosphorus
M.P. (°C)	44	
B.P. (°C)	280	
Density (g/cc)	2.3	1.82^{20}
Vap. pressure at room temperature (mm Hg)	0.04	$< 1 \times 10^{-8}$
Physical appearance	Waxy, off white or yellow solid	Dark red, granular solid.
Chemical reactivity	Very reactive. Can ignite spontaneously in air. Usually stored under water.	Reactive. Easily ignited. Stored in drums with fitted lids.
Toxicity	High by ingestion (LD_{50} ca. 1 mg/kg) and inhalation of vapour.	Fairly low.
Normal handling precautions	Avoid all contact with skin; avoid any inhalation of vapour.	Treat as a hazardous material - avoid contact and inhalation of dust.
Table 2 Some Properties of Elemental Phosphorus		

The vaporisation process of red phosphorus is considered of importance in the commercial production of III-V semi-conductors and was studied by John and Hein [2]. They found that the process was complex: the process was kinetically controlled, and the temperature dependence of the equilibrium vapour pressure varied greatly with the source of the material. Red phosphorus produced by conversion of white phosphorus in a closed vessel had very variable properties depending on the temperature of the reaction and varied in colour from bright red (highly porous) to dark brown-violet (without macroscopic pores). Only amorphous material of compact habit exhibited reproducible behaviour.

This observation of the significant variability of a fundamental physical property of red phosphorus renders less surprising the generally observed variability of chemical reactivity of red phosphorus which can differ significantly from sample to sample even from a single manufacturer.

Phosphorus is obtained primarily by reduction of phosphate rock, essentially calcium phosphate, with coke and silica in an electric furnace in yields of about 90%. Phosphorus volatilises as P_4 (partly dissociated into P_2 above about 800°C) and condenses as white phosphorus.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C = P_4 + 6CaSiO_3 + 10CO$$
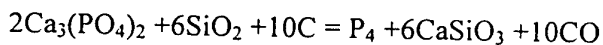
In spite of the heat of combustion of the coke, the overall reaction is strongly endothermic and required about 12 MW hours of electricity per ton of phosphorus.[3] Impurities include arsenic and antimony in quantities up to ~100ppm as well as some silicon, carbon, iron and fluorine. Steam distillation can reduce the concentration of arsenic to 2ppm.

White phosphorus is used industrially primarily as a precursor for red phosphorus, which is used in large quantities as a flame retardant in the plastics industry.

2.2. Uses of Red Phosphorus

The major use of red phosphorus is in the plastics industry where it is used as a flame retardant and fire suppressant. Two main problems seem to be associated with it. The first is the flammability of the material which can cause fires during the processing, the second is the chemical stability of the system and the evolution of phosphine on storage and during the processing. Phosphine production seems to proceed in tandem with an increase in the acidity of the material due to oxidation, although it is difficult to find good comparative data. It is normal practice for the manufacturer to supply red phosphorus which has been treated chemically to suppress these phenomena of excessive flammability and excessive oxidative lability. Although the two phenomena are quite different, some publications do not distinguish clearly between them and the purpose of some additives is not explicit. The fire hazard is countered by the use of an *anti-dusting agent* (or a *phlegmatiser* or a *desensitiser*), the reactivity is suppressed by a *stabiliser*.

In practice, effective flame-proofing seems generally to be achieved with phosphorus concentrations from 1 to 15% by weight of the thermoplastic composition. In the case of glass-fibre-reinforced polyamides, red phosphorus concentrations of from 0.5 to 5% by weight of the fibre-reinforced polyamides provide adequately flame-proofed products. However, the patents generally cover a much wider composition range than that found adequate.

Regardless of the required concentration of red phosphorus, its incorporation into thermoplastic polymers often presents considerable difficulties, especially where such polymers have a high melting point or softening range so as to require high temperatures above 200°C or even up to about 310°C to achieve an effective melt-blending or homogenisation and distribution of the red phosphorus in the polymer itself. Red phosphorus powder, which has particle sizes primarily in the range 0.01 to 0.15 mm (most patents claim below 0.2mm) but which may contain even finer portions, tends to produce a dust and this frequently leads to fires, particularly in the presence of hot surfaces, which are unavoidable, above all when melt-blending or similarly processing thermoplastic polymers with high melting points.

The plastics industry therefore has a similar problem to the pyrotechnics industry. Once the red phosphorus is incorporated into a composition, dusting is no longer a problem, but the processing of the treated stabilised red phosphorus may have an adverse effect on the stabiliser. The advantage for the plastics industry is that phosphorus is a minor constituent of the final product; in a pyrotechnics product, however, it is the major component the amount of which must be maximised to achieve the required effect.

2.3. Manufacture of Red Phosphorus

2.3.1. Discussion

The usual process involves the conversion of white phosphorus by extended heating at about 220° – 280°C in a closed vessel. The reaction is exothermic and the conversion temperature

5

must be controlled as reaction can become too vigorous at sufficiently high temperatures. Catalysts have been proposed to speed up the process.

$$P(white) = P(red) \qquad \Delta H = -17.5kJ$$
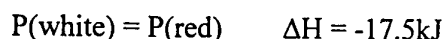
The red phosphorus is usually obtained in massive form which must be broken up and milled to produce particles or the required size. The particles are then treated with aqueous alkali to remove residual white phosphorus. The temperature at which the conversion proceeds affects the degree of crystallinity of the product – the higher the temperature, the greater the crystallinity and, presumably, the less reactive the product.

The Albright and Wilson process used in the UK (in the author's recollection) was a simple process in which the yellow phosphorus was heated in sealed, coffin-like vessels until essentially complete conversion had been achieved. The massive product was broken up coarsely under water and then milled to the required size. The solid was treated with caustic alkali to remove residual yellow phosphorus, dried and oiled (as an anti-dust treatment).

Discussions with Hoechst revealed that all their grades are produced by the same basic method. Yellow phosphorus is converted essentially completely into red phosphorus by a suitable heat treatment. The solid product is then milled to meet the required particle size distribution. Although the material is often of sufficient purity (sufficiently low yellow phosphorus content) to meet the specification, an alkali washing stage is always included.

On the face of it, the two processes are similar. Differences between the processes which might affect the reactivity of the solid product could be sought in the particle size, which governs the specific surface, and in the conversion temperature, which affects the degree of crystallinity. The variation in the physical properties of red phosphorus (equilibrium vapour pressure, density) that have been commented on by several authors suggest that conditions throughout one batch may not be uniform. It may be that the special requirements of pyrotechnics manufacturing processes expose those variations more critically than in other applications.

The patent literature also reveals a process in which yellow phosphorus is reacted in a slurry with red phosphorus and is converted incompletely into it. Under the right conditions a product is achieved of a particle size distribution which does not require grinding to produce a usable material. This process has not been used in the UK, and material from it has not, presumably, been used in UK manufacture, but the Erco plant in the USA (operated by Albright and Wilson) did use it to the technical satisfaction of the US DoD. However, the spherical product was insufficiently reactive for the match industry and, following a lack of financial commitment by the DoD, the plant was closed.

2.3.2. Review of patent literature

All the recent patents searched were variations on the simple theme of heating white phosphorus to convert it into red phosphorus in a continuous or in a batch process. The individual patents are abstracted briefly below. No catalysts were mentioned. Molten lead was used in one patent as an inert heat exchange medium. The main emphases of the patents seem to be production of red phosphorus as a granular powder rather than as a massive lump

which would require breaking up, and managing the heat flow during the conversion. Other than the rough extremes of particle size and occasionally the qualitatively good flow properties of the product, no properties of the phosphorus were claimed. In particular, no treatment to remove residual white phosphorus other than heating was mentioned in any of the patents.

When considering the following patents it should be understood that Hoechst took over the Knapsack plant, and that Albright and Wilson operated the Erco plant.

Most systems react a slurry of red phosphorus in white phosphorus over temperature ranges from about 200°C or 300°C to the boiling point of white phosphorus. The flow rate or removal rate is adjusted to manage the temperature. One claim is for a conversion in aqueous suspension, which seems close to a completely different proposal from a method of manufacturing phosphine!

A variant of the process was described by Wilson and Tusson[4], in which a slurry of red phosphorus in molten white phosphorus at above 200°C was blown with an inert gas to achieve separation by removing the volatile white phosphorus.

Hyman and Chase (American Cyanamid)[5] describe an agitated reactor for the continuous conversion of liquid white phosphorus to red phosphorus. White phosphorus is fed into the slurry at such a rate as to maintain the proportion of red phosphorus in the range 15 to 45% at a temperature in the range 220°C to the boiling point of white phosphorus. Slurry is constantly withdrawn for recovery of red phosphorus at a rate sufficient to maintain constant volume in the reactor. Internal baffles provide an agitation regime such that red phosphorus does not build up inside the reactor.

McGilvery and Singh (Erco)[6] produce red phosphorus by heating white phosphorus to between 250° and 590°C at a pressure above the vapour pressure of white phosphorus. The white phosphorus may be fed into an extrusion head heated to the reaction temperature from which the red phosphorus is extruded into an inert atmosphere. Alternatively, droplets of molten white phosphorus may be fed into an inert immiscible heat exchange fluid such as lead at the reaction temperature.

McGilvery (Erco)[7] proposes a dry process in which white phosphorus is injected onto a bed of red phosphorus particles preheated to a temperature above the thermal conversion temperature and within the range 300° to 595°C (or 350° to 425°C) while controlling the heat generation. The concentration of white phosphorus is maintained below about 20% by weight (of the total).

Lehr et al (Hoechst)[8,9] continuously introduce yellow phosphorus into a ball mill heated to between 280° and 590°C at such a rate that the temperature of the reaction is self sustaining. The red phosphorus is cooled inside the mill, water is poured over it and the whole is subjected to wet grinding. The red phosphorus is finally removed from the mill as an aqueous suspension

Ryan and Yank (Erco)[10] form red amorphous phosphorus is formed by thermal conversion of yellow phosphorus under such conditions that the heat of conversion evaporates the yellow

7

phosphorus which is condensed and used for a subsequent batch. The red phosphorus is essentially free from yellow phosphorus and is in a particulate form. Lead may also be used as the heat transfer medium.

Low and Holmes (Albright and Wilson)[11] claim a process for the manufacture of friable red phosphorus by forming a slurry of 10-45% red phosphorus in molten white phosphorus, reducing the content of yellow phosphorus to less than 20% of the red phosphorus by separation at below 280°C, and then heating the product at above 295°C to convert and also evaporate the yellow phosphorus. Various temperatures and durations, with or without vacuum, and with and without intermediate cooling to various temperatures are also used. The claimed product is readily broken up and does not require washing with caustic soda to achieve the required degree of stability. However, no details of analysis are provided.

Inao et al., (Rinkagaku)[12] prepare red phosphorus by heating yellow phosphorus at its boiling point in the presence of a dispersant which may be a finely powdered inorganic surfactant sparingly soluble in water, an inorganic ammonium salt, or an organic amine. Most of the yellow phosphorus is converted to red, most of the remainder is removed by distillation at its boiling point, and the last traces at a higher temperature. The product is a fine powder of red phosphorus which is less apt to undergo a disproportionation reaction.

2.3.3. Specification and Availability of Red Phosphorus

Red phosphorus for use in UK smoke stores is governed by Interim Defence Standard 68-96/1 (May 1990) (earlier CS5390A phosphorus, amorphous, oiled).

Volatile matter	%	0.25 max
Free phosphorus	%	96.0 min
Oil	%	0.95 min; 1.55 max
White phosphorus	ppm	200 max
Matter insoluble in water	%	1.0 max
Reaction of 5% m/v water extract		
acidity to methyl orange as H_2SO_4	%	0.05 max
acidity to phenolphthalein as H_2SO_4	%	0.50 max
alkalinity to methyl orange as Na_2CO_3	%	0.20 max
Matter insoluble in aqua regia		
total	%	0.30 max
retained on 75μm sieve	%	0.05 max
retained on 250μm sieve	%	Nil
Sieving		
retained on 355μm sieve	%	Nil
retained on 250μm sieve	%	1.0 max
retained on 180μm sieve	%	3.0 max

Table 3 Requirements of Interim Def Stan 68-96/1 Phosphorus, amorphous, oiled

The oil is described as "insulating oil complying with BS 148". As alternatives may be used oil to BS 4475 grade TLS-22 or dioctyl phthalate. This specification limits the acidity of the material on receipt or at the time of use, places limits on the coarsest and finest particles that are acceptable, but makes no comment on the presence or absence of trace impurities other than white phosphorus.

This specification was presumably written around the material originally supplied by Albright and Wilson.

There are now few manufacturers of red phosphorus in the West, which concerns manufacturers of red phosphorus pyrotechnic stores and their customers. Pyrotechnics is a minor user of the total red phosphorus production and most users have tended to take from the suppliers what has been devised for other uses in the plastics industry.

Pyrotechnics compositions containing red phosphorus are treated differently from flame retarded plastics, and they contain different ingredients. Their processing almost invariably takes place at room temperature with intervening stages of drying at modestly elevated temperatures. They are usually granulated moist with a solvent and pressed or perhaps extruded. They often contain significant quantities of inorganic oxidising agents and metal powders which can react with moisture to produce hydrogen. Significantly, perhaps, red phosphorus is by far the major constituent, and all efforts are made to reduce the amount of ingredients which do not directly contribute to the formation of smoke. This may make the problem of phosphine evolution more severe not merely because of the greater amount of potential reactant, but because of the lower amount of potentially protective plastics matrix.

Table 4 shows some grades that have been made available by Hoechst and have been used with success by several pyrotechnics manufacturers, not all of which meet the requirements of the Interim Defence Standard.

		HB300	HB400	HB600	HB700	NF	SMC3	OM3
phosphorus	(% w/w)	>97	92 min	91 min	94 min	97.5 min	97.5 min	96 min
dust suppressant	(% w/w)	0.3-0.7						0.95-1.55
Water	(% w/w)	<0.5	15-25	15-25	0.5 max	0.5 max	0.5 max	
Size distribution								
>400 µm			0.1 max	0.1 max	0.1 max			
>180 µm								3.0 max
>100 µm			3.0 max	3.0 max	3.0 max			
>75 µm						5 max	5 max	
>48 µm		~20						
>45 µm						25 max	25 max	25 max
>24 µm		~50						
Phlegmatising agent					0.3-0.7			
PH		~7				9-11	6.0-8.0	
bulk density		0.8-1.2						
Iron		<0.05						
Copper		<0.001						
white phosphorus		<0.02					0.02 max	
volatile content								0.5 max

Table 4. Some Available Grades of Red Phosphorus (Hoechst)

2.4. Reaction of Red Phosphorus with Moist Air

2.4.1. Introduction

Phosphorus undergoes an important series of reactions at room temperature in the presence of oxygen and moisture to produce acidic oxides and small quantities of the highly toxic gas *phosphine*, PH_3. Although the phenomenon has been known for a long time, the chemistry of the reaction seems to have remained obscure. It seems certain that both oxygen and water are necessary, and that the reaction can be catalysed both positively and negatively by traces of metal ions. It is possible that hydrogen may also be produced by oxidative hydrolysis of phosphorus, although this is uncertain, and any mechanism is equally unclear.

Phosphine can react with moist air to produce similarly acidic products, this time remote from the original sample of phosphorus. Further, it can react rapidly with metals, particularly copper, to cause extensive corrosion at sites well removed from the bulk phosphorus.

2.4.2.   Review of non-patent literature

It has long been recognised that the rate of oxidation is very sensitive to the presence of traces of impurities, and much work, reflecting the importance of red phosphorus in the plastics industry, has been published on the stabilisation of red phosphorus against this reaction.

One of the earliest publications on factors affecting the chemical stability of red phosphorus was by Jakabcin and Silverstein[13] of Frankford Arsenal in 1942 who investigated the stability problems with a small arms priming composition containing red phosphorus and barium nitrate which had been pressed into a brass capsule. They found that the rate of production of acidity was increased in the presence of copper, 70:30 brass and 90:10 brass, and they then investigated mixtures of red phosphorus and powdered metal for which reactivity decreased in the order:

Cu > Cr (sample 2) > Bi > Fe > Ag > Ni > Cd > Sn>
red phosphorus alone>
Pb > Cr (sample 1) > Zn > duralamin > Al.

The order was somewhat changed in the presence of barium nitrate: the tin then decreased the reaction rate considerably, and the cadmium then slightly accelerated the rate relative to a mixture of red phosphorus and barium nitrate. The difference between the two samples of chromium was not resolved. Although the mechanism is obscure, the effect of different metals on the reactivity of red phosphorus is fundamental to many of the subsequent publications.

2.4.3.   Review of patent literature

All the patents searched relating to the use or red phosphorus as a flame retardant in the plastics industry are briefly abstracted below.

Most publications on the subject are in the patent literature, and understanding is fraught with difficulty. While one might accept the internal consistency of the claims within a single patent, the different tests applied in different patents make comparisons between patents uncertain. Many patents give no quantitative evidence for the effectiveness of their claims in suppressing phosphine. Also, while the formation of phosphine and the development of acidity (via phosphorus oxides) presumably proceed hand in hand few quantitatively satisfying links have been found so far in the literature. The rest of this section is devoted to sourcing the published phenomena which are so often incomplete and sometimes apparently contradictory.

Earlier attempts to reduce the reactivity of red phosphorus depended on coating it with hydrophobic layers of paraffin. Knapsack AG improved the method of coating it with about 5% wax[14] and later stabilised it by treating it with magnesium hydroxide or aluminium hydroxide and impregnating it with paraffin, wax or organo-silicon compounds[15]. They also claimed that chloroparaffins, dioctylphthalate, tris(β-chloroethyl) phosphate, tricresyl phosphate and a silicone-polyether block copolymer were also effective[16].

Busch et al.. (Hoechst)[17] use red phosphorus in combination with talc and an alkaline earth metal carbonate.

Horsey et al., (US DoD)[18] use an injection mouldable compositions consisting of 30-80% red phosphorus and 70-20% polymeric binder consisting of polyethylene, polypropylene or their copolymer. Stability may be increased by adding smaller quantities of polystyrene and anti-oxidants such as aluminium oxide.

Dany et al., (Knapsack)[19] passivate red phosphorus with 19-90% molten ε-caprolactam in an inert atmosphere.

Largman et al., (Allied Chemical)[20] claim that polyamide compositions containing an effective amount of red phosphorus flame retardant additive are rendered more flame retardant by heating the composition in the presence of oxygen at a temperature of at least 100°C. No comment is made on phosphine evolution.

Wacky and Cherdron (Hoechst)[21] incorporate in the moulding composition 1 to 120 weight % based on red phosphorus of substances capable of binding with phosphine (See table 5).

	Additive	Additive (on red phosphorus) (%)	Concentration PH_3 in flask ppm
	Standard	-	35-40
1	HgO	2	1
2	MoS_2	2	1
3	PbO_2	2	1
4	active carbon	7	-
5	CuO	10	-
6	$FeCl_3.6H_2O$	10	1
7	$HgCl_2$	1	-
8	$AgNO_3$	1	-
Table 5. Reduction of Rate of Phosphine Production (Wacky and Cherdron)			

These include molybdenum(IV) oxide, mercury(II) oxide, lead oxide, silver nitrate, mercury(II) chloride and iron(III) chloride hexahydrate. The best results were found with copper(II) oxide and activated charcoal. 3g red phosphorus and the compounds given were stored for 12h in a stoppered 100ml flask.

Breitschaft (Hoechst)[22] phlegmatise red phosphorus for use in a retardant for linear polyester sor polyamides by intimately mixing it with a liquid mono- di- or tri-ester of orthophosphoric acid. These materials bind well to the red phosphorus and prevents exposire of grains during processing.

Hilt et al., (BASF)[23] phlegmatise use finely divided red phosphorus with a solid having a melting point from 50°C to 120°C (trioxane and caprolactam are instanced) for use as flame retardant for polyoxymethylenes. They neutralise the surface acidity of the phosphorus with sodium carbonate prior to, or during incorporation.

Dany et al., (Hoechst)[24, 25, 26] propose flame retardants made from red phosphorus and organic nitrogen compounds (specifically melamine or polyacrilonitrile) which carbonise after inflammation (ratio of ingredients from 1:99 to 99:1) and a stabiliser of 1 to 10 weight % (based on red phosphorus) amidosulphonic acid or ammonium bisulphate, or 5 to 15 weight % paraffin oil, or mineral oil, or silicon oil, or 20 to 50 weight % pentaerithritol based on the nitrogen compound.

Kaiser and Cadus (BASF)[27] desensitise red phosphorus against spontaneous ignition, and reduce its tendency to dust during the processing necessary to use it as a flame retardant in plastics, by coating it with a lactam having between 4 and 12 carbon atoms by conventional mixing and homogenising techniques. The flame retardant consists of 25 to 90% red phosphorus and 10 to 75% lactam. Following incorporation into the plastic, the lactam may be partly or wholly recovered by distillation at atmospheric pressure or under vacuum. Suitable lactams are pyrrolidone, caprolactam, enantholactam, octalactam and dodecalactam. These are particularly suitable for flame proofing high melting polymers such as polyamides, polyurethanes, polyacetals and polyester amides.

Wortmann at al., (Hoechst)[28] desensitise red phosphorus with 2 to 20 weight % of a liquid organic or organo-silicon compound which does not react with phosphorus and has a low vapour pressure at room temperature. Desensitisers include chlorinated paraffin oil (30-70% chlorine), tris-(β-chloroethyl) phosphate, tricresyl phosphate, a silicon-polyether block copolymer, and a copolymer of dimethylpolysiloxane and polyoxyalkylene ether.

Raley (Dow)[29] uses red phosphorus as flame retardant for cross-linked halogenated olefin polymers.

Horn and von Rumohr (BASF)[30] add 0.5 to 15 weight % red phosphorus (particle size 0.001 to 0.5mm) to aromatic polycarbonates.

Rainer et al., (BASF)[31] use 0.5 to 12 weight % red phosphorus as flame retardant for thermoplastic nylon used in the electrical industry.

Ducloux (Rhone-Poulenc)[32] uses up to 15% red phosphorus (mean particle size <200μm) as a flame retardant in heat curable compositions based on N,N'-diimide of an unsaturated carboxylic acid.

Dany et al., (Hoechst)[33] use red phosphorus of particle size up to about 100μm coated with a binder which melts between 30° and 180°C consisting of a wax (specifically the ethylene glycol ester of the wax acid product of chromic acid oxidation of crude montana wax) and/or metal soaps and other materials including melamine, polyacrylonitrile amidosulphonic acid, copper(II) oxide, aluminium oxide, and dibromoneopentyl glycol which inhibit the formation of phosphine during incorporation of the flame retardant with plastics.

Staendeke et al., (Hoechst)[34] use as an oxidation stabiliser 0.5 to 5% w/w of a metal compound of the second or third group of the Periodic Table, specifically the neutral aluminium, magnesium, calcium or zinc salt of phosphoric acid. Again the maximum claimed particle size of red phosphorus is 0.2mm (see Table 6). The phosphates are precipitated at controlled pH with orthophosphoric acid from solutions of, for example, aluminium sulphate.

calcium nitrate, zinc sulphate or magnesium sulphate. The treated (or untreated) red phosphorus is suspended in water at 80°C and purged with oxygen. A gas mixture of oxygen and phosphine is passed through solutions of mercury(II) chloride and the extent of oxidation determined by titration according to the following reaction:

$$PH_3 + 3HgCl_2 = P(HgCl)_3 + 3HCl$$
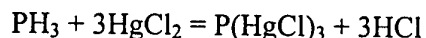
Method of preparation of sample	Evolution PH$_3$ mg/g material/h	Acidity of aqueous suspension Mg KOH/g material/h
100g red phosphorus suspended in 500cc water at 90°C with agitation. Added 5g NaH$_2$PO$_4$ and 12g Al$_2$(SO$_4$)$_3$.18H$_2$O and NaOH added to adjust pH to 3. One hour wait, than filter, wash residue with water and dry at 80°C in stream of N$_2$.	0.27	4.2
As first example, but 11.5g Ca(NO$_3$)$_2$.4H$_2$O added to aqueous suspension in place of aluminium sulphate. pH adjusted to 7 with NaOH.	0.39	5.2
As first example, but 14g MgSO$_4$.7H$_2$O added in place of aluminium sulphate. pH adjusted to 7 with NaOH	0.51	5.8
As first example, but 11g ZnSO$_4$.7H$_2$O added in place of aluminium sulphate. pH adjusted to 7 with NaOH	0.52	5.8
Control: no stabilisation	0.53	7.7

Table 6. Evolution of Phosphine and Development of Acidity. (Staendeke)

Staendeke et al (Hoechst) published four similar methods of stabilising red phosphorus with a compound of a metal of the second or third group of the periodic table.

The compound may be the neutral aluminium, magnesium, calcium or zinc salt of an acid orthophosphoric acid ester[35] of a long chain aliphatic alcohol, which may be ethoxylated, or phenol, the metal compound being present in about 0.25 to 5 weight %. A claimed improvement is that the red phosphorus and about 0.5 to 5 weight % acid orthophosphoric acid ester of a long chain aliphatic alcohol, or phenol, are intimately blended, suspended in water, heated to about 60° to 95°C and treated with the stoicheiometric amount of an aqueous solution of a water soluble salt of aluminium, magnesium, calcium or zinc (aluminium sulphate, magnesium sulphate, calcium nitrate and zinc sulphate are specifically mentioned). The mixture is filtered and the residue dried at elevated temperature (80° to 130°C is mentioned).

The compound may also be the aluminium, magnesium, calcium or zinc salt of an alkyl-, cycloalkyl, aryl- or aralkyl-phosphonic acid having 1 to 20 carbon atoms[36]. Specific mention is made of salts of octane-, decane- dodecane-, benzene-, cyclohexene-, 2-phenylethane-1-, 2-phenylethylene-1-, 2-carboxyethane-1-, cyclohexane-, vinyl-, 2-chloroethane-1 and propane-phosphonic acid. A claimed improvement is that the red phosphorus and phosphonic acid are intimately blended, suspended in water, heated to about 60° to 95°C and treated with the minimum amount of an aqueous solution of a water soluble salt of aluminium, calcium or zinc (aluminium sulphate, calcium nitrate and zinc sulphate are specifically mentioned) necessary to cause precipitation of the corresponding phosphinic acid salt at a pH of 3.0 to 6. The mixture is filtered and the residue dried at elevated temperature (80° to 90°C is mentioned).

The compound may also be the neutral aluminium, magnesium, calcium or zinc salt of orthophosphoric acid[37] present in about 0.5 to 5 weight %. A claimed improvement is that the red phosphorus and about 0.5 to 5 weight % orthophosphoric acid or sodium hydrogen phosphate are intimately blended, suspended in water, heated to about 60° to 95°C and treated with the minimum amount of an aqueous solution of a water soluble salt of aluminium, magnesium, calcium or zinc (aluminium sulphate, magnesium sulphate, calcium nitrate and zinc sulphate are specifically mentioned) necessary to cause precipitation of the corresponding orthophosphoric acid salt at a pH of 3.0 to 7.5. The mixture is filtered and the residue dried at elevated temperature (80° to 130°C is mentioned).

The compound may also be the aluminium, calcium or zinc salt of a phosphinic acid[38] of the general formula R_1R_2POOH-. Where R1,R2 are alkyl, cycloalkyl, aryl or aralkyl groups having 1 to 20 carbon atoms. Specific mention is made of salts of bis-(chloromethyl)-, 2-carboxyethylmethyl- or octylmethyl-phosphinic acid. A claimed improvement is that the red phosphorus and phosphinic acid are intimately blended, suspended in water, heated to about 60° to 95°C and treated with the minimum amount of an aqueous solution of a water soluble salt of aluminium, calcium or zinc (aluminium sulphate, calcium nitrate and zinc sulphate are specifically mentioned) necessary to cause precipitation of the corresponding phosphinic acid salt at a pH of 3.0 to 7.5. The mixture is filtered and the residue dried at elevated temperature (80° to 130°C is mentioned).

Brulet (Rhone-Poulenc)[39] encapsulates red phosphorus of average particle size less than 80μm with waxes, paraffins, chlorinated hydrocarbons, thermoplastic resins and melamines. The encapsulant should not be soluble in any of the ingredients in the polymerisation or moulding process. No specific mention is made of phosphine.

Tacke et al., (Bayer)[40,41] use as a flameproofing material 0.5% to 25% by weight of a mixture of 55-95% phenol/aldehyde condensation resin and 5-45% of red phosphorus having an average particle size below 200μm. They note that the resin and red phosphorus have a synergistic affect on flame retardation. The crosslinking agent may be a polyfunctional epoxide, boric acid, phosphoric acid or its esters, polycarboxylic acids, or polyfunctional isocyanates. It is advantageous to add metal salts to these agents, such as an oxide, hydroxide, carbonate, acetate, formate, phosphate or borate of an alkali metal, alkaline earth metal, zinc, cadmium, tin, lead, antimony, aluminium, copper, manganese, iron, cobalt or nickel. It is noted that the evolution of phosphine is exceptionally low from these materials, but extra suppression can be achieved by adding small quantities of molybdenum(IV) sulphide, mercury(II) oxide, lead(IV) oxide, copper(II) oxide or zinc oxide.

Hira et al., (Hitachi)[42] use red phosphorus coated with a thermosetting resin in the presence of hydrated aluminium oxide as a flame retardant.

Cerny and Vivant (Rhone-Poulenc)[43] prepare a flame retardant from 50-95% red phosphorus and 5-50% epoxy resin for flame proofing plastics without release of toxic products during use. The materials are heated together in an oven, cast into a slab and granulated when cool. In addition may be added metal oxides chosen among copper, zinc, silver, iron, antimony, vanadium, tin, titanium and magnesium. Copper salts are preferred.

Cerny and Vivant (Rhone-Poulenc)[44] encapsulate red phosphorus of particle size below 200μm in a polymer which does not have a melting or softening point below 90°C and which has a molecular weight above 2000. Polycarbonates, polyamides, polyolefines, polytetrafluoroethylenes, silicones, polyimide-amides etc., are used. In addition up to 100% (of weight of red phosphorus) of oxides of copper, zinc, silver, iron, antimony, magnesium, vanadium, tin and titanium may be added.

Dany et al., (Hoechst AG)[45] stabilise red phosphorus with aluminium hydroxide and lead oxide in total quantity 0.1 to 6% w/w of red phosphorus, and with a ratio 0.5 to 2.0 Al_2O_3/PbO. Table 7 gives the effect of various compounds on the amount of phosphine (determined by using it to precipitate insoluble $P(HgCl)_3$ which was then oxidised with excess iodine; the excess determined by titration with sodium thiosulphate) and acidity (determined by titration with sodium hydroxide against phenolphthalein) produced when stored for 28d at 50°C over a saturated solution of ammonium sulphate (corresponding to a RH of 72%).

Cerny and Vivant (Rhone-Poulenc)[46] stabilise red phosphorus with a phenolformaldehyde polycondensate having a molar ratio of formaldehyde to phenol between 0.7 and 0.9, and a molecular weight between 120 and 1500. In addition may be added metal oxides chosen among copper, zinc, silver, iron, antimony, vanadium, tin, titanium and magnesium.

Theysohn and Reimann (BASF)[47] claim a flame retardant for nylon consisting of red phosphorus and melamine cyanurate. Specifically: 100 parts nylon, 10-100 parts inorganic filler, 1-12 parts red phosphorus, 1-40 parts melamine cyanurate. Optionally the phosphorus may be stabilised before coating with the melamine cyanurate.

Staendeke et al (Hoechst)[48] stabilise red phosphorus with a combination of aluminium hydroxide (0.01 to 3% by weight of red phosphorus) and a hardened epoxy resin (0.09 to 4.99% by weight of red phosphorus). The hardened epoxy resin system has an epoxide equivalent weight of about 170 to 500. Specific examples include an epoxy-phenolic resin and an epoxide which is the reaction product of epichlorohydrin and 2,2-bis-4(hydroxyphenyl)-propane (bisphenol A). An water soluble aluminium salt and an aqueous or alcoholic solution or dispersion of an epoxide resin and of a hardener is added to an aqueous suspension of red phosphorus, the pH adjusted to 5 to 9, the mixture stirred for 1 to 3 hours at 20° to 90°C. The aluminium hydroxide precipitates, the epoxide hardens, and the solid is filtered off and dried at elevated temperature. Hardeners include a water soluble polyamine or a water emulsifiable polyaminoamide

Example	MgO	Al_2O_3	CuO	PbO	H_3PO_4	PH_3	Filtration Period (min)	H_2O Content (wt%)
	(g/100g P)				(mg/g P)			
1	0.6	-	-	-	107.6	0.73	55	17.7
2	-	0.6	-	-	66.3	0.18	<70	22.1
3	-	-	0.815	-	220.4	0.04	58	18.8
4	-	-	-	0.925	122.5	1.34	51	17.0
5	0.6	-	0.815	-	154.3	0.03	54	19.1
6	0.6	-	-	0.925	110.7	0.77	50	17.8
7	-	0.6	0.815	-	159.9	0.01	<70	22.3
8a	-	0.6	-	0.925	63.4	0.08	15	14.4
8b	-	2.0	-	1.850	57.1	0.05	19	16.8
8c	-	4.0	-	3.700	52.4	0.05	30	17.9

1 (Comparative example)	30 weight % aqueous solution of 181g $MgCl_2.6H_2O$ added to 6kg red phosphorus. NaOH added to adjust *pH* to 9. Suspension stirred for 1 at 80°C and filtered. Filter cake dried within 15h at 110°C under nitrogen.
2 (Comparative example)	As example 1, but 40 weight % aqueous solution of 235.3g $Al_2(SO_4)_3.18H_2O$ (corresponding to 0.6 part by weight Al_2O_3 per 100 parts phosphorus) in place of magnesium chloride
3 (Comparative example)	As example 1, but 20 weight % aqueous solution of 153.5g $CuSO_4.5H_2O$ (corresponding to 0.815 part by weight CuO per 100 parts by weight phosphorus) in place of magnesium chloride.
4 (Comparative example)	As example 1, but 40 weight % aqueous solution of 94.3g $Pb(CH_3COO)_2.3H_2O$ (corresponding to 0.925 part by weight PbO per 100 parts by weight phosphorus) in place of magnesium chloride.
5 (Comparative example)	As example 1, but 20 weight % aqueous solution of 153.5g $CuSO_4.5H_2O$ (corresponding to 0.815 part by weight CuO per 100 parts by weight phosphorus) also added.
6 (Comparative example)	As first example, but 40 weight % aqueous solution of 94.3g $Pb(CH_3COO)_2.3H_2O$ (corresponding to 0.925 part by weight PbO per 100 parts by weight phosphorus) also added.
7 (Comparative example)	As first example, but 40weight % aqueous solution 235.3g $Al_2(SO_4)_3.18H_2O$ and 20 weight % aqueous solution of 153.5g $CuSO_4.5H_2O$ (corresponding to 0.815 part by weight CuO and 0.6 part by weight Al_2O_3 per 100 parts phosphorus) in place of magnesium chloride
8 (Invention) 8a 8b 8c	As first example but 40 weight % aqueous solutions of Al and Pb salts in place of magnesium chloride: 235g $Al_2(SO_4)_3.18H_2O$ and 94.3g $Pb(CH_3COO)_2.3H_2O$ (corresponding to 0.6 part by weight Al_2O_3 and 0.925 part by weight PbO per 100 parts by weight phosphorus) 784.4g $Al_2(SO_4)_3.18H_2O$ and 188.7g $Pb(CH_3COO)_2.3H_2O$ (corresponding to 1.85 part by weight Al_2O_3 and 2.0 part by weight PbO per 100 parts by weight phosphorus) 1568.7g $Al_2(SO_4)_3.18H_2O$ and 377.3g $Pb(CH_3COO)_2.3H_2O$ (corresponding to 4.0 part by weight Al_2O_3 and 3.7 part by weight PbO per 100 parts by weight phosphorus)

Table 7. Effect of Additives of Phosphine and Acid Production (Dany et al)

Largman et al., (Allied Corporation)[49] use red phosphorus (Exolit, a stabilised red phosphorus flame retardant manufactured by American Hoechst Corporation) and a metal iodide (specifically potassium iodide) as phosphine suppressing agent. The phosphine evolution of a poly(ethylene terephthalate) moulding composition containing 4% red phosphorus is reduced to 0.3ppm at the die and 1.0ppm in storage by the addition of 0.6% potassium iodide (Table 8).

additive (%)		PH_3 concentration (ppm)	
KI	Exolit	Die	Storage
0.6	4.0	0.3	1.0
0.35	4.0	1.5	1.0
0	4.0	2.0	25.0

Table 8. Phosphine evolution from PET during processing (Largman et al.)

Largman (Allied Corporation)[50] uses copper compounds to suppress phosphine evolution from fire retarded polymers containing red phosphorus. Copper(II) chloride, copper(II) acetate, copper(I) acetate, copper metal, and complexes of copper(I) or copper(II) with ligands containing one or more nitrogen atoms are considered. Copper(I) chloride is considered to be particularly effective. The polymer, red phosphorus and phosphine suppressant are blended together prior to extrusion. Pellets were stored in a sealed vessel for 18 hours and the atmosphere above them analysed for phosphine, and the results compared with the concentrations found at the extrusion dye (Tables 9 and 10).

% red phosphorus	PH_3 suppressant	% DARCO 6-60	PH_3 at pelletiser (ppm)	PH_3 in sealed vessel (ppm)
4	1.0 CuEDTA	0	-	0
4	1.0 Cu(ac)$_2$	0	0	0
4	1.0 Cu(cap)	0	1	0
4	1.0 CuCl$_2$	0	0	0
4	1.0 Cu	0	1	1.8
4	0.5 CuCl	0	0.1	0
4	0.5 CuCl	0.7	0	0
4	0.5 CuCl$_2$	0	0	0.4
4	0.5 CuCl$_2$	0.7	0.7	1.0
4	0.4 Cu(ac)$_2$	0	0	0.4
4	0.4 Cu(ac)$_2$	0.7	0	0.4
4	0.5 Cu	0.7	0.5	0.2
4	-	0.7	0.5	0.2
4	0.5 CuCl$_2$	0	2.0	9
4	0.5 CuCl$_2$	0.7	0.1	5
4	0.4 CuCl$_2$	0	0	35

4	0.4 CuCl$_2$	0.7	0.2	4.5
4	0.3 Cu(ac)$_2$	0	0	35
4	0.3 Cu(ac)$_2$	0.7	1	10
4	0.3 CuCl	0	0	7
4	0.3 CuCl	0.7	0	1.8
4	0.5 Cu	0	0	0.3
4	0.5 CuCl	0	0	0.3
4 Exo	0.5 CuCl	0.7	1.5	8
4 Exo	1.5 Cu phthal	-	1.5	8

Darco 6-60: activated charcoal manufactured by MCI Mfg.

Exo: Exolite – 92% red phosphorus manufactured by American Hoechst Corporation

ac: acetate; cap: caprolactam; phthal: phthalocyanine

Table 9.   Phosphine evolution from nylon based compositions (Largman)

% red phosphorus	PH$_3$ additive	DARCO C (%)	PH$_3$ at pelletiser ppm
4	1.0 SnO$_2$	0	0.8
4	1.0 ZnO	0	3
4	1.0 PbO	0	0.6
4	1.0 PbO$_2$	0	1
4	1.0 Pb(ac)2	0	0.8
4	1.0 Al(isopropoxide)		0
4	0.5 PbO	0	5.0
4	0.5 PbO2	0.7	3.0
4	0.5 ZnCl$_2$	0	7.5
4	0.5 ZnCl$_2$	0.7	5.0
4	0.5 Zn(ac)$_2$	0	2.0
4	0.5 Zn(ac)$_2$	0.7	5.0
4	0.5 AlBr$_3$	0	-
4	1.0 CuO	0	0
4	0.5 CuO	0	0
4	0.33 CuO	0	2

Table 10.   Phosphine evolution from nylon 6B (Largman)

Albanesi and Rinaldi (Saffa)[51] use red phosphorus encapsulated in a modified melaminic resin as a flame retardant for paper. The cationised melaminic resin is prepared from formaldehyde, triethanolamine, melamine and a monohydroxyl aliphatic alcohol having less than 5 carbon atoms.

Twardowska (Erco Industries)[52] considers that aluminium oxide gives a product that is difficult to filter and dry and proposes the use of up to 2% titanium dioxide or titanium phosphate as stabilising agents. Titanium appears to have an effect superior to that of aluminium, and red phosphorus stabilised with it can be heated to 300°C without evolution of water. The materials are precipitated onto the surface of the particles from aqueous solution. The effect of titanium and aluminium compounds on the amount of acid formed from red phosphorus is shown in Figures 1a) and 1b) below.

The effect of titanium mixed with the hydroxides of other metals is shown in Figure 1c) and the effect of the pH at which the titanium dioxide is precipitated is given in Figure 1d).
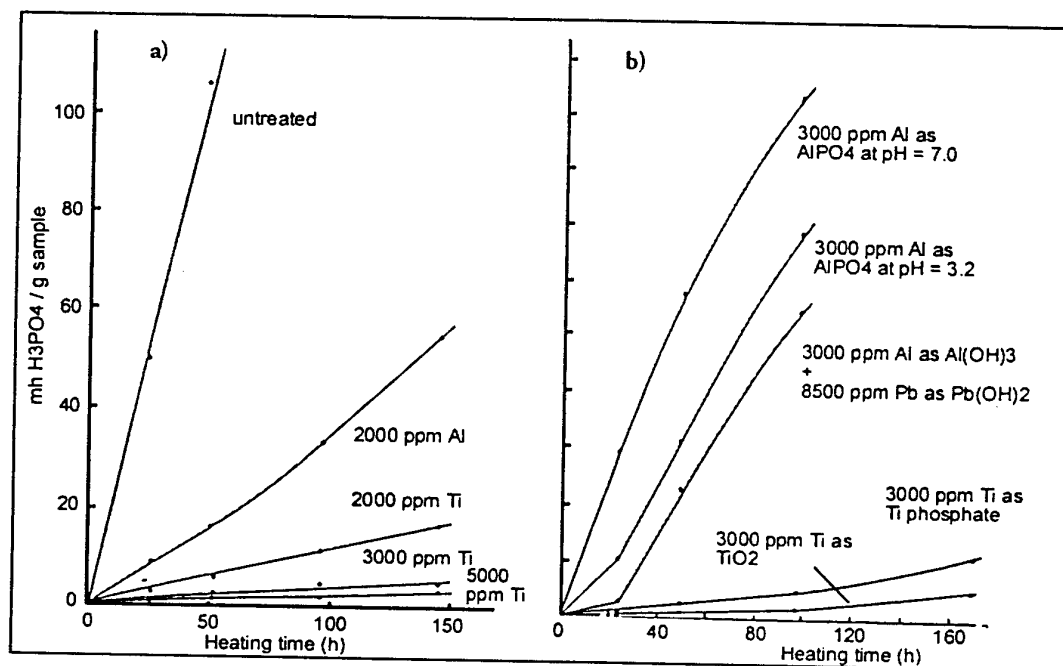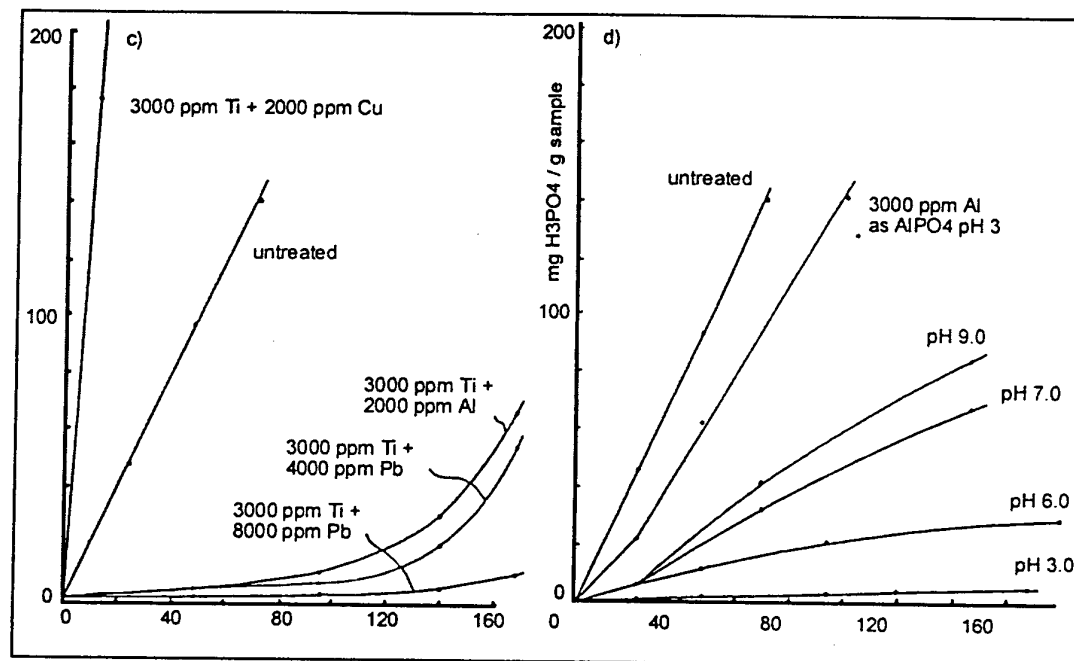
Fig 1   The Effect of Impurities on the Formation of Acid
(Twardowska)

Twardowska [53] later claims that a combination of titanium dioxide and titanium phosphate (0.05 – 1.0% measured as Ti) with an organic resin such as epoxy resin, melamine-formaldehyde resin, or urea-formaldehyde resin (0.1 – 5.0%) gives a particularly well stabilised product. The particle size of red phosphorus is at the greatest 0.2mm, and preferably 0.01-0.15mm. Both oxidation of the phosphorus and the evolution of phosphine are reduced. The process involves adding a titanium compound to a slurry of red phosphorus (in water) and adjusting the pH to between 2 and 4 to allow the titanium dioxide or titanium phosphate to precipitate onto the phosphorus; then adding an aqueous solution or emulsion of unhardened resin which is made to precipitate by hardening. The treated particles are then separated.

Albanesi and Rinaldi (Saffa)[54] encapsulate red phosphorus for use as a flame retardant by preparing a dispersion in an aqueous solution of a melamine condensate (consisting of melamine, formaldehyde, triethanolamine and a monohydroxyl alcohol having up to 5 carbon atoms) cationised with a mineral acid, heating it under stirring to precipitate the condensate onto the red phosphorus in the form of a partly cross-linked melamine resin, and then completing the cross-linking in the final dehydration step at 80° to 130°C.

Marciandi and Relvini (Montedison)[55] claim a self-extinguishing polymeric composition consisting of an olefinic polymer and 1-5% red phosphorus, 0-10% of a substance capable of forming free ammonia by thermal decomposition, and from 0.3% to 2% of a free radical promoter selected from 3,4-dimethyl-3,4-diphenylhexane and 2,3-dimethyl-2,3-diphenylbutane. The compounds (which should not decompose below the temperature of processing) producing ammonia include, amongst others, organic and inorganic ammonium salts, amino-triazines (including melamine). Preferred compounds are ammonium polyphosphates $(NH_4)_{n+2}P_nP_{3n+1}$ which for $n>20$ approximate to ammonium metaphosphate $(NH_4PO_3)_n$.

Rinaldi and Megler (Saffa)[56] stabilise red phosphorus by encapsulating it in a modified cationised melamine resin. An aqueous melamine precondensate is prepared by reacting melamine, formaldehyde, triethanolamine and a monohydroxyl alcohol, then cationising it with a mineral acid until the pH is 7 to 7.5. The red phosphorus is dispersed in this solution and heated to 100°C to precipitate a partly cross-linked polymer. Cross-linking is completed at 100°C under an inert atmosphere. The encapsulated red phosphorus is then mixed with thermoplastic polymers for extrusion.

Hirobe (Kanegafuchi)[57] coats red phosphorus with a thermosetting resin – modified polyethylene terephthalate having a crystallisation temperature of not more than 120°C. Talc is added as a preferred filler.

Itoh et al., (Shin-Etsu)[58] use 1 to 20 parts red phosphorus and an excess (5 to 200 parts) aluminium hydroxide or magnesium hydroxide.

Nielinger at al., (Bayer)[59] stabilise red phosphorus against oxidation with cadmium salts (specifically cadmium oxalate or cadmium adipate) of carboxylic acids to produce a material suitable for use as a flameproofing agent for polyamide moulding compositions Table 11). Curiously, they claim that the materials can be added to the red phosphorus as a powder, precipitated onto it, or added to the melt. They report the amounts of phosphine produced, and the pH of the aqueous extract of the phosphorus.

Additive		as CdO	PH_3	Extract	
	(%)	(%)	(mg)	pH	P (mg)
cadmium adipate	4	2	0.4	5.2	0.2
	2	1	1.1	5.1	0.4
	1	0.5	1.5	5.1	0.4
	0.5	0.25	1.6	5.0	0.6
cadmium oxalate	3.13	2	1.6	4.6	3.1
	1.58	1	1.0	4.3	1.3
	0.78	0.5	1.2	4.0	1.3
cadmium phthalate	2.1	1	1.2	5.2	0.3
cadmium stearate	5.3		0.3	5.8	0.9
cadmium oxide	2	2	nd	6.3	0.8
	1	1	nd	5.9	2.0
	0.5	0.5	1	3.9	6.3
copper(II) oxide	1		nd	2.7	26

Table 11. Effect of cadmium salts on phosphine and acidity suppression (Nielinger et al)

Giroud-Abel (Rhone-Poulenc)[60] uses mixtures of lanthanide or yttrium compounds to reduce the emission of phosphine from red phosphorus. The compounds include salts of monocarboxylic acids having from 2 to 30 carbon atoms, or aliphatic dicarboxylic acids having 3 to 30 carbon atoms which are either saturated, or contain one or more double bonds which may be substituted with halogen atoms, hydroxyl groups, alkoxy groups, mercapto groups, or phenyl, phenoxy, naphthyl or cyclohexyl groups.

Nakamura and Itoh (Shin-Etsu)[61] produce a flame retardant for vulcanised rubber containing red phosphorus and aluminium hydroxide or magnesium hydroxide, zinc carbonate and manganese carbonate.

Alfonso et al., (Consiglio Nazionale)[62] microencapsulate red phosphorus in a synthetic resin, preferably a melamine resin, for use as a flame retardant for articles formed from anionically polymerised ε-caprolactam.

Lee (General Electric)[63] uses red phosphorus or hydrated alumina or both in the presence of a halogenated hydrocarbon.

Seino (Shin-Etsu)[64] uses small quantities 0.1 to 5.0 parts) of red phosphorus in the presence of an excess (5 to 100 parts) of aluminium hydroxide.

Nielinger et al., (Bayer)[65] stabilise red phosphorus with 1 to 30 weight % zinc fluoride which is then incorporated into a polyamide moulding composition as flame retardant.

Albanesi and Rinaldo (Saffa)[66] stabilise red phosphorus for use as flame retardants by encapsulating the particles with 0.2 to 4 weight % aluminium hydroxide covered in turn with 0.8 to 8 weight % of a cross-linked polycondensation resin formed by urea-melamine-formaldehyde. An iron content of less than 180ppm is mentioned. A solution of aluminium sulphate is added to a suspension of red phosphorus and the pH is adjusted to 8 to 9 to precipitate the aluminium hydroxide. The coated grains are separated, washed with water, dispersed in water and a solution of a pre-condensed resin of urea formaldehyde modified with melamine is added. The temperature is maintained at 80°C, a solution of ammonium chloride added, heated to 90°-100°C to cross-link the resin. The product is dried, preferably *in vacuo* at 100°C

Staendeke and Thümmler (Hoechst)[67] stabilise red phosphorus (particle size 2mm maximum) with a coating of hydrated tin oxide. They considered earlier inventions required too much stabiliser. Their results for the daily production of phosphine and water soluble acidic compounds are given in Table 12.

Stabiliser		Storage Conditions			
		65°C/100% RH		80°C/100% RH	
Type	Conc.	mg PH₃/day	mg acid/day	mg PH₃/day	mg acid/day
Al(OH)₃	2.5	0.36	2.3	1.3	11.8
Al(OH)₃	4.7	0.24	2.2	0.87	8.7
Al(OH)₃	6.9	0.22	2.8	0.95	5.5
Al(OH)₃	9.5	0.32	3.2	1.0	8.4
Zn(OH)₂	2.9	0.21	1.3	1.1	7.0
Zn(OH)₂	6.3	0.33	1.6	1.4	6.8
Zn(OH)₂	9.3	0.31	1.6	1.5	7.2
Zn(OH)₂	11.3	0.30	2.0	2.0	9.3
SnO.H₂O	0.9	1.00	7.2	1.8	13.3
SnO.H₂O	1.7	0.30	2.3	0.82	5.4
SnO.H₂O	2.5	0.25	0.63	0.79	3.6
SnO.H₂O	3.3	0.21	<0.05	0.55	2.6
SnO.H₂O	4.4	0.15	<0.05	0.28	0.21
SnO.H₂O	5.7	0.15	<0.05	0.25	0.10
SnO.H₂O	6.4	0.14	<0.05	0.25	0.08
SnO.H₂O	7.4	0.12	<0.05	0.25	<0.05
SnO.H₂O	8.5	0.12	<0.05	0.25	<0.05

Table 12.   Stabilisation of Phosphorus (Staendeke and Thümmler)

Silver (Hercules)[68] uses red phosphorus as part of a polymerisation catalyst system.

Scarso[69] stabilises red phosphorus by encapsulating its particles in a synthetic resin of apparently undisclosed composition.

Staendeke et al., (Hoechst)[70] stabilise red phosphorus with a sparingly soluble, or insoluble metal hydroxide (aluminium, silicon, chromium, manganese, zinc, germanium, zirconium, niobium, cadmium, tin, lead, bismuth and cerium) and a melamine/formaldehyde polycondensation product. They use 1.1 to 25 weight % (based on red phosphorus) of the hydroxide on its own, or a mixture of 0.1 to 5% hydroxide and 1 to 20% condensation product. The polycondensation product may be prepared by adjusting the pH of an aqueous suspension of red phosphorus to 4 to 9, adding the preliminary condensation product, heating to 40° to 100°C for 0.5 to 3h and allowing the preliminary condensation product to harden. The treated particles of red phosphorus are dried at 80° to 120°C in a stream of nitrogen.

Sakon et al., (Rinkagaku) [71,72] claim that red phosphorus formed from white phosphorus with no pulverising presents a completely different shape and has a superior combination of

24

chemical and physical properties particularly with regard to corrosion resistance, moisture resistance, mechanical strength and dielectric properties. Coating with thermosetting resin and/or the hydroxides of aluminium and/or zinc greatly improve its stability. They produce the red phosphorus by converting a maximum of 70% at 250° to 600°C under an inert atmosphere. Magnesium hydroxide or titanium hydroxide may also be used as inorganic stabilisers. The material may be incorporated to 0.1 to 30 parts by weight into a thermoplastic resins such as polyamide, polyester, polyether, polycarbonate, polystyrene, polyurethane or polyacrylate

Alder and McCallum (UK MoD)[73] find radical inhibitors effective, preferably 4-(p-nitrophenyl-azo)-1-naphthol and phenolic, quinolic and quinonic compounds and their sulphur analogues which are mono and fused bi- and tri-cyclic compounds bearing two substituents in such combinations that:

1st substituent	2nd substituent
hydroxy-, mercapto-	hydrogen, hydroxo- mercapto-
oxo-, thioxo-	oxo-, thioxo-

The 2nd substituent is located on the same ring as, and *ortho* or *para* to, the first. About 1% stabiliser is required, and it may be added as a dry powder or in a suitable organic solvent.

Samples weighing 1g consisting of 94% w/w red phosphorus (ex works or oven dried for 3-4 hours at 70°C), 5% binder (polyvinylbutyral) and 1% test additive were stored at 50°C for 30h in an atmosphere of high humidity (>80% in the presence of water). The phosphine concentrations in the atmosphere are given in Table 13:

	Additive	PH_3 Concentration Relative Response	
		Oven dried	Ex works
Blank	none	100	100
Invention	1,4-naphthaquinone	-	0; 1.3
	p-benzoquinone	-	0.4; 4.0; 12.5
	phenanthraquinone	-	15.5; 25
	p-nitrophenol	-	26.7; 44.4; 38.8
	chloranil (tetrachloro-1,4-benzoquinone)	-	37.8; 40
	quinol	38	46
	4-*tert*-butylcatachol	20	48.8
	4-(*p*-nitrophenylazo)-1-naphthol	-	26.7; 66.7; 47.5
	phenol	-	42.7; 76.7; 83.8
Reference	sodium diethyldithiocarbamate	168	115
	sodium dimethylthiocarbamate	200	88.5
	ammonium tetramethyldithiocarbamate	100	100
	resorcinol	45	100

	m-cresol	-	73.3; 82.2; 81.3
	p-cresol	-	60.0; 68.9; 87.5
	2-hydroxybiphenyl	-	60.0; 55.6; 72.5
	3-dimethylaminophenol	-	72.0; 70.0; 76.3
	1-(2-pyridylazo)-2-naphthol	-	56.0; 71.1; 88.8
	4-(p-nitrophenylazo)resorcinol	-	64.0; 90.0; 80.0
	resorcinol (sodium salt)	-	61.1; 64.4; 56.3
	anthraquinone	-	108; 120
Comparison	Ex works material, no additive	244	

Table 13. Atmospheric Concentrations of Phosphine (Alder and McCallum)

Chilles at al.,[74] (Allbright and Wilson) claim that the evolution of phosphine from red phosphorus is reduced by means of alicyclic compounds having at least one carbon double bond in the alpha-position relative to an electron withdrawing group (such as aldehyde, ketone, carboxylic acid, carboxylic anhydride, carboxylic ester or their thio analogues) and proposed *trans*-cinnamaldehyde as being particularly suitable. Their invention is intended to stabilise master batches of red phosphorus and polymeric materials (such as polyethylene, polystyrene, styrene/butadiene copolymers etc.,) for storage pending further processing by the customer. They mixed equal masses of red phosphorus and the stabiliser and stored the mixture in glass flasks at approximately 70% relative humidity (saturated mixed solution of ammonium chloride and potassium nitrate). The phosphine content of the atmosphere was measured by gas chromatography (flame photometric detector) after 14 days. The results are reported (values relative to the unstabilised sample) in Table 14:

additive		additive	
- (control)	100	2-nitro-cinnamaldehyde	1.8
cinnamamide	64.7	citral	1.4
methyl methacrylate	54.9	cinnamyl chloride	0.56
cinnamonitrile	19.6	*trans*-2-methyl-2-butenal	0.56
trans, trans-benzylidineacetone	14.6	*trans*-2-ethyl-2-butenal	0.44
4-phenyl-3-butene-2-one	9.0	3-methyl-2-butenal	0.34
cinnamoyl chloride	5.8	*trans*-cinnamaldehyde	0.22
α-amylcinnamaldehyde	4.5	2,4-hexadienal	0.06
trans-3-pentene-2-one	4.4	crotonaldehyde	0
α-methyl-*trans*-cinnamaldehyde	3.6	α-chlorocinnamaldehyde	0

Table 14. Atmospheric Phosphine Concentration (Chilles et al)

7.5g suppressant was mixed with 150g red phosphorus and 150g low density polyethylene added. The mixture was stirred and extruded in a single cavity extruder. The master batch was pelletised and a 1g sample was placed in a 250ml flask at 70% RH. The phosphine produced was 3.7% of that from the red phosphorus control.

Bonin and LeBlanc (Rhone-Poulenc)[75] stabilise polyamide based molding compositions containing red phosphorus with at least one lanthanide compound (specifically the stearate, oxide or chloride of lanthanum(III) or cerium(III), talc and zinc sulphide and/or zinc oxide. The particle size of the red phosphorus is below 200μm. They also claim[76] for similar compositions the use of a hydrotalcite stabiliser of the general formula $Mg_{1-a}Al_a(OH)_2H_2O$ and expand the description of the metal salt to any compound of the entire lanthanide series.

Reimann at al., (BASF)[77] use zinc oxide, cadmium oxide or a mixture in a thermoplastic moulding composition red phosphorus in the presence of ε-caprolactam and sebacic acid

Schreiber and Saur (Gurit-Essex)[78] use red phosphorus as one of many alternatives (including aluminium oxide, magnesium hydroxide, inorganic salts of phosphorus oxyacids and boric acid)

Sakon et al., (Rinkagaku)[79] convert yellow phosphorus into red phosphorus particles and coat it with at least one of a resin and aluminium hydroxide or zinc hydroxide The resin may be a thermosetting resin such as phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin, furfural alcohol-formaldehyde resin, aniline-formaldehyde resin and polyhydric alcohol-polybasic acid resin The resin may be a polyolefin resin such as polyethylene, polypropylene, ethylene-acrylate copolymer, ethylene-vinyl acetate copolymer, polybutene, cross-linked polypropylene, ethylene-propylene rubber, poly-4-methylpentene-1, ethylene-butene copolymer butyl rubber, styrene-butadiene rubber or mixtures of these. Basic magnesium carbonate may also be used as a filler.

Steiert at al., (BASF)[80, 81] phlegmatise red phosphorus of particle size up to 2mm with 0.05 to 5% polyurethane or polyester-polyurethane. Phosphine suppression is also claimed.

Staendeke and Thümmler (Hoechst)[82] stabilise red phosphorus with 4 to 20% hydrated tin oxide.
Lee and Gim[83] use red phosphorus as flame retardant in polyphenylene ether compositions, but do not comment on the stability.

Williams (Bip)[84] prepares an injection mouldable polyamide composition in two steps. A magnesium compound (mixtures of magnesium hydroxide and magnesium carbonate) and an ungrafted copolymer of ethylene and vinyl acetate are blended to form a masterbatch. This mixture is compounded with a thermoplastic polyamide, red phosphorus (1-15% by weight) and glass fibre reinforcement.

Kober at al., (Freudenberg)[85, 86] prepare a flame-resistant cover for flexible circuit boards by treating an insulating film of a non-woven polymer fabric with a flame-resistant, halogen free polymeric adhesive. The adhesive consists of an aqueous mixture of a copolymerisate of acrylic acid esters and styrene, and an aminoplastic or phenolic precondensate to which has been added a mixture of fine particle red phosphorus and fine particle ammonium polyphosphate.

Chilles et al., (Albright and Wilson)[87] reduce the rate of evolution of phosphine from red phosphorus with acyclic, aliphatic compounds having at least one carbon-to-carbon double bond in the alpha position relative to an electron withdrawing group. A preferred compound is

trans-cinnamaldehyde. The claim covers 0.1 to 100% additive!. Additive could also be crotonaldehyde, α-chlorocinnamaldehyde, cinnamoyl chloride, 2-nitrocinnamaldehyde, α-amylcinnamaldehyde, α-methyl-*trans*-cinnamaldehyde, 2,4-hexadienal, 3-methyl-2-butenal, and *trans*-3-penten-2-one.

Yagawa et al., (Bridgestone)[88] use a maximum of 24% red phosphorus as flame retardant for rubbers. Aluminium hydroxide (6 to 30 weight % of the rubber) may also be added.

Baierweck et al., (BASF)[89] use 1 to 20% by weight red phosphorus in plastics containing various dyes such as copper phthalocyanine, manganese violet. No comment is made on stability.

Gareiss and Baierweck (BASF)[90] produce flame proofed thermoplastic polyamide molding materials containing 1-30% red phosphorus, 1-15% mono- or di-phenolic compound and fillers.

Kao et al., (ITRI)[91] use red phosphorus in polycarbonate plastics.

Imahashi (Kyowa)[92] describes a flame retardant consisting of 2 to 750 parts by weight red phosphorus, 100 parts by weight magnesium hydroxide and 0.2 to 250 parts by weight of an epoxy resin. The magnesium hydroxide has a particle size in the range 0.2 to 5μm, and the red phosphorus 1 to 50μm.

Zeltner et al., (BASF)[93] use red phosphorus as a flame retardant in polyphenylene ethers and polystyrene. No comment is made about stability.

Aoki et al., (Mitsubishi)[94] use red phosphorus and magnesium hydroxide or aluminium hydroxide flame retardants.

Bonin and LeBlanc (Rhone-Poulenc)[95] propose a flame retardant for polyamide compositions suitable for the electrical industry. It consists of red phosphorus and a corrosion/migration-reducing ingredient for example zinc oxide, zinc sulphide, and an oxygen containing salt such as zinc borate.

Lee and Gim (GEC)[96] use red phosphorus as one of several preferred elements in a flame retardant for flexibilised polyphenylene ether compositions.

Keough et al., (Union Carbide)[97] use red phosphorus in the presence of about 0.5 to 5 parts zinc oxide as flame retardant in a plastic copolymer of ethylene and an unsaturated ester copolymer.

Okisaki et al., (Tosoh)[98] make a flame-retardant from a resin (polyester, polyamide), a heat expandable graphite and red phosphorus. The red phosphorus may be treated with thermosetting resins or inorganic compounds.

Brynseels and Homann (Shell Oil Company, USA)[99] incorporate red phosphorus into epoxy resins but do not claim any method of stabilisation.

Ueda (Sumitomo)[100] uses red phosphorus coated with aluminium hydroxide and then with a phenol resin. The red phosphorus content in the flame retardant is 60 to 95%. The epoxy resin contains an ion trapping agent $BiO_x(OH)_y(NO_3)_z$ or $Mg_4.3Al_2(OH)_{12}.6CO_3.3.5H_2O$ or a combination of these to minimise migration of corrosive ions to the surface of metallic electrical components.

Among the patents on smoke compositions:

Palmer and Ball (Albright and Wilson)[101] prepare a pyrotechnic composition suitable for smoke production. They use red phosphorus coated with a liquid unsaturated organic compound such as vinyl hydrocarbons, hydrocarbon substituted ethylenes, unsaturated carboxylic acids, or a polymeric resin formed by autoxidation of such compounds. As oxidant they use carbonates, alkali metal sulphates, alkaline earth sulphates, and oxalic acid or urea.

Seales (USA DoD)[102] proposes to render explosive compositions insensitive to water and water vapour by coating the ingredients with an organosilane capable of polymerising on contact with water or water vapour. As an example is given a red phosphorus, potassium chlorate, ground glass composition coated with γ-(β-aminoethyl)aminopropyltrimethoxysilane applied in a volatile solvent such as 1,1,2-trichloro-1,2,2-trifluoroethane. Other suitable materials are γ-aminopropyltriethoxysilane, methyltriethoxysilane, phenyltrichlorosilane, dimethyldichlorosilane, n-butyltrichlorosilane and methylphenyldichlorosilane. The reaction is:

$$R_{4-n}SiX_n + nH2O = R_{4-n}Si(OH)_n + nHX$$
$$R_{4-n}Si(OH)_n = polymer + H_2O$$
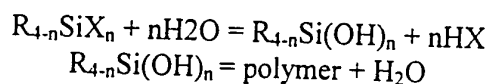
where: R is halogen, amino, alkoxy, aryloxy, and X is alkyl, aryl, aminoalkyl, aminoaryl, alkylamino, arylamino, alkoxy or aryloxy.

Liberman (DREV, Canada)[103] uses calcium carbonate as an acid absorber to reduce the acidity of oxidation products of red phosphorus in the following composition:

smoke producer	red phosphorus	55-80%
oxidising agent	sodium nitrate or ammonium nitrate	10-30%
metal fuel	aluminium or magnesium	5-10%
acid absorber	calcium carbonate	1-5%
synthetic rubber binder		1-8%
titanium alcoholate		1-4%

He comments that magnesium reacts with the water always present to produces hydrogen, and that it promotes the formation of phosphine from the red phosphorus. Zinc oxide used in other compositions has inadequate acid absorbing capacity. The titanium alcoholate (preferably titanium isopropoxide) reacts with water to form titanium hydroxide. No comment is made on the use of stabilised grades of red phosphorus.

2.4.4. Summary of literature

Red phosphorus has been treated for two different reasons. The first and older reason is to suppress the formation of flammable dust on handling. In other words, the treatment was to provide phlegmatisation. The second reason is to suppress the low temperature surface reaction with moist air to form phosphine and acid oxides, that is, to stabilise the phosphorus. Almost all the published information concerns the suppression of phosphine from compositions (pyrotechnic or plastics) containing red phosphorus. Little specific attention (other than the addition of calcium carbonate) has been paid to the formation of acidic surface contaminants, presumably because this is not a general problem in the plastics industry. However, many of the inorganic materials used as stabilisers are in fact basic. Only one reference was found (Breitshaft, Ref 22) to the desirability of using coatings which adhere well both to the red phosphorus and to the plastics matrix.

Several methods for the suppression of phosphine from compositions may be supposed on the basis of published information

- reduction of the reactivity of the phosphorus surface by treating it with metal compounds;
- reduction of the reactivity of the phosphorus surface by coating it with organic compounds;
- reduction of the reactivity of the phosphorus surface by treating it first with metal compounds and then with organic compounds;
- absorption of phosphine by reaction with constituents (phosphine traps) in the matrix.

Of these, the first three are stabilising processes, the last is not. These differences are not distinguished in the patent literature, and it is sometimes unclear whether certain organic materials are added to suppress phosphine, or whether their purpose is to modify the physical properties of the plastics matrix.

The various materials and combinations of them that have been claimed to be effective include:

Coating with an inorganic compound.
alkaline earth carbonate;
aluminium hydroxide;
aluminium hydroxide and lead oxide;
aluminium, magnesium, calcium or zinc salt of orthophosphoric acid, organo-orthophosphoric acid, organo-orthophosphonic acid or organo-orthophosphinic acid;
ammonium bisulphate;
ammonium metaphosphate;
cadmium adipate;
cadmium oxalate;
cadmium oxide;
cerium(III) stearate, oxide or chloride;
lanthanum(III) stearate, oxide or chloride;
magnesium hydroxide,

manganese carbonate;
tin oxide hydrated;
titanium dioxide;
titanium phosphate;
zinc carbonate;
zinc fluoride;
zinc sulphide;

Coating with an organic compound.
ε-caprolactam;
organosilane which polymerises in the presence of water;
polyvinyl, polyethylene, unsaturated carboxylic acids;
trioxane, caprolactam;
waxes, paraffins, chlorinated hydrocarbons;
melamine cyanurate;
melamine resin;
modified polyethylene terephthalate;
acyclic, aliphatic compounds having at least one carbon-to-carbon double bond in the alpha position relative to an electron withdrawing group. A preferred compound is *trans*-cinnamaldehyde;
radical inhibitors such as quinones;

Coating with an inorganic compound and an organic compound.
magnesium and aluminium hydroxides, coated with waxes or organosilicon compounds;
polyalkalenes and aluminium oxide;
orthophosphoric acid esters and polyester or polyamide;
organic compounds which carbonise after inflammation (polyacrylonitrile, melamine) and amidosulphonic acid or ammonium bisulphate;
phenol/aldehyde condensation resin and the oxide, hydroxide, carbonate, acetate, formate, phosphate or borate of an alkali metal, alkaline earth metal, zinc, cadmium, tin, lead, antimony, aluminium, copper, manganese, iron, cobalt or nickel;
thermosetting resin and hydrated aluminium oxide;
epoxy resin salts of copper, zinc, silver, iron, antimony, aluminium, copper, manganese, iron, cobalt, nickel;
phenol/formaldehyde resin with oxides of copper, zinc, silver, iron, antimony, vanadium, tin, titanium and magnesium;
aluminium hydroxide and hardened epoxy resin;
TiO_2 or Ti phosphate and an organic epoxide resin, a melamine-formaldehyde resin or a urea-formaldehyde resin;
Sparingly soluble, or insoluble metal hydroxide (Al, Si, Cr, Mn, Zn, Zr, Nb, Cd, Sn, Pb, Bi, Ce and a melamine/formaldehyde polycondensation product;
aluminium hydroxide and a hardened epoxy resin;

Adding a phosphine absorbent (phosphine trap)
molybdenum(V) oxide;
mercury(II) oxide;
silver nitrate;
mercury(II) chloride;

iron(III) chloride hexahydrate;
copper(II) oxide;
activated charcoal;
magnesium oxide;
aluminium oxide;
lead(II) oxide;
amidosulphonic acid;
ammonium bisulphate;
melamine;
copper(I) chloride;
copper(II) chloride;
copper(II) acetylacetonate;
potassium iodide;
organic and inorganic ammonium salts (compounds capable of producing ammonia);

The mechanisms by which many of these compounds could have an effect one way or another is unclear.

The inorganic compounds used directly onto the red phosphorus granules as stabilisers tend to be basic or amphoteric or can be components of pH buffers..

The more favoured organic compounds tend to contain nitrogen groups and are also somewhat basic.

Many of the materials used as phosphine traps are capable of complexing with phosphine but some, such as potassium iodide, are apparently not.

It seems reasonable to suggest that the use of phosphine traps in pyrotechnic formulations could be explored. It is noteworthy that plastics often contain additives of metals some of which are known to *promote* the reactivity of red phosphorus, and some of which are known to *reduce* it. These materials are often added as cross-linking agents, but probably also act as phosphine traps. It is of interest that in one report where the phosphine and acid formation are both reported, copper(II) oxide was found to suppress the phosphine, but to raise the acidity of the aqueous extract and the amount of phosphorus entering solution. It seems unwise, if it can be avoided, to introduce any element into a pyrotechnic composition which is suspected of accelerating the reaction of phosphorus, no matter how well the phosphorus is stabilised and coated. Copper seems to be particularly objectionable.

2.5.   Other Aspects of Phosphorus Chemistry

2.5.1.   Combustion

Phosphorus burns energetically in the presence of air to produce dense clouds of phosphorus oxides. White phosphorus is spontaneously flammable at room temperature, and red phosphorus ignites above about 260°C. *Phosphorus pentoxide* forms in an excess of air, *phosphorus trioxide is* present when the air supply is restricted:

$$4P + 5O_2 = P_4O_{10} \qquad \Delta H = -3010 \, kJ$$

$$4P + 3O_2 = P_4O_6 \qquad \Delta H = -2260 \text{ kJ}$$
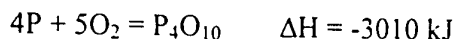
This combustion reaction occurs at the surface of the solid fuel, and therefore the rate at which it occurs (the rate of consumption of the fuel) is dictated primarily by the mean specific surface of the solid exposed to a suitably oxidising environment.

These materials are acid anhydrides and absorb water to form oxyacids of phosphorus, the exact products depending upon, amongst other factors, the amount of water available. For example:

$$P_4O_{10} + 6H_2O = 4H_3PO_4 \quad \Delta H = -343 \text{ kJ}$$
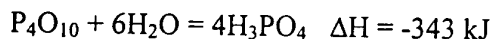
Although this reaction is very energetic, it should be remembered that complete combustion may not occur in the presence of plastics.

### 2.5.2. Phosphorus hydrides

Several hydrides have been reported.

The most common hydride is *phosphine* PH_3, a colourless gas with the odour of garlic, boiling at $-88°C$, solidifying at $-133.8°C$ which may be produced in sufficient quantities to be a problem when red phosphorus is exposed to moist air. Phosphine is sparingly soluble in water (0.26 volumes at 20°C) to give a neutral solution which slowly disproportionates into phosphorus, hydrogen and a sub-hydride of approximate formula P_2H (see van Wazer page 187). It is a strong reducing agent and will reduce many metal salts to free metal.

Phosphine is unstable with respect to its elements; the decomposition is first order but immeasurably slow at temperatures below several hundred degrees Celsius. The product is usually red phosphorus.

Pure phosphine is flammable, but not spontaneously so, in air with an ignition temperature of about 150°C. The higher hydride *diphosphine* P_2H_4, (a colourless liquid boiling at 56°C) however is spontaneously flammable and may be a contaminant of phosphine produced by the reaction of metal phosphides with water.

2.5.3. Other Indications of Reactivity

Ripley and Lipscomb[104] investigated the reactivity of red phosphorus from six commercial manufacturers with sulphuryl chloride in benzene.

$$2P + 3SO_2Cl_2 = 3SO_2 + 2PCl_3 \qquad \Delta H = -365 \text{ kJ}$$
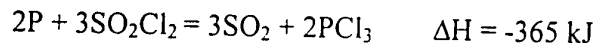
The reaction was followed by monitoring the rise in temperature, and was found to be pseudo first order. The surface of the particles was found to be more reactive than the bulk. Not surprisingly the reactivity was found to vary inversely with the particle size. The reactivity of samples from different manufacturers differed, but then a further experiment sampling production batches from a single manufacturer produced even greater variations. Overall, the stabilised phosphorus (containing aluminium oxide) was the least reactive. The density of

individual particles was found to vary from below 2.05 g/cc to about 2.23 g/cc. No single factor examined was adequate to account for the observed variation in reactivity.

3. Red Phosphorus Pyrotechnic Compositions

3.1. Introduction

Red phosphorus is normally manufactured as a granular powder which is pressed into a payload in the presence of burning rate modifiers and a suitable binder which desensitises it adequately for the pressing operation, and which should reduce the rate of the non-pyrotechnic reactions mentioned above. This pressing operation is necessary to provide a robust payload which can survive the environmental forces to which it is subjected on deployment, to provide control over the burning surface to improve the duration of the desired effect, and also to maximise the amount of smoke producing agent in the fixed volume available for the payload. Red phosphorus is not spontaneously flammable in air below about 260°C, and the munition must be furnished with an ignition system to ensure that the payload ignites adequately on deployment.

Because of the cost of requalifying new types of material and new sources of ingredients for use in UK military stores, pyrotechnic manufacturers tend to be conservative and use ingredients with which they are familiar rather than being more adventurous. Pyrotechnics use is a small fraction of the total use of red phosphorus and most grades were developed for purposes other than pyrotechnics. Discussions with manufacturers of red phosphorus reveal a willingness to work with the industry to develop grades of optimum properties, and this offers a good way forward.

The early work of Jakabcin and Silvester[13] on raw phosphorus has been reported earlier.

Pearce (CDE)[105] published a study on the stability in moist air at 25°C of compositions containing only red phosphorus and butyl rubber. The red phosphorus was obtained from Albright and Wilson and the following typical analysis was provided by the firm:

> copper < 10ppm;
> iron 0.15% as Fe_2O_3;
> aluminium 0.10% as Al_2O_3

The reaction of phosphorus was followed by measuring the gain in weight of samples (Table 15) stored for up to 6 weeks at relative humidities of 45%, 70% and 90%. No measurements of phosphine evolution were made.

The results are not surprising in general. The addition of oil had no effect, and the reaction rate increased as the relative humidity increased. Coating with binders reduced the rate with butadiene-styrene rubber and polyvinyl butyral performing better than butyl rubber, This was attributed to the better coating achievable with the first two which are soluble in dichloromethane whereas butyl rubber merely swells to form a very viscous gel.

The effect of several additives considered to be likely impurities or contaminants or possible additional ingredients was studied at 80% RH. Only copper showed a marked detrimental effect and increased the rate of weight gain considerably. Surprisingly, perhaps, manganese (as manganese dioxide or as manganese sulphate) decreased the rate.

Attempts were made to counter the effect of copper with compounds known to be successful in inhibiting the oxidation of rubber which is also catalysed by traces of copper. These were successful and reductions by a factor of ten were achieved with materials such as N,N'-dioctyl *p*-phenylene diamine (UOP 88).

No.	Red Phosphorus		Additive or Contaminant		Binder	
	form	%		%		%
1	dry	100	--		--	
2	oiled	100	--		--	
3	oiled	95	--		butyl rubber	5
4	oiled	97	--		butadiene styrene rubber	3
5	dry	95	--		polyvinyl butyral	5
6	dry	99	boron	1	-	
7	dry	99.8	iron	0.2	-	
8	dry	99.8	zinc	0.2	-	
9	dry	99.8	aluminium	0.2	-	
10	dry	99.8	manganese dioxide	0.2	-	
11	dry	99.8	manganese sulphate	0.2	-	
12	dry	99.8	lead(II,IV) oxide	0.2	-	
13	dry	99.8	copper(II) oxide	0.2	-	
14	dry	99	anti-oxidant Santowhite	1	-	
15	dry	99	anti-oxidant UOP88	1	-	
16	dry	99	copper deactivator, regular grade	1	-	
17	oiled	94	copper deactivator, grade UOP88	1	butyl rubber	5
18	oiled	94	copper deactivator, regular grade	1	butyl rubber	5
19	oiled	96	copper deactivator, grade UOP88	1	butadiene styrene rubber	3
20	oiled	96	copper deactivator, regular grade	1	butadiene styrene rubber	3
21	oiled	95	--		butyl rubber	5

Table 15   Samples for Stability Testing (Pearce)

The results showing the increase in weight of red phosphorus powder in humid air alone and in the presence of traces of copper(II) oxide and manganese(IV) oxide are shown in Figure 2 below. Also shown are the difference between red phosphorus powder and pellets containing anti-oxidant. The overwhelming effect is that of available surface area which is much decreased by pelleting. The effect of the antioxidant obscures the small improvement that Intol rubber shows over Butyl rubber in its absence.
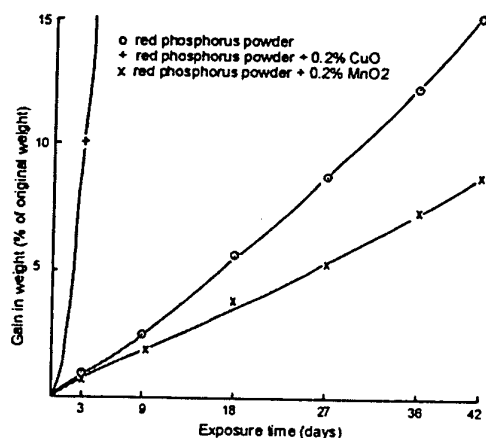
Effect of Additives on Red Phosphorus
(80% RH and 25°C)
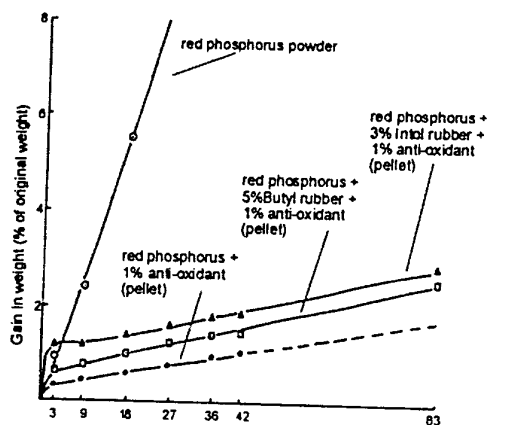
Effect of Anti-Oxidant on Red Phosphorus
(80% RH and 25°C)

Fig 2 Effect of Additives and Binders on the Formation of Acid
(Pearce)

Robertson and Glyde[106] studied the effect of coating red phosphorus to reduce the emission of phosphine from composition SR622 (oiled red phosphorus, anhydrous calcium sulphate, oxalic acid dihydrate) used in Marker Marine. The most significant improvement was the removal of the small quantity of oxalic acid (used as a blowing agent) and its associated water (see Table 15).

Compositions containing LOCC (linseed oil, coated and cured) phosphorus (Albright and Wilson to TS50181) were more stable than compositions containing phosphorus, amorphous, oiled (Albright and Wilson to CS5390A) coated with 5% polyvinylbutyral and the latter was more stable than composition containing uncoated phosphorus.

Tarantino and Brown[107] study the effect of moisture on the production of phosphine, and suitable desiccants to prevent its formation, and suitable absorbents to remove it if formed. They find that aluminium silicate clay was an effective desiccant, and activated charcoal a good absorbent. Use of both materials in a perfectly sealed munition provides a non-corrosive environment.

		Phosphorus		Calcium sulphate		Oxalic acid	Atmosphere	Moisture	Initial rate of PH₃ evolution
		Identification	(%)	Identification	(%)	(%)		(%)	(vpm/h)
1	SR620	TS548	46	DS13/69	51.1	2.9	air	0.36	4.8
2	SR622	TS548	46	TS567B	51.1	2.9	air	0.34	4.4
3	SR622	CS5390	46	DS13/69	51.1	2.9	air	1.49	19.4
4	SR622	CS5390	46	TS567B	51.1	2.9	air	1.49	17.4
5		TS548	47.4	DS13/69	52.6	-	N₂	0.13	0.94
6		TS548	47.4	TS567B	52.6	-	N₂	0.02	0.85
7		CS5390	47.4	DS13/69	52.6	-	N₂	0~35	0.90
8		CS5390	47.4	TS567B	52.6	-	N₂	0.25	1.56
9		5%PVB on CS5390	47.4	DS13/69	52.6	-	N₂	0.53	0.08
10		5%PVB on CS5390	47.4	TS567B	52.6	-	N₂	0.36	0.10
11		LOCC TS50181	47.4	DS13/69	52.6	-	N₂	0.57	0.04
12		LOCC TS50181	47.4	TS567B	52.6	-	N₂	0.4	0.04
13		5%PMMA on CS5390	47.4	DS13/69	52.6	-	N₂	0.87	1.65
14		5%PMMA on CS 5390	47.4	TS567B	52.6	-	N₂	0.77	1.10
15		5%PMMA on CS 5390	47.4	TS567B	52.6	-	N₂	0.72	1.29
16		5%PVB on CS5390	47.4	DS13/69	52.6	-	N₂	0.79	0.16
17		5%PVB on CS5390	47.4	TS567B	52.6	-	N₂	0.6	0.16
18		5%PVB on CS5390	47.4	TS567B	52.6	-	N₂	0.57	0.16

Table 15. Phosphine evolution from RP and from RP/anhydrite/oxalic acid smoke composition (Robertson and Glyde)

No reports of the production of *diphosphine* P_2H_4 have been found, which is perhaps fortunate, as the gas is spontaneously flammable in air.

A curious observation[108] is the occasional formation on the surface of pellets of pressed composition containing red phosphorus of a very thin hard layer of a yellow material which analysed almost entirely as phosphorus. It was suggested that it was a subhydride of phosphorus of approximate formula P_4O earlier produced by the dehydration of metaphosphoric acid with acetic anhydride. Detailed examination of the position of the layer indicated that light and access to the atmosphere were necessary for its formation. Fortunately, the thermal stability of the material was high and no change other than the cosmetic was observed in the properties of the pellets.

3.2. Pyrotechnics Processing of Red Phosphorus

The following stages are typical. Each has its problems.

Receipt and storage.

Red phosphorus to the desired specification is received in, say, 25kg drums which are stored sealed until required. The length of storage and the life of a drum once opened depend on the

local practices. In the UK the phosphorus will probably be handled in an atmosphere of relative humidity between 65% and about 70%, although local excursions due to temperature fluctuations could be severe.

The drums should have lids that can be resealed, and any internal plastic bags should be of conducting material to reduce any danger of electrostatic ignition of dust or solvent vapours. Ideally the size of the drum should be matched to the batch size of the composition so that exposure to the air is minimised, and the storage of part empty drums is discouraged. Consideration could be given to the use of local dehumidification of the air when red phosphorus is being weighed.

Processing - Mixing

The red phosphorus is usually slurried in a solvent and a solution of binder is added. Solvents include acetone and other ketones, and methylene chloride and other chlorinated hydrocarbons. Other solid ingredients are added (metal powders and oxidants) and the mixture stirred until the solvent has more or less evaporated. The damp material may be granulated by persuading it through a mesh. It is then dried on trays in an oven at, say, 60°C.

The composition is likely to be exposed at all stages to air and to solvents which may contain significant quantities of water. Also, if the mixing is carried out open to the air chilling due to evaporation of solvent can cause atmospheric moisture to condense in the vessel. In the drying stage it is usual to rely on a fan to exchange the air within the oven, and on the elevated temperature to reduce the relative humidity. Although this is perfectly standard pyrotechnics practice, it is open to the simple objection that although the *relative* humidity is reduced, the *concentration* of water in the air is unchanged, and any chemical reactions are likely to proceed faster at the higher temperature. It must be remembered that phosphorus oxides are excellent desiccants. Preferably, therefore, the incoming air should be reasonably dry. Consideration could be given to bleeding dry nitrogen into the ovens with twofold advantage – reduction of the moisture level in the atmosphere and reduction of the probability of spontaneous ignition of dust because of the lower oxygen concentration in the atmosphere around the trays. It is not necessary to replace the entire atmosphere by nitrogen.

Obviously the combination of solvents (perhaps mixed), vigorous agitation and finally granulation may remove stabilising coating from the granules, and the plastics matrix with which they are coated by the pyrotechnics process has been selected more for its physical and pyrotechnics properties than for its effect as an oxidation inhibitor.

Materials known to promote the reactivity of red phosphorus (copper, brass etc.,) should be avoided in the mixing equipment.

Mason and Paikos (Crane, USA)[109] reviewed the use of rubber binders for red phosphorus but only from the point of view of ease of processing and coating. It was suggested that acrylic acid ester polymer and acrylonitrile – butadiene copolymer could be considered as replacements for butyl rubber binder. Mixtures were examined for the formation of phosphine with none detected.

Although it does not immediately affect stability, the use of solvents such as acetone and chlorinated hydrocarbons is a great inconvenience for the pyrotechnics manufacturer. Chlorinated hydrocarbons in particular are toxic and environmentally objectionable and their long term availability may not be certain. Ideally, water would be used, but that too has its problems with red phosphorus and inorganic nitrates. Alcohols are probably less objectionable than many organic compounds and the availability of an effective binder with good properties which could be added in such a solvent should be welcomed. This aspect should be considered if new binder systems are being investigated.

Processing - Pressing

The composition is almost invariably consolidated by pressing. The loose composition must be allowed to cool before pressing to avoid undue friction sensitiveness. Ideally, it would be cooled in a dry atmosphere and transferred to containers that can be sealed until use. Once pressed, the material is less susceptible to atmospheric effects because of the much reduced surface area. Nevertheless, the pellets should be stored as soon as possible in dry, sealed containers in the absence of any sources of moisture (cardboard, expanded polystyrene etc.,). Pellets left on the bench may eventually show signs of the growth of crystals of inorganic oxidants on the surface as a result of moisture absorption.

While material for bursting grenades is pressed relatively lightly to produce large pellets that break up quite easily, pellets for use in artillery ammunition have to survive high stresses on launch and deployment without breaking up, and so are pressed at several tens of tonnes per square inch to achieve adequate mechanical properties. The high pressures exerted in the die may help remove stabilising coating from the grains, particularly if it has been attacked by the solvents in the previous stage of the process. The red phosphorus may therefore be more reactive to moisture from the air and from within the composition. Naturally, materials that promote the reactivity of red phosphorus (such as brass) should not be used as pressing tools.

It seems that phosphine evolution requires both air and moisture. However, reaction of metals (for example magnesium) with water can proceed anaerobically with the formation of hydrogen. This is known to cause cracking of pellets of other pyrotechnic compositions (illuminating flares and infrared decoys) and although it does not seem to have been reported for red phosphorus pellets, it remains a potential hazard.

Assembly

The pressed pellets are assembled into the final product which may or may not be hermetically sealed. Assembly is carried out under similar conditions to manufacture and the pellets may be exposed to the air for many hours.

If the final product is well sealed then only the moisture and air enclosed are of concern as reactants, but undue pressurisation of the store by phosphine (and perhaps hydrogen) may be a problem. Absorbents for phosphine, particularly charcoal cloth impregnated with copper or silver, may be included somewhere in the enclosed volume. The designer should make himself aware of the maximum amount of gas that can be generated form a correctly manufactured payload to ensure that the mechanical design can cope with it. Storage of

unused cloth should be such that it cannot absorb contamination from the atmosphere with consequent reduction in its capacity when sealed within the store.

Attention should be paid to preventing contamination of the red phosphorus with charcoal cloth impregnated with metal salts that could promote its reactivity. The components in the store that would be exposed to phosphine (rubbers, adhesives, metals etc.,) should have been cleared at the design stage and any deterioration assessed and approved.

Discussion

At all stages of the process the two hazards of accidental ignition and phosphine evolution are present. It is reasonable to expect that the finer grades of phosphorus (or grades containing more fine material) will be more likely to cause problems both with higher sensitiveness and with higher reactivity because of their higher specific surface. Once in the store, it is only the phosphine (and perhaps hydrogen) evolution that is of great concern. The production of these should be quantified for each design.

Accurate measurement of the absolute rate of phosphine evolution from a particular surface is not an easy matter but it is necessary for the quantitative understanding of the effects of processing variables. However, it is not a type of test that a manufacturer would wish to undertake routinely during production as an aid to quality control. There is a clear need for a simple, reasonably rapid and easy test which can demonstrate at least the amount of phosphine produced by a sample under given conditions in a given time. The manufacturer could then apply the test to material on receipt or before use, to the intermediate product during processing, and to his final product ready for assembly. The routine application of such a test to new ingredients and finished pyrotechnic composition, and the demonstration of the robustness of the manufactured product to ageing would provide the manufacturer and the customer with considerable confidence in the entire process. In particular, a value for the final product could form part of the acceptance process for the product. However, before this could be implemented, considerably more needs to be known about the time dependence of phosphine evolution and the effect on it of temperature, moisture and air. A test based on the known rapid corrosion of copper may be feasible.

The author is aware of commercial work in which the effect of processing variables (the order of addition of ingredients to the composition, the extent of drying of the granules and pellets etc.,) on the pressure rise in a sealed steel vessel containing pellets of the composition at elevated temperature was measured. Significant variations were found between different methods. The work proved its value in that a preferred process could be selected and adopted for production.

If a suitable test were available and well understood it could be applied to red phosphorus on receipt, to freshly prepared composition, freshly pressed pellets and to payloads assembled into dummy bombs (for example) in parallel with manufacture. The test on the manufactured article would give the Customer confidence in the long term survival of the product in storage, and consideration could be given to the eventual use of such a test as part of the acceptance. Any earlier tests during the manufacturing process would give the manufacturer greater confidence in achieving the desired ultimate result.

41

Kok at al.,[110] studied the attack of brass by phosphine after tropical storage of a red phosphorus grenade, and recommended that the composition be manufactured in a humidity not exceeding 50% to reduce the amount of moisture taken into the product by the phosphorus. This is unlikely to be achieved reliably by manufacturers in the UK without investment in air conditioning equipment. This investment would not be huge, but the safety of the process would have to be investigated. There is a general opinion in the UK that a minimum relative humidity of 65% is necessary to minimise the hazard of accidental ignitions by electrostatic discharge. It is likely, given modern materials for clothing and earthing, and paying close attention to dusting of the ingredients that safety would not be compromised in any way. Such a hazard assessment would be a valuable exercise because the absorption of water by pyrotechnic ingredients is a general problem in the industry. With certain types of material (particularly initiatory compositions, for which the 65% limit was first set) a reduction in the lower level of humidity would be dangerous.

Because it is known that certain metals catalyse the oxidation of red phosphorus, it seems sensible to avoid copper or brass tooling in any processing operation.

It seems to be current practice to rely on the supplier of red phosphorus to provide a grade adequately stabilised against phosphine evolution but then to subject it to extended processing that might degrade its stability. Little attention has been paid to this possible effect, and it is most desirable that pyrotechnics manufacturers seek to quantify it by a comparison of the rates of evolution from suitable samples of red phosphorus as received and composition after processing.

Perusal of the patent literature concerned with the use of red phosphorus as a flame retardant in the plastics industry suggests that consideration could be given to incorporation of additional stabilisers and phosphine traps in the pyrotechnic matrix. Small quantities of materials such as aluminium hydroxide, titanium dioxide etc., would have insignificant effect on the pyrotechnic behaviour, and marginal effect on the rheology of the mix. Radical changes of the binder system to those used in the plastics industry (many of them containing nitrogen atoms which perhaps allow them to bind more effectively to the phosphorus particles) and the incorporation of perhaps more powerful phosphine traps including transition metals will require considerable research, but should be considered.

4. Phosphorus Smokes

4.1. The Constitution of Phosphorus Smoke

The mass of smoke produced by a munition per unit mass of payload, and the chemical constitution of the smoke are essential parameters for the estimate of its effectiveness. Red phosphorus burns to produce highly hygroscopic oxides which absorb water from the atmosphere to form oxyacids of phosphorus. The mass of smoke therefore depends upon the relative humidity of the air as well as on the phosphorus content of the payload and its efficiency of combustion.

Rubel[111] investigated the growth of phosphoric acid droplets in humid air in order to derive a relationship between relative humidity and yield factor of a phosphorus smoke. He found that the droplets attain equilibrium very rapidly with unsaturated atmospheres. The derived yield factors (mass of smoke per unit mass of phosphorus) at various relative humidities is given below. Note that most of the growth occurs at relative humidities above 80%.

RH %	10	20	35.8	40	50	60	70	80	90
Yield Factor	3.82	4.42	4.91	5.04	5.36	5.97	7.13	9.33	16.29

Rubel[112] earlier had shown significant differences between the absorption characteristics in the $8 - 12$ μm region of phosphorus smokes and comparable orthophosphoric acid mists. He concluded that the smoke was better described as 75% pyrophosphoric acid ($H_4P_2O_7$) and 25% orthophosphoric acid (H_3PO_4).

4.2. Toxicity of Phosphorus Combustion Products

There has been much recent debate about the acceptability of different types of smoke composition for modern munitions. The main areas of concern are:

- the degree of toxicity of the smoke;
- the environmental impact of the residues;

It is reasonable not to distinguish between the types of phosphorus (red or white) when the toxicity of the smoke is the main concern provided that inhalation occurs remote from the combustion zone. Both forms burn in air to form exactly the same products. The following brief summaries of published reports are given for reference.

An early (1957) British report by Cullumbine[113] from CDE Porton considered the acute effect of (white) phosphorus smoke on troops and commented that "experiments have shown that a concentration of 700 mg/m^3 (0.7 mg/l) is required before the effects compel men doing moderate work to adjust their respirators; 1700 mg/m^3 (1.7 mg/l) is needed to harass men similarly at rest. Even with concentrations as high as 3600 mg/m^3 (3.6 mg/l) it was impossible to produce explosive coughing and so hinder the adjustment of facepieces". However, no comment on the toxicity was made.

A literature search in 1978 by Wasti et al,.[114] on behalf of The US Army Medical Research and Development Command, Fort Detrick, USA revealed virtually no information on the

toxicity of red phosphorus/butyl rubber, plasticised white phosphorus or epoxy white phosphorus, and nothing substantive on the toxicity of red phosphorus. It had been reported that mice died from carbon monoxide poisoning after breathing the fumes of burning styrene-butadiene rubber

A more recent (1984) paper reported a study at CDE Porton[115] on 30 minute exposure of rats and rabbits to the combustion products of red phosphorus/butyl rubber 95/5 and red phosphorus/butadiene styrene 97/3 at concentrations of 3200 mg/m³ (3.2 mg/l) and 3100 mg/m³ (3.1 mg/l) respectively. It was commented only that the second composition appeared more toxic than the first, and that both were of lower toxicity than the smoke from zinc oxide / hexachloroethane at a similar concentration.

A 1987 report by Burton et al,.[116] from the Biology Department, Battelle, Pacific Northwest Laboratories, USA noted that studies of the inhalation toxicity of (red) phosphorus smoke had not been published in the open literature, although some studies of white phosphorus smoke had been reported (by Edgewood Arsenal and Aberdeen Proving Ground), and that the effects of smokes from red and white phosphorus should be similar. The results of exposure of rats to the combustion products of pellets of red phosphorus/butyl rubber/mineral oil 95/5/1 were reported. Four groups of ten Sprague-Dawley rats were exposed for 1 hour to average smoke concentrations of 3.15, 4.33, 5.36 and 8.46 mg/l. Some rats died during exposure except in the group exposed to the lowest concentration. One group of ten rats was exposed for 4 hours to an average smoke concentration of 1.53 mg/l with the result that one died during exposure, and one after 7 days. Although the types of damage observed (primarily in the laryngeal region) were reported, no conclusions were drawn about the toxicity of the smoke. The authors warned that direct comparison with results reported by others should be interpreted with caution because of the different concentration levels employed, and because of the possibly differing extent of coagulation and hydration of aerosols.

A brief 1990 abstract from the US Department of Agriculture, Animal and Plant Health Inspection Service of the Denver Wildlife Research Centre[117] reported that four, daily, 80 minute exposures to red phosphorus smoke (at concentrations up to 4.0 mg/l) caused no mortality or other significant effects on prairie dogs (*Cynomys ludoviticus*), but that two such exposures caused deaths among rock doves (*Columbia livia*). It was considered unlikely that damage to wild life would result from training.

The following calculation, while very simplistic, may put these figures into perspective:

Mass of red phosphorus in payload	kg	7
Yield factor		3
Dimensions of (rectangular) smoke screen	m	100 x 20 x 10
Average particle concentration	mg.m⁻³	1050
	mg.l⁻¹	1.05

That means that, in relatively dry air, the concentration in an unrealistically small volume of smoke screen is below that at which mortality occurred in test animals over periods of an hour or more. In reality, the yield factor may be higher in more humid air, but the average concentration will be markedly reduced by growth and dispersal of the smoke cloud.

However, all red phosphorus compositions contain other ingredients, particularly organic binders. Much attention has been paid to selecting the binder for good smoke and mechanical properties, but less to the effect that the binder has on the toxicity of the combustion products. This consideration should not be ignored and a database of combustion products of some red phosphorus / binder compositions would be a useful guideline for the pyrotechnics designer.

4.2 Environmental Aspects.

Little appears to have been published on possible environmental dangers of *red* phosphorus, but the persistence of both forms in the environment, and the dangers of *white* phosphorus have been commented on.

Cullumbine[7] commented upon the danger to livestock grazing land contaminated by white phosphorus from munitions, because small pellets of phosphorus could be driven into tufts of grass and remain unoxidised in the absence of air, presumably as had been reported in *J. Min. Agric.*, in 1930 and 1942 [118, 119].

Although phosphorus is chemically reactive, particularly with oxygen, even white phosphorus can persist for years in environments where the oxygen supply is limited. Spanggord et al,. [120] estimated the half life of red phosphorus/butyl rubber as 1.8 years in air, about 3 years in aerated water (dependant upon particle size and oxygen concentration) and some thousands of years in soils where the reaction is limited by oxygen diffusion. They estimated the half life of the much more reactive white phosphorus/felt to be about 5 minutes in air, about 2.4 years suspended in water and much longer in soil. The minimum life of a 1 cm^3 chunk of white phosphorus buried 12 cm below the surface was estimated to be 10 years.

Racine et al,.[121] of the US Army Cold Regions Research and Engineering Laboratory described a serious consequence of the use in training of white phosphorus ammunition over wetlands in Alaska. Particles of white phosphorus were extinguished on falling into the water and remained unreacted in the anaerobic conditions within the river sediments. Large numbers of waterfowl were now dying because of ingestion of these white phosphorus particles.

The considerable difference in toxicity of red and white phosphorus should be remembered, and it is unlikely that the *toxicity* of *red* phosphorus is a serious concern. Attention better focuses on the environmental impact of compositions containing red phosphorus, where two concerns seem to be expressed:

- incomplete combustion of the composition (either because of the formation of smothering combustion products, or because of quenching in water or snow), with a subsequent inadvertent incendiary hazard;

- formation of white phosphorus by condensation of phosphorus vapour and the consequent production of a toxic residue.

In addition, there is the justified concern about littering training grounds with any sort of unnecessary residue or contaminated hardware.

Considering the first problem (complete combustion) it should be remembered that red phosphorus is used as a flame retardant in the plastics industry. Combustion of a simple red phosphorus / organic binder smoke composition probably depends on the fierce heat flux to which it is initially subjected, to the high content of phosphorus, and to the relatively fine fragments into which the composition is dispersed. Perhaps it is not surprising that pellets which have been partly extinguished in water or by impact do not burn to completion.

One can attempt to minimise this problem by the incorporation of an energetic fuel and inorganic oxidant which permit some combustion under anaerobic conditions, and which generate sufficient heat to promote combustion of the phosphorus. With the selection of a suitable binder (fluorinated hydrocarbons seem to be better than epoxy binders), combustion of pressed pellets leaves very little residue, and a much reduced incidence of subsequent burning compared with standard red phosphorus/butyl rubber compositions.

Residues from such combustion trials of a proprietary red phosphorus composition were sampled by Royal Ordnance's laboratories at Glascoed. No white phosphorus was identified after extraction with organic solvents. However, these are single results, and the effect of conditions of combustion needs to be made clear. It is certain that white phosphorus can form from red phosphorus only by the process of vaporisation and condensation, and the effect of the binder char in providing a medium in which this can occur in the absence of air might deserve study.

5. Demilitarisation and Reclamation

The USA in particular has given thought to the possible reuse and to the ecologically acceptable disposal of smoke payloads containing red phosphorus. Serious consideration should be given to the problem of disposal which is likely to constitute an increasing part of the cost of ownership of munitions containing red phosphorus.

Johnson et al,.[122] in 1974 investigated the disposal of smoke compositions from Naval smoke markers containing red phosphorus, pyrolusite, magnesium, zinc oxide and linseed oil. Acid dissolution of the material yielded a solution which, after adjustment of the *pH*, was proposed for use as a fertiliser. It would seem unlikely in today's ecologically sensitive climate that such a use would be acceptable without extensive and prohibitively costly tests.

Grassi et al,.[123] studied the problem with the specific aim of reusing the phosphorus from the original red phosphorus/butyl rubber/talc composition of the L8A1 grenade in the red phosphorus/butyl rubber/silica reformulation for the L8A3 grenade. The original pellets were soaked in sufficient dichloromethane to make them capable of being processed and the composition (still presumably containing talc) was blended with silica and produced acceptable pellets.

Environmentally acceptable destruction of the L8 grenade is not simple. The phosphorus composition can be extracted and burned in the open, but that practice may not be permitted in the future. Phosphorus manufacturers are not interested in the material because of all the contaminants in it. The rubber boot cannot reasonably be burned in the open because of the black smoke produced. However, it is contaminated with phosphorus which can attack the lining of conventional furnaces. Suitable incinerators do exist and continued dialogue between MoD and the owners of such incinerators seems advisable.

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<u>6.</u> Summary

Red phosphorus can be incorporated into pyrotechnic compositions which produce copious white smoke of lower toxicity than other materials. The smoke is very effective as a visual screen, and can be made very effective in the infrared. Red phosphorus is likely to be an important pyrotechnic ingredient for many years.

The use of red phosphorus has certain problems associated with it, and specific the topics to be addressed are:

- The reduction in the quantity of phosphine produced in storage by compositions containing red phosphorus;
- The reduction in the quantity of hydrogen produced in storage by compositions also containing metal powders;
- The quantification and minimisation of the amount of white phosphorus formed under different conditions of combustion;
- The assessment of the toxicity of combustion products of, and optimum selection of ingredients and formulations devised to minimise it.
- Establishment of environmentally and economically acceptable methods of demilitarising, reusing and destroying red phosphorus compositions and components.

The approach of the pyrotechnics industry has generally been to select from the grades that exist commercially a grade of red phosphorus that provides acceptable properties (usually burning rate, processability and phosphine evolution), or to encourage the manufacturer to produce a grade with the required properties. The stabilised material is then subjected to further chemical and physical processing (mixtures of solvents, vigorous stirring, consolidation at high pressure) which could remove the stabilisers from their site of effectiveness. The materials with which the red phosphorus is compounded are currently selected primarily for pyrotechnic effect and not as contributors to the stability of the composition or to the toxicity of the combustion products.

Red phosphorus is used extensively in the plastics industry as a flame retardant, and much work has been published on the phlegmatisation of the material against inadvertent ignition and the stabilisation of it against low temperature oxidative reactions. Although most of the information is in the patent literature, and phrased more for legal than scientific precision, the types of materials that have been found suitable are reasonably clear, even if the mechanisms of effectiveness are obscure. A significant difference between the requirements of the plastics and the pyrotechnic industries lies in the fact that red phosphorus is a minor ingredient in a plastics material, and overwhelmingly the major ingredient in a pyrotechnic smoke composition. The pyrotechnist must therefor seek among the most effective of the stabilisers which can be used in small concentrations.

Consideration of the plastics patent literature suggests that the pyrotechnists could approach the problem differently by selecting the stabiliser and processing conditions so that the phosphorus remains stabilised, and by incorporating additional stabiliser into the plastic

matrix of the composition. This seems to demand a close collaboration between the manufacturer and the user of the red phosphorus.

Improvements are required to manufacturing processes to reduce the amount of moisture present in the finished product.

A rapid and simple test is required which can be used by the pyrotechnics manufacturer to assess the rate at which phosphine is produced over a specified time from ingredients, composition and pressed pellets.

7. Conclusions and Recommendations

It is concluded that no definite solution exists to the problem of the variability in the non-pyrotechnic reactivity of red phosphorus, but that are indications in the literature which should be followed.

The chemistry of the slow reaction of phosphorus with moist air, and the mechanisms by which certain compounds can change the rate at which it occurs remain unclear. The effect of pyrotechnics processing on the stability of red phosphorus is not understood. Processes which do not degrade the original stability of the phosphorus are required, and the use of phosphine traps may be learned from the plastics processing industry. Convenient standard tests to establish the quantity of phosphine produced are not available.

The interaction between the surface of red phosphorus and organic binders should be investigated so that binders can be selected which bind better to the red phosphorus (and may therefore suppress oxidation by the largely physical effect of shielding the surface) and which are themselves good binders, or which also bind well to the selected binder to improve the mechanical properties of the final product.

Close co-operation between the Customer, the pyrotechnics manufacturers, research organisations and the manufacturers of red phosphorus is necessary to grasp the entirety of the problem.

It is therefore recommended that:

- Research be undertaken into the basic mechanisms of phosphine and acid production as a basis to the identification and understanding of improved types of formulations and processing conditions.

- A reproducible, simple and convenient non-destructive test be devised to determine the amount of phosphine produced (or the time to the production of a defined concentration in a defined volume) by compositions containing red phosphorus.

- A working party including red phosphorus manufacturers, pyrotechnics designers and manufacturers, and academic chemists be established to consider more satisfactory combinations of phosphorus treatments and pyrotechnics processing ,and to produce guidelines for future developments.

- Experimental samples arising from the recommendations of the working party be produced and subjected to ageing trials.

- The toxic and environmental hazards of the combustion products (smokes and residues) be quantified and guidelines for selection of ingredients be sought.

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