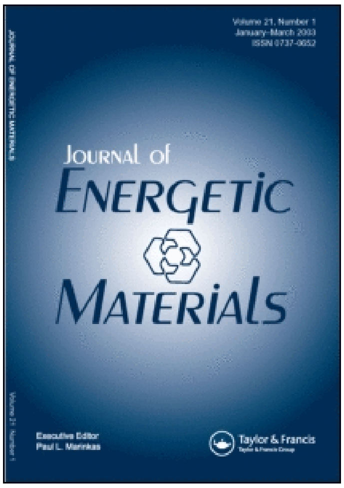

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Studies on Characterization and Burning of Red Phosphorus–Based Smoke Compositions

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Burning of red phosphorus leads to attenuation of electromagnetic radiation in the visible and infrared regions. Red phosphorus and potassium nitrate–based compositions exhibit favorable smoke screen formation with high obscuration characteristics at low oxidizer content as indicated by radiometric studies. The rapid vaporization of excess red phosphorus leads to quick dispersion in air. The obscuration is mainly due to formation of P_2O_5 *followed by its reaction with moisture/humidity in the atmosphere. The compositions are highly sensitive to impact and friction, and oxidation of phosphorus occurs in moist air. Coated red phosphorus is used to suppress excess flammability and prevent dust formation. The thermograms of coated red phosphorus and smoke composition show the general trend of thermal stability of the mixtures under specified experimental conditions. The SEM photographs of the smoke composition of the sliver sample indicate bubbled surfaces for entrapped phosphorus vapors as well as valley-like holes from which the vaporized phosphorus escaped through the surface. Hot-stage microscopy indicates escape of red phosphorus before complete oxidation. Although loose*

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composition may absorb moisture because of the porous structure, the moisture ingress into the filled munitions where particles are compacted is expected to be less. The data indicate that processing of red phosphorus—based compositions needs controlled humidity conditions and storage in hermetically sealed systems to avoid moisture ingress.

Keywords: red phosphorus, smoke, IR and visual obscuration, scanning electron microscope, thermal analysis, hot-stage microscope

Introduction

Red phosphorus (RP)—based smoke compositions are fast burning and quick smoke screen forming due to fast inorganic reactions as compared to generally used hexachloroethane (HCE)—based smoke compositions. These smoke compositions constitute an important class in the family of smoke generators and are extremely useful for screening troop movements, signaling, marking position on the sea as a spotting aid, and as an infrared counter measure [1—4]. White dense smoke formed by burning of RP becomes denser with increased humidity and leads to attenuation of electromagnetic radiation in the visible and infrared regions. This smoke shields reconnaissance and defeats observations by night vision aids. For military use, white phosphorus must be considered undesirable because of its toxicity and unacceptable handling hazards [5]. Despite several advantages of smoke generated by burning RP [6,7], these compositions are highly sensitive to impact and friction. Also, RP rapidly absorbs moisture with generation of o-phosphoric acid and phosphine in humid conditions. Coated RP [8—10] is used to suppress excess flammability and prevent dust formation. The reactivity of RP is retarded by using a polymeric binder. In the present study, RP has been coated with a binder. Thermal stability and sensitivity behavior have been studied along with humidity/moisture-related problems. The burning process was followed on a hot-stage microscope, and quenched slivers of the pellet were analyzed by a scanning electron microscope (SEM). Obscuration in the visible and IR regions was measured.

Experimental

Compositions were processed by mixing coated RP and potassium nitrate. Experiments were carried out using organic binders as encapsulants for safe processability and thermal stability. The experiments conducted include evaluation of friction sensitivity by the Julius-Peter apparatus, impact sensitivity by the Drop Hammer method, and thermal analysis by NETZSCH STA 409. Determination of the effectiveness of coating and sliver analysis were carried out using an SEM. Moisture absorption of ingredients and composition were tested under 70% and 30% relative humidity conditions. Obscuration characteristics were measured using a spectroradiometer by burning 5 g composition in a smoke chamber of $1.8\,\mathrm{m}^3$ volume. The stabilized RP (stabilizer content 1.5%) as obtained from M/ S United Phosphorus, Vapi, India, was used as such in this study without any further treatment except as specified in the individual experiments. Various binders like nitrocellulose, polybutadiene, polybutene (molecular weight 950 and 2700), polyvinyl butyral, linseed oil, castor oil, polyester resin, phenolic resin, and crepe rubber were incorporated to the extent of 5% by using suitable solvents.

Results and Discussion

The sensitivity data of RP-based compositions are shown in Table 1. The impact sensitivity of RP is increased by coating with the binder, indicating that either the binder acts as an oxidizer as well, or it introduces a resistance to flow, thus localizing the heat energy during the impact. Although ignition occurs to a RP sample at 170 cm impact with 2 kg weight and at 36 kg friction, RP coated with 5% polyester, phenolic resin, or polybutene exhibits increased sensitivity, which is probably due to the formation of gritty granules and agglomerates. However, addition of a dust suppressant reduced the impact sensitivity. During the selection phase of an oxidizer, three factors were considered, viz., (1) non-hygroscopicity, (2) burning rate, and (3) restricted oxidizer content to give maximum phosphorus loading to achieve a high percentage of obscuration. It is seen from the data that the oxidizers other than alkali nitrates make the mixtures comparatively insensitive, but they all exhibit poor burning characteristics and delayed smoke generation. As sodium nitrate is more hygroscopic, potassium nitrate was chosen as the oxidizer.

The composition with RP (80%) + KNO_3 (20%) without a binder exhibited high sensitivity to impact and friction. Therefore, coating of both RP and potassium nitrate with a binder was considered essential. Thermochemical calculations (Table 2) indicate that the volume of gases evolved and flame temperature are minimum at 10% oxidizer content, and they increase with increased oxidizer content, reaching a

Table 1
Impact and friction sensitivities of red phosphorus−based compositions

Sr. No.	Composition	Impact sensitivity* (cm)	Friction sensitivity (kg)	Remarks
1	Red phosphorus (60 μm)	170**	36	
2	(i) coated with 5% polyester	40	26	
	(ii) coated with 5% phenolic	65	36	
	(iii) coated with 5% polybutene-2700	45	36	
	(iv) coated with 5% phenolic & 2% dust suppressant	85	36	
3	80% red phosphorus + 20% oxidizer			
	(i) RP + $NaNO_3$	20	10	Hygroscopic
	(ii) RP + KNO_3	10	08	
	(iii) RP + Ba $(NO_3)_2$	20	20	
	(iv) RP + Bi (OH) CrO_4	50	32	Slow burning
	(v) RP + $CaSO_4 2H_2O$	50	36	Slow burning
	(vi) RP + ammonium oxalate	170**	36	Prolonged ignition
4	80% red phosphorus + 20% oxidizer (coated with 5% binder separately)			
	(i) Phenolic resin: 5%	15	24	
	(ii) Phenolic resin: 10%	18	28	
5	80% Red phosphorus + 20% oxidizer			
	(i) RP (binder coated) + KNO_3 (binder coated)	22	29	Binder mixed dry
	(ii) RP (binder coated) + KNO_3 (binder coated)	21	36	Binder coated using organic solvent

*Height for 50% explosion with 2 kg drop weight.
**No explosion at this height.

Table 2
Thermo-chemical data of RP:KNO_3 compositions

Composition No.	RP:KNO_3	Flame temperature (°C)	Volume of gases m^3/kg
I	90:10	516	0.49
II	80:20	1077	0.92
III	70:30	1239	1.27
IV	60:40	1324	1.65

maximum value at 40% in the compositions under study. Since a favorable condition for smoke generation is maximum volume of gas evolution at minimum possible flame temperature with faster smoke generation rate, composition II is a good choice. The flame temperature thereafter raises slowly with rise in volume of gases generated. The large difference in flame temperature and volume of gases between compositions I and II is due to the melting endotherm of RP, which occurs at 597 °C, and the exothermic decomposition of potassium nitrate in the same temperature range.

Burning of phosphorus leads to formation of P_2O_3 and P_2O_5 compounds in smoke. However, experimental investigations by a number of authors [4,5] could detect only P_2O_5 compounds. Obscuration is governed by the formation of P_2O_5 and its subsequent reaction with moisture from the atmosphere. Phosphorus pentoxide surrounded by the absorbed atmospheric water produces condensed phase o-phosphoric acid, and additional atmospheric water condensation on these liquid droplets leads to growth in drop size. Obscuration is better at high humidity conditions as water condensation around the o-phosphoric acid molecule increases formation of the aerosol and consequent obscuration.

The highest percentage obscuration is observed for composition I, though the flame temperature and volume of gases are minimum in this case. This is attributed to the vaporization of excess unreacted phosphorus, which gets oxidized, with the participation of about 230 g of oxygen available in the 1.8 m^3 volume of atmosphere in the smoke chamber. As the calculated flame temperature is low, it is expected that the burning and obscuration are also likely to be slow phenomena under this condition. Since the flame temperature is on the order of 516 °C (Table 2), complete RP is not fully available for efficient obscuration, as melting of RP occurs at 597 °C. With the increase of oxidizer to 20% in composition II, the burning rate increases with increase in flame temperature to 1077 °C, which contributes to rapid vaporization of phosphorus, leading to quick obscuration. Further increase in oxidizer content only marginally increases the flame temperature, reducing the unreacted phosphorus content, though obscuration becomes quicker. Obscuration is expected to become poorer with increase in flame temperature because of a higher rate of diffusion at higher temperature. Thus obscuration is lowest at the higher oxidizer content.

The extinction coefficient (α) (Table 3) calculated at $\lambda = 0.4-13.0\,\mu m$ decreases from 1.74 to 0.41 when calculated per unit mass of composition at 85% relative humidity. The corresponding α-values at 45% RH are lower and decrease from 1.05 to 0.35, which indicates that the shadow cast per unit mass of the sample is smaller in the absence of particle growth at low humidity. Extinction coefficient values for compositions I–IV vary from 0.97 to 0.61, whereas the same when calculated per unit mass of RP remains constant (Table 4). Examination of the residue of the reaction indicates that all the phosphorus has participated in the reaction. This confirms that it is the RP content of the composition that is responsible for the obscuration, and the role of the binder in obscuration is not significant.

The summary of thermal analysis data is given in Table 5. Pure RP shows a sharp exothermic ignition reaction in air at a peak

Table 3
Obscuration and extinction coefficient of composition II in visible and IR ranges at 85% and 45% relative humidities

	Obscuration (%)		Extinction coefficient (α) (m^2/g)	
Range (μm)	85% RH	45% RH	85% RH	45% RH
0.4–0.7	99.7	97.0	1.74	1.05
2.0–2.4	90.7	88.0	0.71	0.64
3.0–5.0	80.0	74.0	0.48	0.40
8.0–13.0	75.0	69.0	0.41	0.35

Charge mass (g) = 5; chamber volume (m^3) = 1.8.

Table 4
Extinction coefficient (α) of smoke composition and its RP content

Composition No.	RP content in composition (g)	% obscuration	α for composition (m^2/g)	α for RP content (m^2/g)
I	4.5	96	0.97	1.07
II	4.0	94	0.84	1.06
III	3.5	91	0.72	1.03
IV	3.0	87	0.61	1.02

Note: Charge mass (g) = 5; chamber volume (m^3) = 1.8; range (μm) = 0.4–0.7; RH (%) = 30.

temperature of 410 °C. A mixture of uncoated RP and potassium nitrate shows sharp ignition corresponding to a peak temperature of 321 °C. The mixture of RP, potassium nitrate, and binder shows multiple exotherms with one sharp exotherm at 422 °C. These thermograms

Table 5
DTA data of red phosphorus/KNO_3/resin-based compositions

Sr. No.	Composition	Binder	Ignition exotherms T_i(°C)	T_p(°C)	T_f(°C)
1	RP	Uncoated	390	410	440
2	RP	Coated with phenolic resin	380	420	446
3	RP + KNO_3	Uncoated	318	321	440
4	RP + KNO_3 + binder	Powder coated	328	378	450
5	RP + KNO_3 + binder + dust suppressant	Separately coated & granulated	368	422	455

T_i = inception temperature
T_p = peak temperature
T_f = final temperature.

indicate the increased thermal stability of the mixtures under specified experimental conditions. No change in ignition temperature was observed as a result of long-term storage. It can be seen that the temperature of ignition of all samples was dependent only on ignition of phosphorus. Thermogravimetric analysis indicates 98% weight loss in the sample of commercial RP at 262°C, whereas the smoke composition indicated a loss of 60% at 260 °C, indicating an ignition reaction of phosphorus, KNO_3, which is exothermic in nature. The Thermogram (TG) of smoke composition shows that 80% of the RP content of the composition goes out in a vapor state without undergoing oxidation. It is expected that as this vapor passes through the flame/reaction zone of 1077 °C, it gets oxidized with atmospheric oxygen.

Radiometric studies carried out in the spectral mode at different intervals during the smoke screen formation process indicate that highest obscuration is observed in the visible region for the entire duration with marginal decrease toward the latter half. Also the obscuration in the infrared region is initially less and increases toward the middle with a rapid decrease toward the end. This can be attributed to the fact that shorter-wavelength radiations are obscured during the formation of aerosol, whereas the longer wavelengths are obscured when the size of $P_2O_5{\cdot}xH_2O$ aggregates are comparable to the wavelength of the radiations.

The burning process of smoke composition was recorded by color video through a hot-stage microscope, and it was observed that RP starts subliming from the composition at around 260−270 °C. Figure 1 shows entrapped RP under the layers of binder and in contact with oxidizer. At ~350 °C (Figure 2) molten RP and decomposed oxidizer species bubble out with spurting and are ejected into the reaction zone above the surface. At the right-hand top corner of the figure, the deposits of the spurted species are seen, and the same process is also seen in the SEM photograph of the quenched sample (Figure 6), where the tunnels indicate the surface after the release of oxidative species with molten RP, and the bubbles in between indicate the entrapped species trying to leave the surface. Since quenching occurred at this instance, the enlarged surface remained with the vapors getting condensed inside.

An SEM photograph of the RP is shown in Figure 3, and one of the RP sample coated with 5% binder is given in Figure 4. The effect of coating can be seen in Figure 4 by the absence of sharp edges and by the dull but uniform finish. Figure 5 is the SEM photograph of the smoke composition based on RP without the dust suppressant. Grains of RP and KNO_3 are distinct, and the dullness and

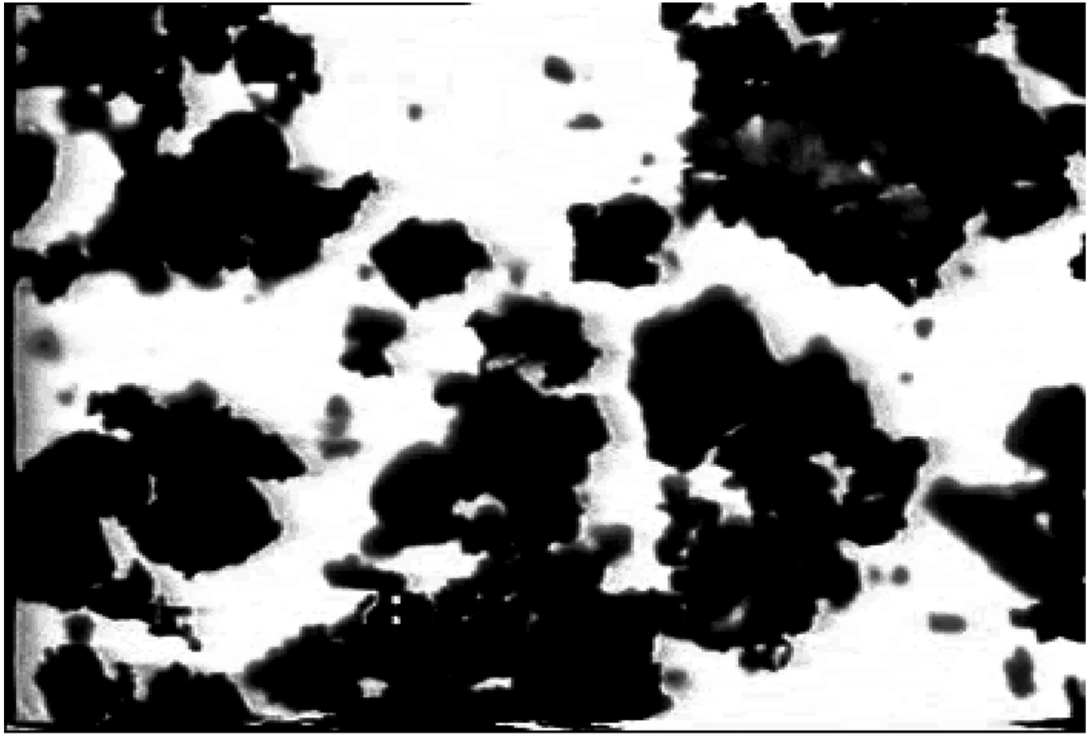

Figure 1. Hot-stage microscopic view of $RP + KNO_3 + Binder$ at $\sim 270\,^{\circ}C$.

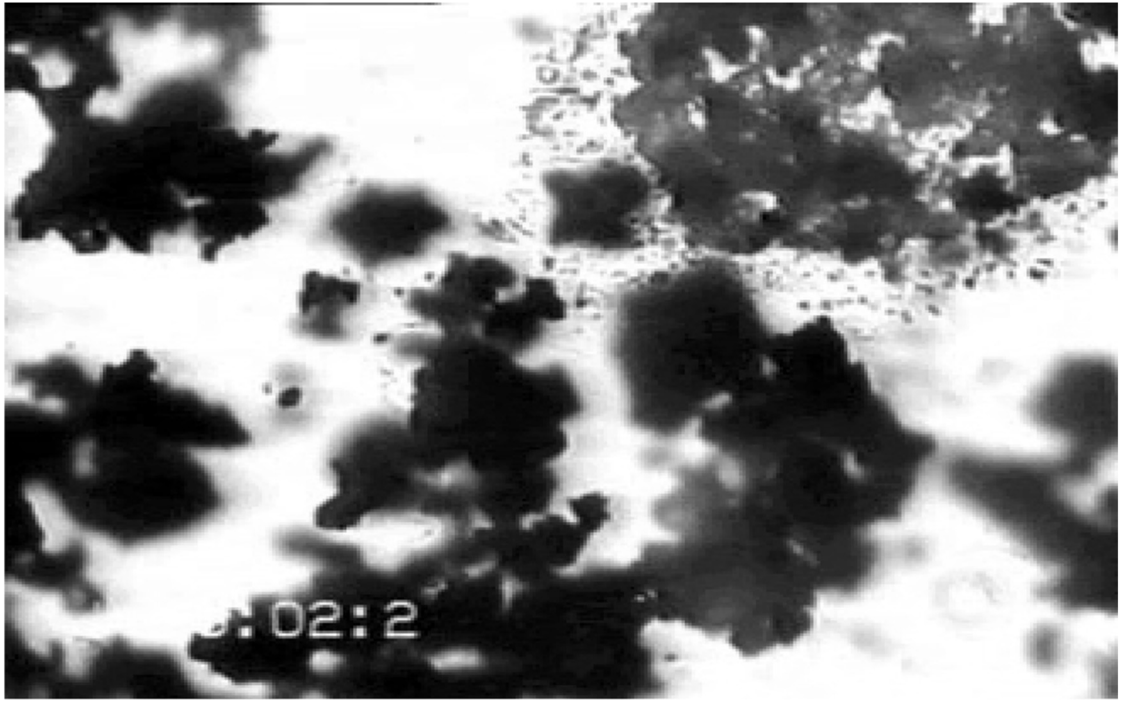

Figure 2. Hot-stage microscopic view of RP + KNO_3 + Binder at ∼350 °C.

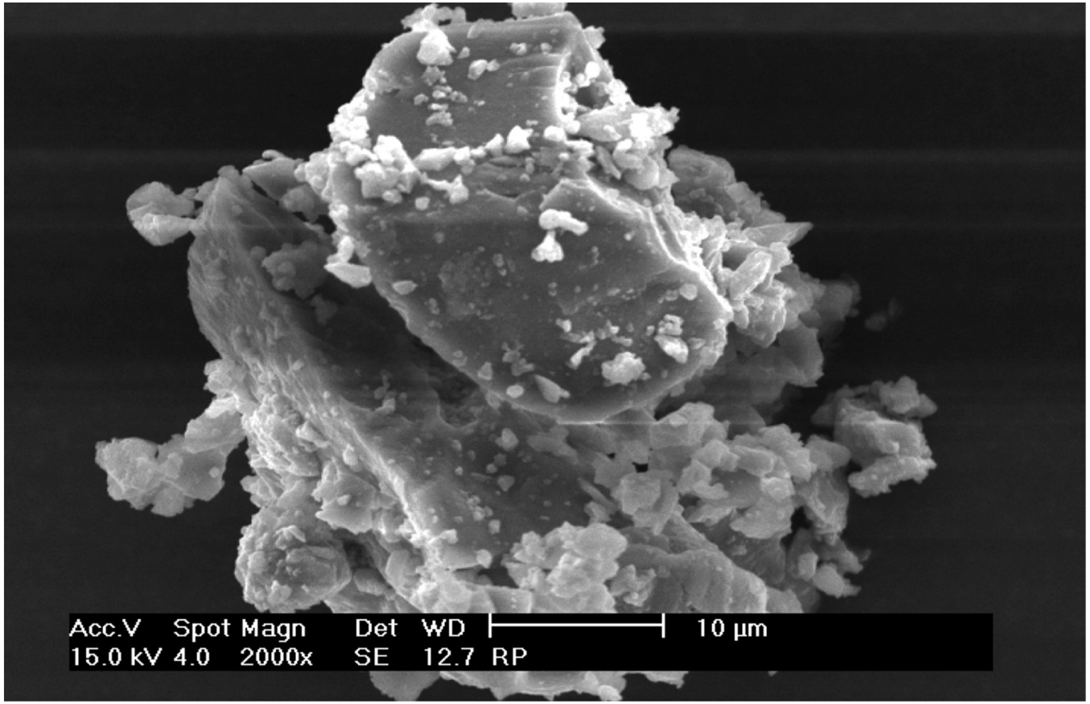

Figure 3. Red phosphorus.

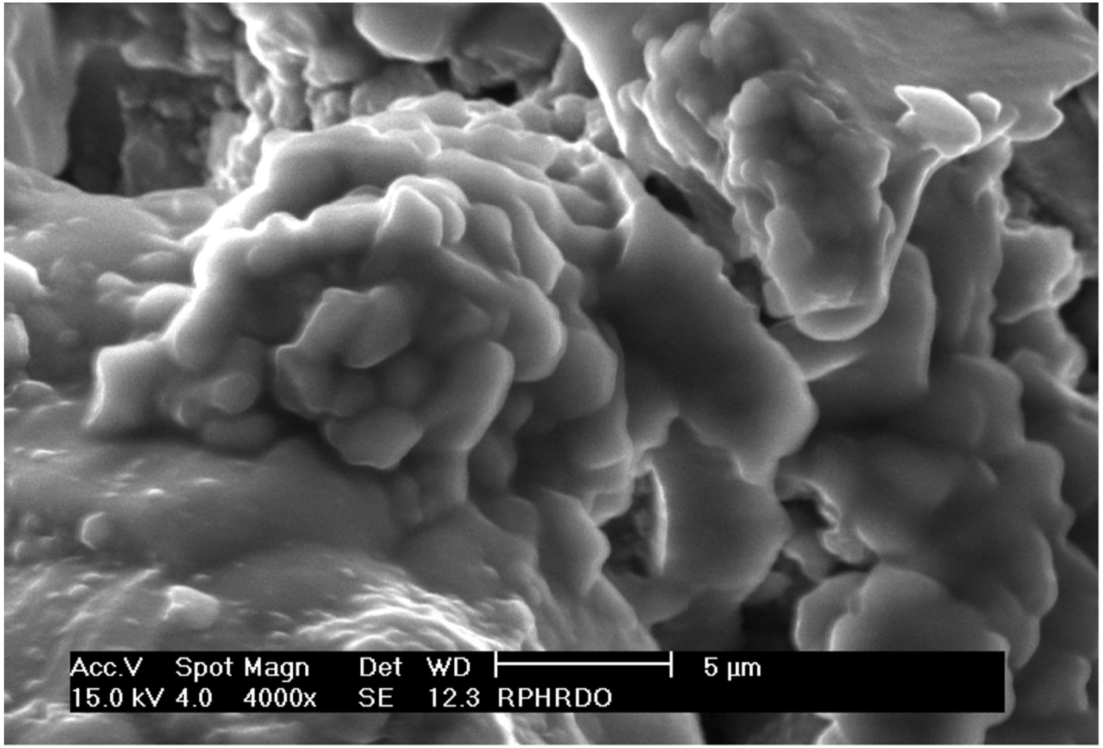

Figure 4. Red phosphorus coated with phenolic binder.

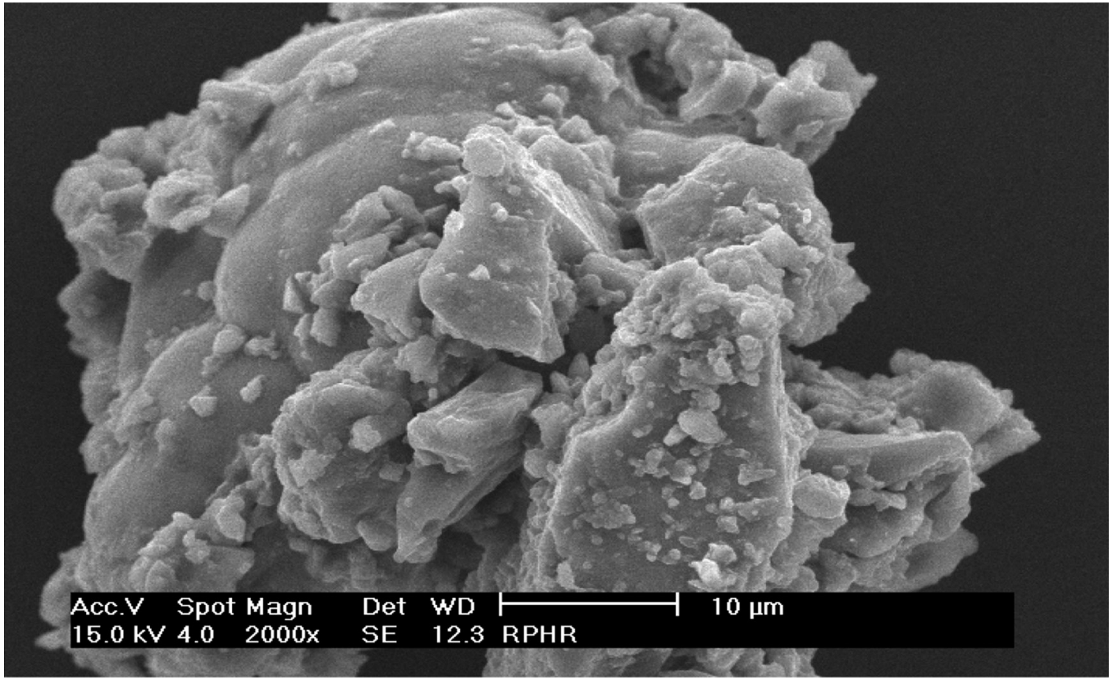

Figure 5. Red phosphorus−based smoke composition.

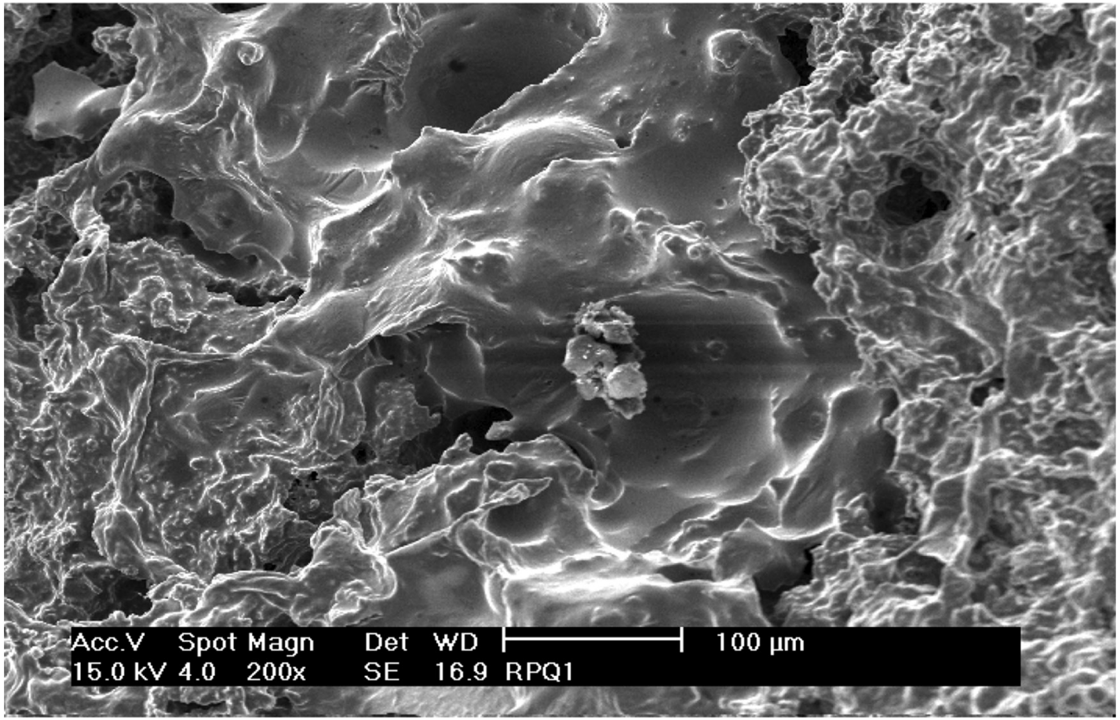

Figure 6. Sliver sample (quenched surface).

Table 6

Moisture absorption at 70 and 30% RH

Days	1		2		3		5		16		25		34	
Material	30*	70*	30	70	30	70	30	70	30	70	30	70	30	70
Red phosphorus	2.07	3.97	2.65	5.25	4.18	7.22	9.14	13.61	14.39	17.18	17.79	21.53	20.18	27.27
RP coated	1.15	2.96	1.54	3.12	1.75	3.36	1.81	3.38	2.13	3.46	2.39	3.73	2.52	3.85
RP composition	1.15	2.96	1.54	3.36	1.75	3.42	1.81	3.50	2.13	3.68	2.39	3.70	2.59	3.73
Binder	0.53	1.13	0.70	1.17	0.88	1.19	0.89	1.25	0.91	1.29	0.94	1.43	0.98	1.45
KNO_3	0.04	0.04	0.06	0.06	0.06	0.07	0.06	0.07	0.06	0.07	0.06	0.07	0.06	0.07
KNO_3 coated	0.05	0.15	0.05	0.17	0.10	0.15	0.16	0.19	0.19	0.21	0.24	0.32	0.29	0.35

*30 and 70 are RH%.

absence of sharp edges indicate the effectiveness of coating. Thus it is expected that the binder is effective in its role of providing a barrier to avoid moisture absorption. The quenched sliver sample in Figure 6 shows tunnels in the surface formed as a result of the escape of phosphorus vapor or the phosphorus oxides. This corresponds to the view seen through the hot–stage microscope in Figure 2.

Table 6 shows moisture absorption data of RP and potassium nitrate and the mixtures at 30% and 70% RH. The absorption of moisture by uncoated RP is around 27%, while coated RP absorbed 3.8% after 34 days at 70% RH. At 30% RH, it is 20% and 2.5%, respectively. The composition made by coating also indicates 3.7% and 2.6 % moisture absorption at 70% and 30% RH. The moisture absorption by binder and KNO_3 is comparatively less. This moisture absorption will lead to increase of acidity in RP and formation of phosphine. The level of phosphine generation at different RH conditions is being studied in a separate set of experiments. The remedial acid adsorbents and their role in stabilizing the composition are being studied. Although uncoated ingredients absorb a large amount of moisture over a period of time (Table 6), absorption by coated ingredients is comparatively less, indicating the effectiveness of coating. Although moisture ingress is mostly reduced because of the binder, the 3% absorption will also affect the stability of the phosphorous composition on prolonged storage. The moisture ingress into the filled munitions in which the composition is compacted and sealed may be less, but compared to the loose grains, the effect of moisture absorption on prolonged storage needs to be studied in view of the hazards associated with the liberation of PH_3.

Conclusion

Processing of red phosphorus–based compositions needs controlled humidity conditions. Also, encapsulation by a binder and addition of a stabilizer to maintain neutral pH are essential to have satisfactory storability. Storage in hermetically sealed systems is essential to avoid moisture ingress. The SEM studies offer an interesting tool for studying the effectiveness of polymeric coating and correlation with moisture absorption. The thermal studies and the hot-stage microscopy provide an insight into the reactions occurring in the composition. The radiometric studies show that RP–based smoke serves as an efficient obscurant in the 0.4–13 μm region with increased efficiency at higher humidity conditions.

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