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Radiometric Screening of Red Phosphorus Smoke for its Obscuration Characteristics

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ABSTRACT

Red phosphorus and potassium nitrate-based compositions exhibit favorable smoke screen formation with high obscuration characteristics at low oxidiser content. The rapid vaporisation of excess red phosphorus at higher flame temperature leads to quick aerodispersion. The obscuration characteristics are due to formation of P_2O_5 and subsequent reaction with moisture/ humidity in the atmosphere. Obscuration increases with increasing humidity. Extinction coefficient, the shadow cast per unit mass of the composition, is higher in visible and comparatively lower in far infrared.

Keywords: Smoke screen, pyrotechnic compositions, red phosphorus, obscuration characteristics, radiometric screening

1. INTRODUCTION

Pyrotechnic compositions based on red phosphorus gained worldwide attention[1-5] since the smoke particle emanating from the burning of these compositions attenuate not only visible but also infrared radiation. Sudden spurt in research activity in this field is due to the deployment of sophisticated electrooptic instruments using laser and IR sensors as tools of target detection. Taking advantage of the absorption characteristics[6-8] of the products of burning of red phosphorus, effective shielding from being seen and engaged by the night vision aids/IR homing missiles can be obtained. The aerodispersion of smoke could occupy relatively large volume instantaneously, which can help the tank to move to a safer position. Since most work carried out on red phosphorus-based smoke compositions is either classified or in the form of patents, an attempt has been made to screen a few compositions with varying oxidiser content for their obscuration characteristics by generating red phosphorus smoke in a smoke chamber.

2. EXPERIMENTAL

2.1 Materials

Red phosphorus (97 %) used in the experiments is conforming to IS-2012 specification and is obtained from M/s United Red Phosphorus. The material was dried at 60 °C and passed through 240 BSS. Potassium nitrate (grade I) conforming to IS-301-1963 specification was dried at 110 °C for 3 h and passed through 120 BSS, phenolic resin of 240 BSS size is a proprietary item of M/s Bakelite Hylam Ltd, Hyderabad, and was used as obtained from the Firm.

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2.2 Methods

Composition (100 g) was mixed in a porcelain dish using a wooden spatula. All the compositions contained 5 parts binder by weight. Red phosphorus was mixed with 4 parts of binder, potassium nitrate was mixed with 1 part of binder and both the coated red phosphorus and KNO_3 were then thoroughly mixed for 5 min in the dish. Pellets (20 mm dia) were pressed at 3 ton load for a dwell time of 10 s. Four compositions containing red phosphorus and KNO_3 in the ratios 60:40, 70:30, 80:20, and 90:10, respectively were processed. The pellets were burnt at 1 atm pressure and the time of burning was evaluated using a stopwatch and the smoke generation rate was calculated. In addition, the pellets were burnt in an electrical muffle furnace inside a smoke chamber of volume 1.8 m^3 and the percentage obscuration was calculated from the formula

$$\text{Per cent obscuration} = \frac{I_o - I}{I_o} \times 100$$

where I_o is the initial radiant intensity, and I is the radiant intensity through the smoke column.

The extinction coefficient (α) for the composition was calculated using the formula

$$\ln \frac{I}{I_o} = e^{-\alpha . c . l}$$

where c is the concentration of the composition/ red phosphorus in the given volume, and l is the length of the smoke column.

3. RESULTS & DISCUSSION

3.1 Results

Thermochemical calculations were made at different oxidiser loading conditions. The flame temperature, smoke generation rate, and sensitivity figures for each composition is presented in Table 1. Pellets weighing 2 g were burnt in smoke chamber and the obscuration and the extinction coefficient in visible and IR regions are shown in Table 2.

Obscuration for composition II in visible and IR regions measured at different humidity conditions are shown in Table 3.

3.2 Discussions

Thermochemical calculations (Table 1) indicate that the flame temperature is minimum at 10 per cent oxidiser content and go on increasing with the oxidiser content, reaching a maximum value at 40 per cent in the compositions under study. This is in line with the general expectations. Since a favourable condition for smoke generation is maximum volume of gas evaluation at minimum possible flame temperature with faster smoke generation rate, composition II will be a good choice. Since red phosphorus smokes are known for their pillaring effect, minimum flame temperature is mandatory. The flame temperature thereafter rises slowly with rise in the volume of gases generated. The rapid change in flame temperature and volume of gases for only 10 per cent rise in oxidiser content can be attributed to the melting of red phosphorus, which occurs at 870 K.

All the compositions ignite in less than 100 ms and the smoke generation rate is minimum at 10 per cent

Table 1. Data on red phosphorus: KNO_3 smoke compositions

Composition No.	Red phosphorus: KNO_3*	Flame temp (K)	Smoke generation rate (g/s)	Impact sensitivity ** (cm)	Friction sensitivity (kg)
I	90 : 10	789	0.08	27	28.8
II	80 : 20	1350	0.10	21	25.2
III	70 : 30	1512	0.11	18	25.2
IV	60 : 40	1597	0.12	16	21.6

***** with 5 % binder

****** Height for 50 % explosion with 2 kg drop weight

Table 2. Obscuration perdentage and extinction coefficient in visible and differant infrared regions

Composition No.	Obscuration (%)				Extinction coefficient* (α), (m^2/ g)			
	0.4- 0.7 µm	2.- 2.4 µm	3 –5 µm	8 –14 µm	0.4 -.7 µm	2.- 2.4 µm	3 –5 µm	8 –14 µm
I	99.7	89	72	62	4.36	1.66	0.95	0.73
II	99.8	90	75	68	4.66	1.72	1.04	0.85
III	99.6	85	66	59	4.14	1.42	0.83	0.67
IV	99.5	82	57	51	3.97	1.28	0.64	0.54

Charge weight - 2 g, Chamber volume - 1.8 m^3, Relative humidity - 55 %

oxidiser loading and reached a maximum value at 40 per cent oxidiser loading. When 2 g pellets are burnt, the obscuration is 100 per cent in all cases in visible region as could be seen from Table 2. However, per cent obscuration gradually decreases from 89 per cent to 62 per cent from near-IR to far-IR regions in the case of composition I. The same tendency is seen in all the other compositions. Obscuration is governed by the formation of P_2O_5 and its subsequent reaction with moisture/ humidity in the atmosphere. Phosphorus pentoxide surrounded by the absorbed atmospheric water produces condensed phase o-phosphoric acid at the surface of the solid particles and additional atmospheric water condenses on the vapour particles surface, thus leading to growth in drop size. The pellets were burnt at a very low (15%), and high (85%) relative humidity conditions to identify the most efficient obscuration system under all the conditions (Table 3). Obscuration has to be better at high humid conditions as water condensation around the o-phosphoric acid molecule will increase the formation of the aerosol and consequent obscuration.

Although existence of P_2O_3 in the smoke has been suggested, experimental investigations by a number of authors could detect only P_2O_5. Highest percentage obscuration was observed for composition II with comparatively low flame temperature and high smoke generation rate. This can be attributed to the vaporisation of excess of unreacted phosphorus, which will get oxidised, 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 rather low, it is expected that at this condition burning and obscuration will be a slow phenomena. Since the flame temperature is of the order of 789 K (Table 1) and melting of red phosphorus occurs at 870 K, complete red phosphorus is not available for efficient obscuration in the case of composition I. With the increase of oxidiser to 20 per cent in compostion II, burning rate increases with rise in flame temperature to 1350 K, which contributes to a rapid vaporisation of phosphorus, leading to quick and enhanced obscuration. Any further rise in oxidiser content will only marginally raise the flame temperature, reducing the unreacted phosphorus content, though obscuration becomes quicker. Obscuration is expected to become poorer with rise in flame temperature since the surrounding atmospheric moisture tends to spped up vaporisation and reduction in drop growth size. Thus, obscuration is the lowest at the higher oxidiser content. Corresponding extinction coefficient values calculated for different wavelengths show the same tendency, which in actual indicate the amount of shadow cast per unit mass of the composition. Also, extinction coefficient calculated at different regions of the visible and IR spectrum goes on decreasing for compositions II to IV, the same when calculated for red phosphorus content of the composition remains at a constant value. Examination of the residue of the reaction indicated that all the phosphorus has

Table 3. Obscuration of compositions II at different humidity conditions

Relative humidity %	Obscuration (%)			
	0.4-0.7 (µm)	2-2.4 (µm)	3–5 (µm)	8–14 (µm)
15	94	82	70	45
55	99.8	90	75	68
85	100	100	88	76

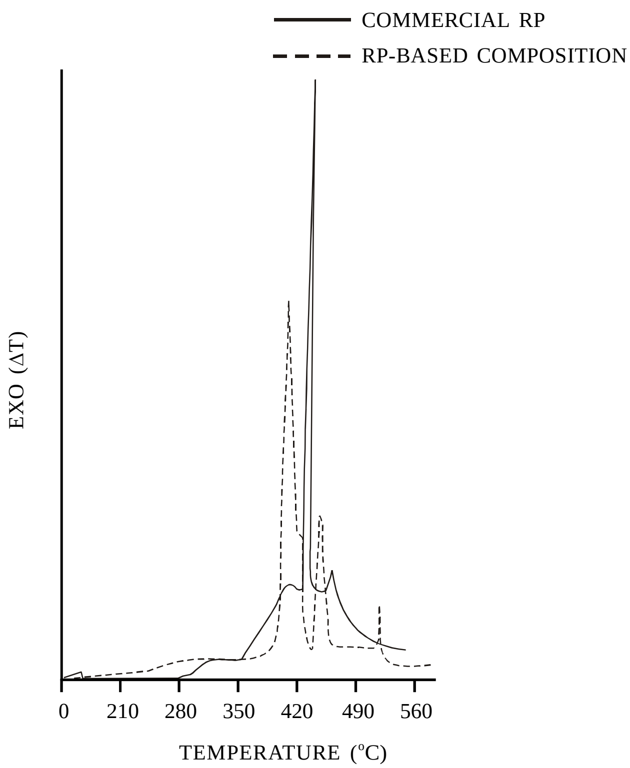

Figure 1. DTA of commercial red phosphorus and red phosphorus-based composition.

participated in the reaction. This also shows that the red phosphorus content of the composition alone is responsible for the obscuration character and not the binder.

The thermal analysis curve (Fig. 1) indicates a sharp exotherm for pure red phosphorus, which is the ignition reaction in air (683 K). The mixture of red phosphorus, potassium nitrate, and binder shows multiple exotherms with one sharp exotherm at 725 K. The increase in ignition temperature shows the increased thermal stability of the composition as well as safe processing since the red phosphorus particle is encapsulated by the binder.

4. CONCLUSION

Red phosphorus and potassium nitrate compositions exhibit favourable smoke screen formation conditions with highest obscuration. Since a rapid change in flame temperature and volume of gases occurs for a small rise in oxidiser content and also quickens the rate of aerodispersion, a combination containing 80 per cent red phosphorus and 20 per cent KNO_3 is preferred in high humid conditions, as the obscuration characteristics are considered to be due to the formation of P_2O_5 and subsequent reaction with moisture/humidity in the atmosphere.

REFERENCES

1. Holst, G.C. Tactical smoke increases survivability. *Armor*, 1984, **94**(3), 20.

2. HopFgarten, F. IR-screening smoke. *In* Proceedings of the 10th International Pyrotechnics Seminar, Karlsruhe, Bundesrepublik Deutschland, 1985. pp. 79-1 to 79-13.

3. Somayajulu, M.R.; Gautam, G.K.; Jayaraman, S. & Agarwal, J.P. Studies of characterisation and burning of red phosphorus-based smoke composition. *J. Energ. Mater.*, Jan-March 2003, 15-31.

4. Somayajulu, M.R.; Gautam, G.K.; Joshi, A.D.; Narayana & Agarwal, J.P. Phosphorus-based smoke compositions–towards safe processibility. *In* Proceedings of the 3rd International Seminar of High Energy Materials Society of India, 6-8 December 2000. pp. 539.

5. New infrared countermeasure grenades for Swiss Army. *Janes Int. Def. Rev.*, 2000, **33**, 16.

6. Milham, M.E.; Anderson, D.H. & Frickel, R.H. Infrared properties of phosphorus-derived smoke. *Applied Optics*, 1982, **21**, 2501-507.

7. Klusacek, L. The time characteristics making exact the screening by aerodispersion from smoke grenade with the charge based on red phosphorus. *Propell. Explos. Pyrotech.*, 1999, **24**, 314-18.

8. Hua, G.; Li, J. & Guang, W. Research on red phosphorus anti-thermal smoke composition and it its manufacturing process. *In* the 27th International Seminar on Pyrotechnic, Colorado, USA, 2000. pp. 239-43.

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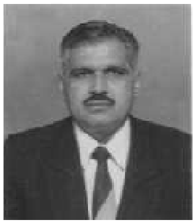

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