研究論文

IR-Screening properties of red phosphorus smoke

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Recently, red phosphorus is widely used in military applications as the base material in screening smoke munitions. In this study, in order to clarify the IR-screening properties, the IR transmission spectrum of red phosphorous smoke was measured in our laboratory. As the result, it was found that *far*- and *middle*- IR screening factor was absorption of phosphoric acid. It was also found that IR-screening performance was not dependent on the combination of oxidizer and metal, but dependent on the amount of red phosphorus.

1. Introduction

Red phosphorus (RP) is widely used in military applications as the base material in screening smoke munitions. It has an excellent visible and infrared screening performance, reduced reactivity compared with white phosphorus, and much less toxicity properties than either white phosphorus or zinc/hexachloroethane. It is said that RP will continue to remain the most important smoke producing material for military applications for at least the next 20 years [1].

However, there are few reports [2) 3) 4)] on IR screening mechanism of RP. In order to develop a smoke-producing reagent with high IR screening performance, it is indispensable to solve the IR screening mechanism.

Many night vision systems employ infrared (IR) devices with a wavelength ranging from 8μm to 12μm.

The objectives of this study are to understand the followings:

1) A fundamental characteristic of red phosphorus-derives infrared screening smoke.
2) A screening factor and performance in 8μm-12μm.
3) A relation between infrared screening performance and composition of smoke-producing agent.

Received : May 17, 2002
Accepted : August 23, 2002
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1.1 Formation mechanism of smoke

When phosphorous is being heated, phosphorus begins to evaporate, and at the temperature of 323K-333 K the vapors become to be oxidized with air oxygen where 75%-80% of initial material will react. Phosphorus consisted of RP and WP (white phosphorous) was mixed with oxidants and the mixtures are applied to different types of smoke system. Phosphorus can be oxidized with air oxygen or the oxygen generated from oxidants into phosphoric oxide, which could be changed to trihydrogenphosphoric acids with heat release as the result of reaction with moisture in air. The following scheme has been proposed for this process [5]:

$$4\ P + 5\ O_2 \rightarrow 2\ P_2O_5 + \text{heat}$$
$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4 + \text{heat}$$
$$H_3PO_4 + n\ H_2O \rightarrow H_3PO_4 \cdot n\ H_2O$$

1.2 Consideration of screening factor

Three factors should be considered for IR screening by smoke-producing agents: absorption, dispersion, and radiation.

1.3 Lambert-Beer's Law

Lambert-Beer's Law is well-known as an expression of relations indicating absorption of light for not only infrared radiation but also all the other radiation.

Logarithm of the reciprocal of transmittance (I/Io) is proportional to the absorption coefficient α (m^2/g), which is a constant for a medium, concentration C (g/m^3), pass length L (m). These relations will be expressed in the following formula.

$$\ln(Io/I) = \alpha \cdot C \cdot L \qquad (1)$$

In this study, the smoke concentration C (g/m^3) was defined in the following formula, where rate of smoke formation c (-), mass of agent w (g), and chamber volume V (m^3).

$$C = c \cdot w/V \qquad (2)$$

Eq.(2) and $V = 1$ (m^3) are substituted for Eq.(1), and the following equations can be obtained.

$$\ln(Io/I) = \alpha \cdot c \cdot w \cdot L \qquad (3)$$

$$\alpha \cdot c = \ln(Io/I)/(w \cdot L) \qquad (4)$$

A value $\alpha \cdot c$ has been used to evaluate IR screening performance under the condition of fixed quantity and distance.

2. Experimental

2.1 Equipment

Fig. 1 shows the experimental set-up and instruments used in this study. Burning tests were conducted by using a combustion chamber. IR transmittance (I/Io) was measured before and after combustion of smoke-producing agents.

Two equipments were used for smoke characterization. One was an IR spectral analyzer, which can measure the infrared spectrum radiated from the black body furnace before and after combustion, and then calculates a transmittance rate. The other one was a thermal imager, which can evaluate the screening situation of a hot plate as an image, and measures the hot plate temperature and the background temperature before and after combustion. The details of the equipments are described as below:

1) Smoke chamber

Smoke chamber with a volume of 1 m^3 was a highly gas tight-cube constructed with acrylics boards. In order to uniform the smoke concentration, the small fan was attached into the smoke chamber.

2) IR spectral analyzer

An IR spectral analyzer SA200 made by Minarad Co. was used for measurement of the amount of IR transmissions. This equipment has a measurement range from 1.4μm-13.4μm. A black body furnace (1000℃) made by the same company was used as an IR reference.

3) Thermal imager

A thermal imager 6T62 made by NEC SANEI Co. was used for measurement of hotplate temperature. The infrared detecting element is

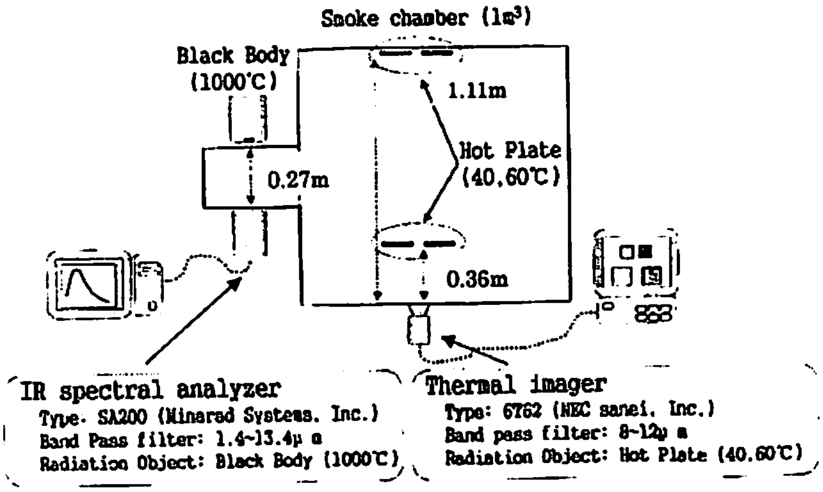

Fig. 1 Experimental set-up and performance of instrument.

Hg-Cd-Te. This equipment has the performance to measure an IR spectrum ranging from 8μm-12μm by using band pass filters. Temperature measurement range is 50-2000℃ with a minimum detection differences in temperature of 0.1℃ with an accuracy of ±0.5%. As an IR radiation reference, a hotplate made by our company was used and temperature can be adjusted by changing input voltage.

4) Ignition device

An electric heat line was used for ignition in order not to generate gas other than a smoke-producing agent.

2.2 Sample

Combinations of red phosphorus, an oxidizer, and a metal were employed to three kinds of compositions, A, B, and C, as basis compositions. In addition to these basis compositions, red phosphorus ratios were changed under a fixed condition for an oxidizer and a metal. All the detailed compositions are shown in Table 1.

Table 1 Composition of smoke-producing agents

	Base material	Oxide + Metal	Binder
Smoke A	Red Phosphorus 55,60,65,70,75%	Nitrate A + Mg, Zr/Ni	5 %
Smoke B		Sulfate B + Mg	12 %
Smoke C		Sulfate C + Mg	5 %

3. Analysis

3.1 IR spectral analyzer

Transmittance (I/Io) in 8μm-12μm region was calculated from the IR transmission spectra(Fig. 2, 3). A relation between the abscissa mass w (g) and the ordinate $\ln(Io/I)$ is shown in Fig. 4.

$\ln(Io/I)$ and w exhibited a linear relationship. By setting proportionality constant to be k, they are expressed as follows.

$$\ln(Io/I) = k \cdot w \qquad (5)$$

IR screening performance $\alpha \cdot c$ becomes the following simple expression from equations (4) and (5) (see Table 2).

$$\alpha \cdot c = k/L \qquad (6)$$

Table 2 IR screening performance of unit mass and unit distance.

	Smoke A	Smoke B	Smoke C
αc*	0.355	0.438	0.374
γ**	0.342	0.403	0.357

*ac= $\ln(Io/I)/(w \cdot L)$ is the value which calculated by L=0.27m and w=1g.

**g=$\ln\{(To\text{-}to) / (T1\text{-}t1)\} /(w \cdot L)$ is the value which calculated by L=1.11m and w =1g

3.2 Thermal imager

The following analyses were performed from the images (Fig. 5) obtained by the thermal imager. The hotplate and the background temperature before burning by thermal imager are set to be Tb and to, and similarly T_1 and t_1 after 3 minutes passed from the end of burning. The temperature change rate $(T_1\text{-}t_1)/(To\text{-}to)$ before and after the burning can be obtained, which is the difference in temperature of the hotplate and the background temperature.

A plot of the mass of smoke-generating agent against $\ln\{(Tb\text{-}to)/(T_1\text{-}t_1)\}$ is shown in Fig. 6 for the smoke-producing agents A, B, and C. $\ln\{(Tb\text{-}to)/(T_1\text{-}t_1)\}$ and w showed a linear relationship. Thus the following equation can be obtained where k' is a proportionality constant:

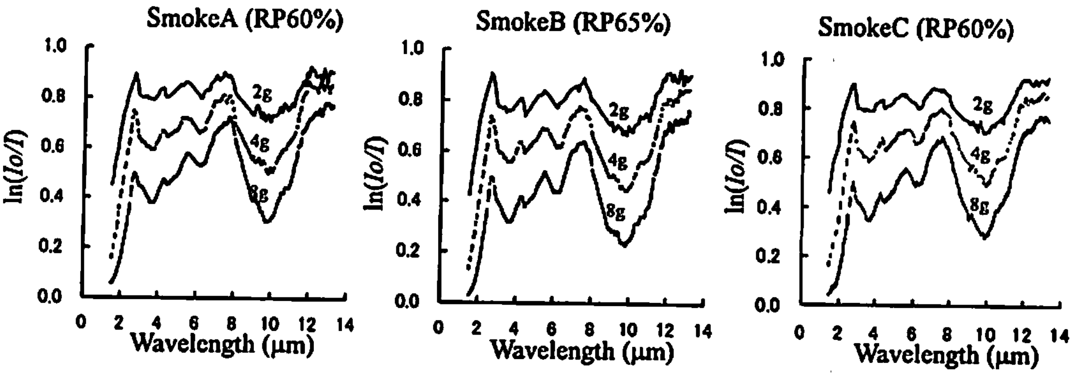

Fig.2 IR transmission spectra – effect of mass of agent.

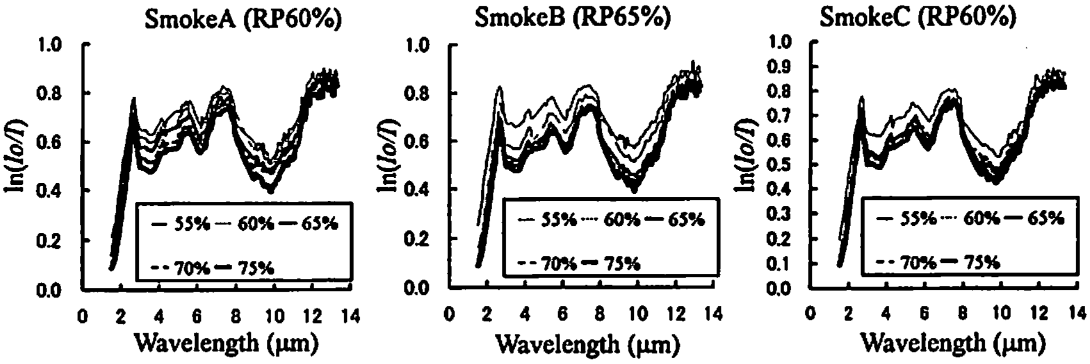

Fig.3 IR transmission spectra – effect of RP content.

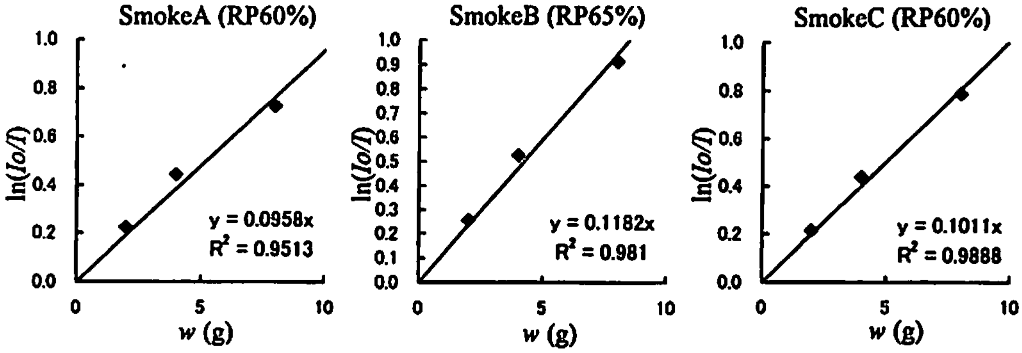

Fig.4 Relationship between ln (Io/I) and w (8-12μm range).

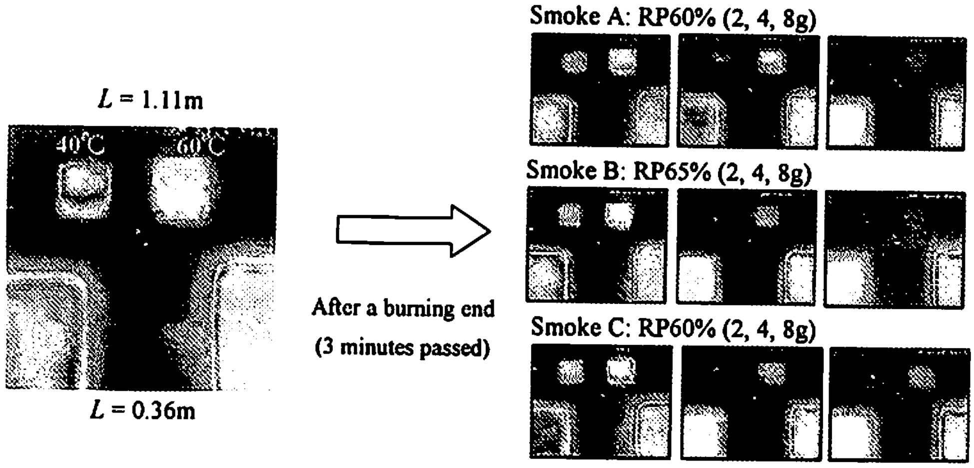

Fig.5 Results of images measured with the thermal imager.

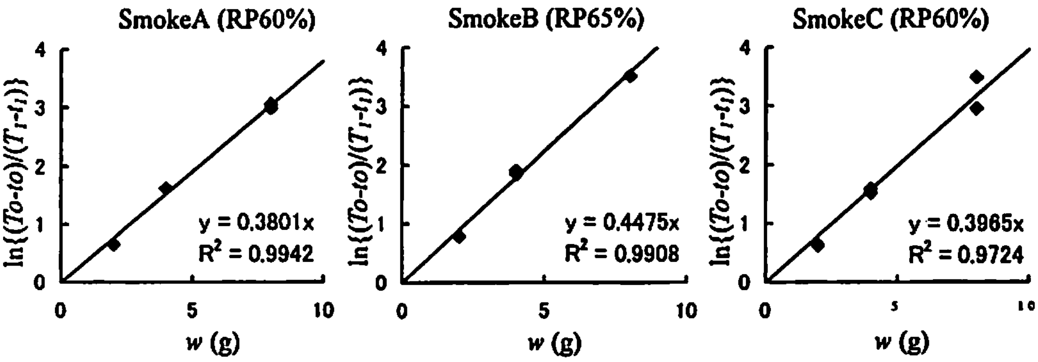

Fig.6 Relationship between ln $\{(To\text{-}to)/(T_1\text{-}t_1)\}$ and w (8-12μm range).

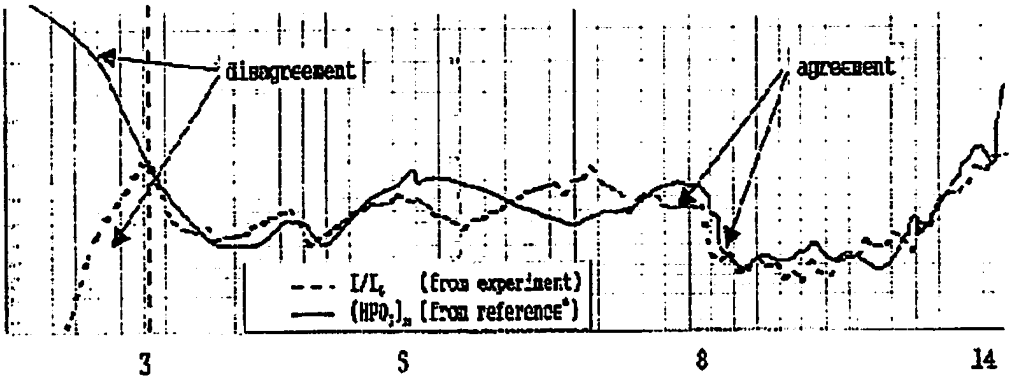

Fig.7 Comparison of *I/Io* and the absorption spectrum of $(HPO_3)n$

$$\ln\{(Tb-to)/(T_1-t_1)\}=k'\cdot w \quad (7)$$

γ is the rate of change as below (see Table 2).

$$\gamma = k'/L \quad (8)$$

4. Discussions

4.1 IR screening factor

The IR transmittances of each red phosphorus smokes obtained in this experiment was the same. A comparison between the absorption spectrum of metaphosphoric acid $(HPO_3)_n$ [6] and the typical IR transmittance (*I/Io*) obtained from this experiments is shown in Fig. 7. Since the transmittance (*I/Io*) is in good agreement with the absorption spectrum (reference) of phosphoric acid on larger wavelength than 3μm, it can be thought that the far- and middle-IR screening factor in this region is absorption. Moreover good agreement between the IR transmittance (Fig. 4) by IR spectral analyzer and the Lambert-Beer' law strongly suggests that a screening factor is absorption.

But, since the transmittance (*I/Io*) is not in agreement with the absorption spectrum (reference) of phosphoric acid in smaller wavelengths less than 3μm, near-IR screening factor in this region is considered to be anomalous absorption. According to the Mie theory, dispersion serves as the maximum in the wavelength of the same length as the diameter of a particle of smoke (Fig. 8)[7]. In this study, although dispersion was not taken into consideration, the IR-screening factors in visible and near-infrared region are based on dispersion.

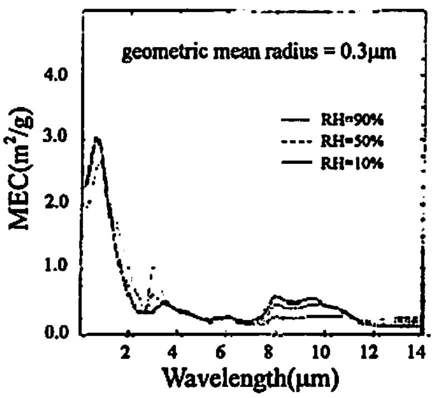

Fig.8 Examples of a calculation of a mass extinction coefficient (MEC)estimated by Mie's dispersion theory.

4.2 IR screening performance and composition

When RP content was changed in the smoke-producing agents A, B, and C, the value of $\alpha\cdot c$ changed as shown in Fig. 9. In the range of 55%-75% of RP(s), the value of $\alpha\cdot c$ was proportional to RP content (%). Thus we could understand that the IR screening performance become higher as RP content increases. Conversely, it can be said that there will be little influence of an oxidizer and

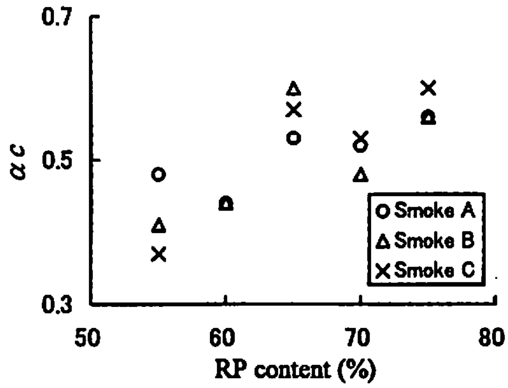

Fig.9 IR screening performance αc and RP content

a metal on IR screening performance.

Although RP content should be increased in order to increase IR screening performance, there is a practical limit in this method.

4.3 IR spectral analyzer and Thermal imager

About each composition, a graph plotting of the IR screening performance $\alpha \cdot c$ and the rate of change γ is shown in Fig. 10. Since γ correlated with $\alpha \cdot c$, we consider that γ from a thermal imager is applied to the Lambert-Beer's law. We can estimate the temperature of- change rate from the observed IR transmission spectrum.

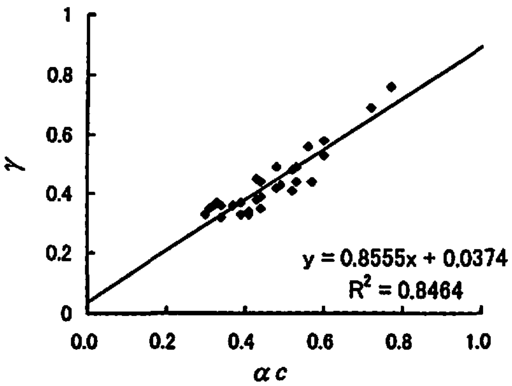

Fig.10 Correlation αc and γ

5. Conclusions

We obtained the following infrared screening properties of red phosphorus smoke.

1) *Far* - and *middle*- IR screening factor was absorption of phosphoric acid.
2) IR screening performance was not dependent on the combination of oxidizer and metal, but dependent on the amount of red phosphorus.
3) Observed results of thermal imager can be predicted from the results of spectral analyzer.

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