Defence Science Journal, Vol. 57, No. 6, November 2007, pp. 817-824

# Stabilisation of Red Phosphorus to Prevent Moisture Absorption and Suppression of Phosphine Release

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## ABSTRACT

Red phosphorus (RP) is an essential ingredient to generate smoke for multi-spectral obscuration and is receiving wide attention throughout the world for military applications. However, oxidation of phosphorus occurs in moist air resulting in the formation of various phosphorus acids and subsequently the evolution of the toxic gas, phosphine ($PH_3$), even in the sealed systems. Entrapped moisture leads to deterioration of the stores. The commercial-RP at ambient temperature and 95 per cent RH conditions indicates 15 per cent moisture absorption and 13 per cent acidity development with the generation of more than 100 ppm of phosphine gas. Efforts were made to overcome this problem by suppressing acid formation. The technology adopted was: (i) use of stabiliser, and (ii) doping stabiliser-coated particles with polymeric substance. The aim to use metal oxide as stabiliser was to neutralise the phosphorus acids, which are catalysing the phosphine generation. $MgO$ due to its basic nature seems to be faster than amphoteric $Al_2O_3$, in removing the acid from site of reaction, thus suppressing the phosphine release effectively. Though $MgCO_3$ as stabiliser suppresses moisture absorption and acidity development, phosphine release is not controlled effectively. Study of RP coated with these materials independently and monitoring them at different RH conditions indicated superiority of $MgO$ in suppressing acidity and phosphine formation.

**Keywords:** Smoke, red phosphorus, multi-spectral obscuration, phosphorus acids, phosphine, stabiliser

## 1. INTRODUCTION

Development of red phosphorus (RP) smoke composition has brought about extensive attention[1-5] because the yield of phosphorus smoke increases quickly with the increase of relative humidity increasing smoke for multi-spectral obscuration[6-8] (visible light, infrared radiation of 1-3 µm, 3-5 µm, 8-14 µm and the laser among this wave band) . The chief ingredients of the composition are RP, oxidiser and binder. The RP used in this study was commercially manufactured by heating white phosphorus to 250 °C-300 °C in the absence of air. The hard lumps of the RP obtained is grinded with water, boiled with sodium nitrate solution to remove unreacted white phosphorus and finally washed with boiling water. The red allotrope of phosphorus is distinguishable from the white form by its reduced reactivity, insolubility in solvents and essentially non-toxic character. The extinction quality of the RP smoke compositions is excellent. But one significant problem with RP powder is that it decomposes in moist air and releases toxic phosphine gas and formation of different phosphoric acids as per the reactions:

Received 10 April 2007, revised 30 August 2007

$$4P + 5O_2 \longrightarrow 2P_2O_5 \uparrow$$

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4 \uparrow$$

$$4P + 6H_2O \longrightarrow 2H_3PO_3 + 2PH_3 \uparrow$$

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3 \uparrow$$

The decomposition rate depends directly on the availability of moisture and temperature[9]. Phosphine is a flammable, chemically reactive and highly toxic gas. The fatal dose for phosphine is 0.0003 mg/kg/d based on body weight and clinical parameters.

Phosphorous acids and phosphine also have the propensity to react with metal components particularly copper and brass which can lead to the failure of munitions to function due to internal corrosion and also these metals serve as catalysts in the oxidation of phosphine. The present investigation acquires important dimensions since human exposure to this smoke, either during storage or combustion, causes harm. A systematic study is carried out by storing RP, RP doped with different stabilisers, and RP-based formulations at different humid conditions. Commercially available quick reaction tubes are used for quantitative measurement of phosphine liberation though literature mentions about other analytical methods[10] as well.

## 2. EXPERIMENTAL

### 2.1 Materials

Commercial RP (98 %) conforming to IS Specification no. IS - 2012, obtained from M/s United Phosphorus, Vapi, India was used as a chief constituent of the compositions. Different metal oxides/salts were selected for stabilisation and doping of RP. The stabiliser and their specifications are:

- Magnesium oxide, light pure (Specification no. IS-11803: 1998)
- Alumna activated, neutral (Specification no. IS-9700: 1991) and
- Magnesium carbonate (Specification no. IS-1420:1989)

Potassium nitrate Grade I conforming to IS-301 -1963 specification was dried at 110 °C for 3 h. Grinded $KNO_3$ after passing through 120 BSS and retained on 240 BSS was used as an oxidiser. Phenolic resin, HR6312 of 240 BSS size dissolved in a suitable solvent was used as a binder.

### 2.2 Methods

#### *2.2.1 Coating of Red Phosphorus*

Commercial red phosphorus received from M/s United Phosphorus, was coated with 3 per cent, of stabilisers in an incorporator. The RP thus stabilised was used in all the experiments.

#### *2.2.2 Preparation of Composition*

100 g of composition was mixed in an antistatic bowl using an antistatic spatula. All the compositions contained 5 per cent organic binder by weight. Stabilised RP was mixed with four parts of binder, potassium nitrate was mixed with one part of binder and both the coated-RP and $KNO_3$ were then mixed for 5 min for intimate mixing.

Composition was then passed through 12 BSS and granulated material kept for drying for 24 h at ambient conditions in a vacuum desiccators.

#### *2.2.3 Test Set-up for Phosphine Measurement*

Commercial RP, stabilised RP and compositions were stored under 30 per cent, 70 per cent and 95 per cent relative humidity conditions and at room temperature. Moisture absorption was monitored at periodic intervals. A house made 1 litre glass apparatus (Fig. 1) was fabricated for the purpose with three outlets. The central outlet was used for suspending the sample (in a glass holder) over the standard saturated solution for different humid conditions.

One of the side outlets fitted with a rubber septum for sample gas withdrawal through a specifically designed syringe while the remaining outlet is used for air recoup. 3 g of sample was taken in the glass holder.

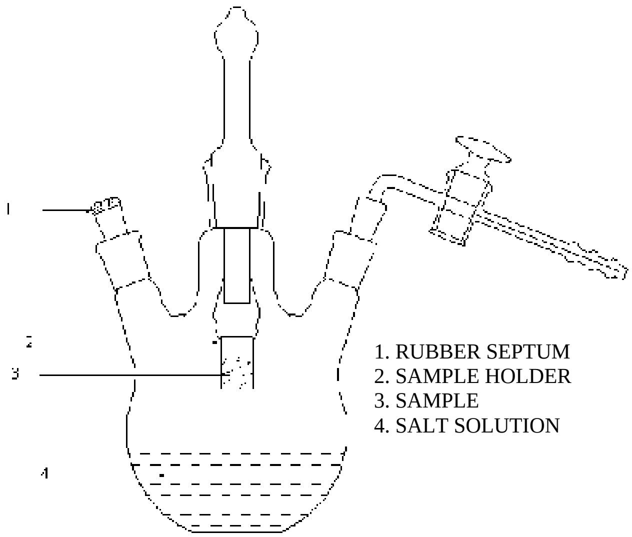

**Figure 1. Phosphine measurement set-up.**

### *2.2.4 Phosphine Measurement*

Evolved phosphine was measured using a precision gas detector, which consists of two parts, viz., (i) gas detector tubes and (ii) air sampling pump. The air sampling pump is used to draw a precisely defined volume (100 cc) of sample air through the detector tube for determining the impurity gas concentration in the air sample. A solid carrier material impregnated with sensing chemical is sealed in glass tube with tapered tips. When the sensing chemicals come in contact with a specific gas or vapour a discoloured stain develops. The tubes are calibrated for a fixed volume of air sample, which is drawn using a sample draw pump. The scale of on the glass tube reads the stain length in ppm of contaminant gas concentration. This method of measurement is accurate and values found to be reproducible. The set up of sampling tube and pump is a proprietary item of M/s United Phosphorus Ltd., Vapi, India and is shown in Fig. 2.

**Figure 2. Sampling pump and phosphine detection tube.**

### *2.2.5 Moisture Content*

10 g of different samples in a silica crucible 30 mm dia were weighed and kept in a desiccator, wherein different RH conditions are maintained. Weight was monitored at periodic intervals.

### *2.2.6 Acidity and Alkalinity Measurement*

Percentage acidity and alkalinity was determined as sulphate and carbonate respectively. Moisture absorption monitored for the commercial RP during its storage at different RH conditions is shown in Fig. 3(a), while phosphine release by commercial red phosphorus at different RH conditions is plotted

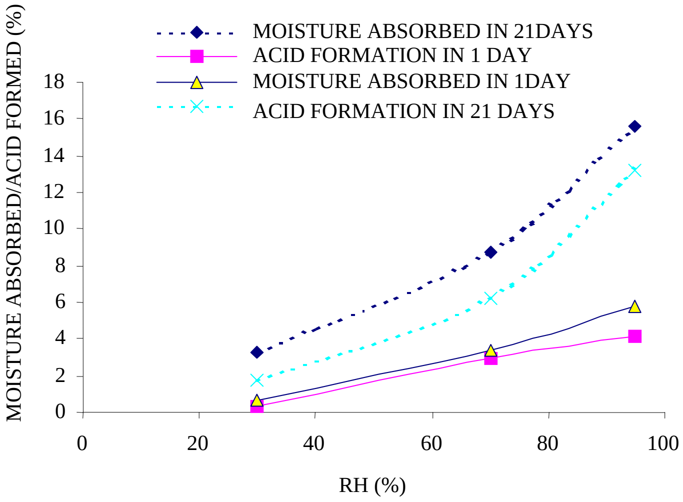

**Figure 3(a). Behaviour of commercial red phosphorus.**

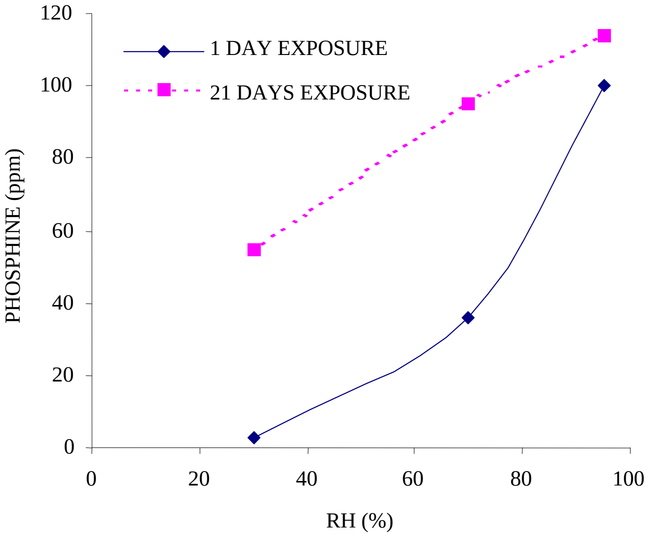

**Figure 3(b). Phosphene formation in commercial red phosphorus.**

in Fig. 3(b). Moisture absorption followed by alkalinity/acidity with different stabilisers and phenolic resin-doped stabilised RP data is shown in Table 1. Figures 4 and 5 indicate behavioural trends of coated-RP and compositions processed. The phosphine gas liberated by different stabilisers–coated samples and compositions at different RH conditions are shown in Figs 6 and 7.

## 3. RESULTS AND DISCUSSION

Commercially available RP shows the tendency to absorb moisture with increased humidity and it is exponential at higher humid conditions. It can be observed that this value increases from 0.7 per cent at 30 per cent RH in one day to 15.6 per cent at 95 per cent RH in 21 days[11]. While moisture absorption, acidity/alkalinity development and phosphine release are slow initially the slope drastically changes beyond 70 per cent RH as can be seen from Figs 3(a) and 3(b). Since moisture absorption and acid/alkali formation curves follow the same trend for one day or 21 days exposure, it can be deduced that humidity complicate the storability, it also leads to simultaneous acidity development and phosphine release. While acid content goes up from 0.3 per cent to 13.2 per cent, phosphine release goes up from 3 ppm to >100 ppm. One point of observation is even at the same RH prolonged storage also leads to increase of acidity as well as phosphine release. The limitation of the experimentation is that phosphine release beyond 100 ppm could not be monitored under the present experimental setup.

Classical chemistry of phosphorus indicate that the reactions of phosphorus trioxide produced during the oxidation of stored phosphorus, are very complicated and produces among other products $PH_3$, phosphoric acid, and elemental phosphorous. It may be point of noteworthy that phosphorus acid itself and all trivalent phosphorus acids are thermally unstable leading to phosphine formation as per the equation:

**Table 1. Moisture absorption and acidity data on red phosphorus with stabilisers and binder at different RH conditions.**

| Sample | (%) | 30 % RH |  | 70 % RH |  | 95 % RH |  |
|---|---|---|---|---|---|---|---|
|  |  | 1 day | 21 days | 1 day | 21 days | 1 day | 21 days |
| RP coated with 3 % $Al_2O_3$ | Moisture absorption | Nil | 2.1 | 0.9 | 3.9 | 1.2 | 8.6 |
|  | Acidity/ Alkaline | Nil | 0.9 Acidic | Nil | 3.4 Acidic | 0.7 Acidic | 6.3 Acidic |
| RP coated With 3 % $MgO$ | Moisture absorption | Nil | 0.8 | Nil | 1.4 | 0.4 | 2.3 |
|  | Acidity/ Alkaline | 0.1 Alkaline | 0.09 Alkaline | 0.1 Alkaline | 0.06 Alkaline | 0.1 Alkaline | 0.03 Acidic |
| RP coated with 3 % $MgCO_3$ | Moisture absorption | Nil | 0.49 | Nil | 1.7 | 0.7 | 5.7 |
|  | Acidity/ Alkaline | 0.09 Alkaline | 0.07 Alkaline | 0.09 Alkaline | 0.6 Acidic | 0.09 Alkaline | 1.2 Acidic |
| Composition containing 3 % $Al_2O_3$ and phenolic resin | Moisture absorption | Nil | 1.8 | 0.4 | 2.5 | 0.8 | 6.4 |
|  | Acidity/ Alkaline | Nil | 0.5 Acidic | Negligible Acidic | 1.4 Acidic | 0.3 Acidic | 3.2 Acidic |
| Composition containing 3 % $MgO$ and phenolic resin | Moisture absorption | Nil | Nil | Nil | Nil | 0.1 | 0.6 |
|  | Acidity/ Alkaline | 0.07 Alkaline | 0.07 Alkaline | 0.07 Alkaline | 0.06 Alkaline | 0.07 Alkaline | 0.04 Alkaline |
| Composition containing 3 % $MgCO_3$ and phenolic resin | Moisture absorption | Nil | 0.3 | Nil | 0.9 | 0.5 | 2.9 |
|  | Acidity/ Alkaline | 0.06 Alkaline | 0.06 Alkaline | 0.06 Alkaline | 0.04 Alkaline | 0.08 Alkaline | 0.6 Acidic |

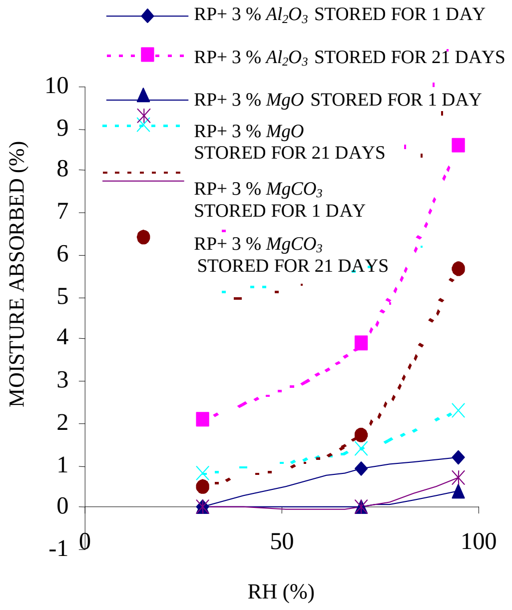

**Figure 4. Moisture absorption of red phosphorus with different stabilisers.**

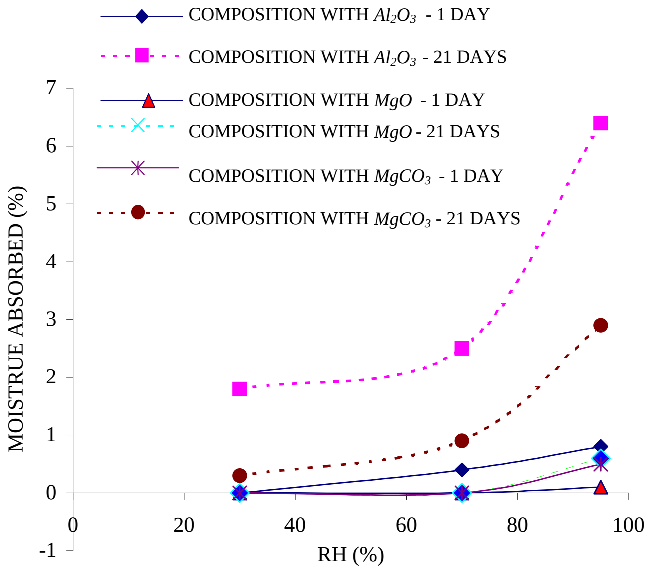

**Figure 5. Moisture absorption of composition using different stabilisers.**

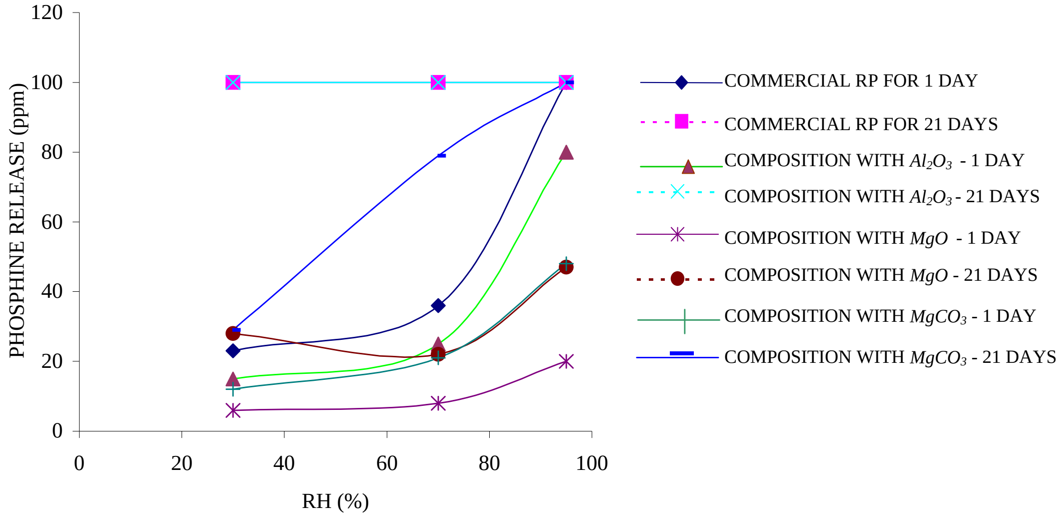

**Figure 6. Phosphine release of red phosphorus using different stabilisers.**

$$2H_3PO_2 \longrightarrow H_3PO_4 + PH_3 \uparrow$$

$$3H_3PO_2 \longrightarrow 2H_3PO_3 + PH_3 \uparrow$$

$$4H_3PO_3 \longrightarrow 3H_3PO_4 + PH_3 \uparrow$$

In basic solution

$$1/4P_4+3H_2O+3e \longrightarrow PH_3\uparrow+3OH^- \quad E^o=-0.89 \text{ v}$$

Pure phosphine alone is not inflammable but inflames due to the traces of $P_2H_4$ and literature mentions that phosphorus alone forms diphosphine ($P_2H_4$), which is unstable and decomposes on exposure to light.

$$3P_2H_4 \quad 4PH_3\uparrow + 2P$$

It may be mentioned that phosphine generation in the higher humid conditions even in sealed systems, at times leads to accidental initiation as well. Therefore it is necessary to treat RP before incorporating

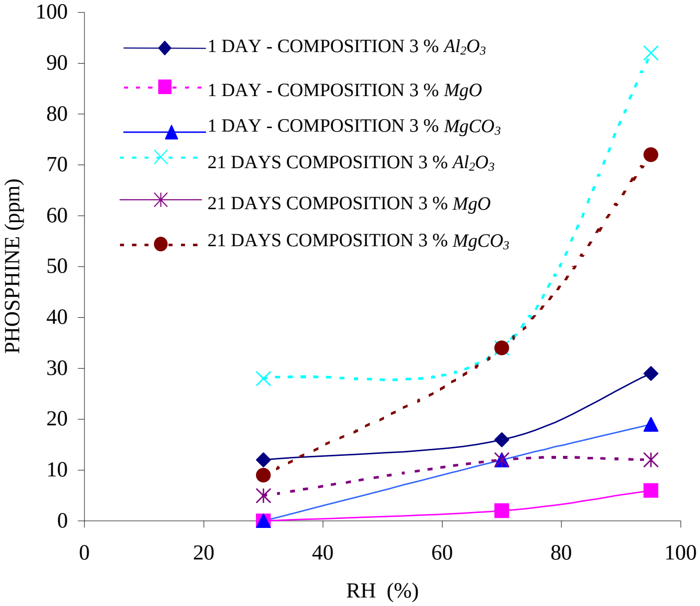

**Figure 7. Phosphine release from composition.**

into composition preparation and use in further applications.

To reduce acid/alkali formation and to suppress phosphine generation, commercial red phosphorus was coated with different stabilisers. The selection criteria was: pH measurement of phosphine show that the solution is neither acidic nor basic and the acid constant is ~$10^{-29}$ and the base constant is ~$10^{-26}$. Basic oxide therefore leads to suppression of acidity. *Mg* salts are thus one of the favorable additives. It can be seen from Table 1 that the moisture absorption has been drastically reduced to 2.3 per cent from 15.6 per cent maximum in 21 days, with simultaneous reduction in phosphine release to 47 ppm in highest humid conditions. At the same time acidity also has shown lower values of 6.3, 0.03 for $Al_2O_3$ and $MgO$, respectively, though this figure is minimum when coated with $MgO$ even at 95 per cent RH (Fig. 4).

The observation was different in case of $MgCO_3$-coated RP. $MgCO_3$-coated RP shows alkalinity from day one and moisture absorption was minimum with 1.7 per cent moisture absorption even after 21days at 70 per cent RH.

Contrary the phosphine release at the same period was highest. This can be explained due to the weak $H_2CO_3$, which may not contain acidity development under high humid conditions. The on sight oxy acids readily influences phosphine formation thus explains the highest phosphine formation of >75 ppm even at 70 per cent RH conditions.

In case of $Al_2O_3$ as stabiliser moisture absorption is higher which influences higher acidity and higher phosphine release. RP with 3 per cent $MgO$ stabiliser stored even for 21 days at 95 per cent RH has absorbed 2.3 per cent and rate of absorption is also very slow as can be seen from the slope in Fig. 4. In case of $Al_2O_3$ and $MgCO_3$ stabilised RP the moisture absorption rate is exponential beyond 70 per cent RH, while the RP stabilised with $MgO$ the moisture absorption rate is slow. Same tendency is seen in case of composition with $Al_2O_3$ and $MgCO_3$ stabilised, though the extent of moisture absorption is low as seen in Fig. 5. This observation is assigned due to the encapsulation of stabilised RP with phenolic resin.

The contrast of phosphine release between commercial RP and composition with different stabilisers can be seen in Fig. 6 wherein it can be observed that phosphine release is more than 100 ppm at all humid conditions for commercial RP stored for 21 days. The straight line parallel to X-axis is not a true representation of the behaviour because of the experimental limitation.

It is also the case with $Al_2O_3$ stabilised composition stored for 21days.Therefore, it emerges from the above observations that moisture absorption is poor for $MgO$-coated RP as well as the rate of absorption over prolonged period is also small. On the contrary in case of $MgCO_3$-coated RP, over prolonged period of storage at higher humid conditions-moisture absorption increases exponentially.

From Fig. 4, it can also be seen that moisture absorption values at 30 per cent RH are very close in these cases, though the slopes differ drastically.

Further, in case of $MgO$-coated RP, while moisture content increase from 0.8 per cent –> 1.4 per cent –> 2.3 per cent, the RP particle environment changes from alkalinity –> near neutrality –> acidity (Table 1).

Though general tendency of more phosphine release in acid and high humid conditions is obeyed, at 70 per cent RH, a near-neutral RP environment causes mild decrease in phosphine release as can be seen from Fig. 6.

While RP doping with stabiliser is adsorption phenomenon, binder coating is expected to provide better encapsulation thus a thin layer around RP particle that of stabiliser followed by binder minimises moisture absorption as could be seen from the reduced levels of moisture followed by reduced acidity. Comparison of phosphine release levels in Figs 6 and 7 indicates the influence of binder on composition. There is an overall reduction in phosphine release in case of composition at all RH conditions.

It can also be seen in Fig. 7, while compositions with $Al_2O_3$ and $MgCO_3$ show growth in phosphine release with increased days of storage, only composition with $MgO$ stabiliser becomes a constant value reduced to the minimum level. Thus the study indicates that red phosphorus stabilised with 3 per cent $MgO$ is maximum effective in suppressing the acidy and phosphine release. Any increase of stabiliser will only add to inert addition with no gain in terms of stabilisation. It has also been observed that 3 per cent $MgO$-coated RP after storing at sealed ambient conditions for 16 months also indicate basicity with lower phosphine liberation.

## 4. CONCLUSIONS

It can be said that the stability of RP against air and humidity can be improved by addition of $MgO$ as stabiliser. Doping further by binder improves stability. The coated and stabilised RP developed reduce the hazards in the manufacturing and can lead to shelf life improvements in the RP-based smoke compositions. At different RH conditions acid formation and phosphine liberation was suppressed effectively by $MgO$ stabilised RP.

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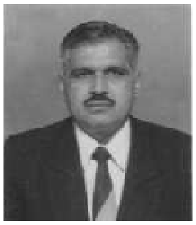

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