Phosphine Retention in New and Aged Fumigation Sheets

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Newly acquired, and naturally- and accelerated-aged fumigation sheets of different types were tested for retention of phosphine under a lab setup. In a 24-h test the decreasing order of retention of the gas by the newly acquired sheets was: carbon impregnated low density polyethylene (LDPE) (225-250 µ, 0 per cent gas loss) > polyvinyl chloride (PVC, 255 µ) > PVC coated fabric (310-335 µ) > high density polyethylene (HDPE, 85 µ) > LDPE without carbon impregnation (140 µ) > multilayered cross laminated (280 µ) > HDPE woven fabric with LDPE coating (260-330 µ) > LDPE (75 µ) and HDPE (70 µ) > multilayered cross laminated (140 µ) > rubberised fabric painted with aluminium on one side (650 µ, 16 per cent loss). Sheet samples after accelerated ageing (exposed to 70 ± 1 °C for 7 d) showed higher gas retention than the newly acquired sheets. Phosphine retention decreased significantly after natural ageing of sheets by keeping in the open and exposed to sunlight, wind and rain for 5 months. The results indicate that all sheet types tested, except the rubberized fabric, and carbon impregnated LDPE, multilayered cross-laminated and HDPE woven fabric coated with LDPE were suitable, for indoor and outdoor fumigation with phosphine, respectively. The accelerated ageing improved the phosphine retention properties of sheets in general.

Introduction

Sheeted or cover fumigation using phosphine for insect pest control is commonly practiced in India and other countries adopting a bag-storage system for food grains. Sheeted fumigations are carried out for stacks held indoors as well as outdoors. Different types of gas-proof or fumigation covers and sheets are available for bag-stack fumigation. Factors such as cost, local availability, strength, resistance to damage and permeability of fumigant gases are considered in the selection of fumigation sheets. For a successful fumigation, retention of insecticidal concentration of phosphine inside a stack during the exposure period is important. Phosphine retention, however, is known to vary with different types of gas-proof sheets. The gas retention property of sheets is likely to be affected by repeated handling during fumigations. Fumigation sheets or covers manufactured and marketed in India are expected to conform to the standards prescribed by The Bureau of Indian Standards (BIS), viz., for low density polyethylene films, double texture rubberized fabrics, polyvinyl chloride and polyethylene woven and coated and laminated films/fabrics, and multilayered cross laminated sheets and tarpaulins/ covers. Data on phosphine retention property of various films available in this country as tested by the methods prescribed by BIS are lacking. Furthermore, very little information is available about the changes, if any, in the retention property of these sheets upon ageing, either naturally or by that achieved by accelerated methods. It was, therefore, intended to examine phosphine retention property of different types of gas-proof sheets available in India as new and aged ones.

Materials and Methods

Different types of gas-proof sheets, as new ones, were obtained from fumigation sheet manufacturers/suppliers and user organizations. A dead load micrometer was used to measure thickness of sheets. The phosphine retention by the sheets, as new and after ageing, was tested according to the BIS standard method carried out at 27 ± 2 °C and 65 ± 5 per cent relative humidity (RH). The above test is essentially

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based on the vapour transmission test developed by Muldoon et al. The sheet was sandwiched between two specially designed stainless steel cells or chambers of 1.4 L capacity with rubber gaskets on either side. 'G' clamps were used along the rims of cells for tight fitting. Phosphine was generated from commercially available aluminium phosphide tablets in a gas burette on 10 per cent sulphuric acid solution. The phosphine thus generated was used in dosing chambers for testing. The top chamber was dosed with phosphine at 3 g/m². After 24 h the amount of phosphine that has permeated through the test-sheet into the lower chamber containing 10 per cent mercuric chloride solution was estimated by titrmetry. Two to six replicates were carried out for each sheet type. The average loss of phosphine was determined after deducting blank values in each case.

A duplicate batch of samples was aged by the accelerated ageing method of BIS. Samples of size 30 cm X 30 cm were placed in an incubator maintained at 70 ± 1 °C for 7 d. After ageing, the sheets were tested for phosphine retention as described above. Another set of duplicate samples was kept hung in the open, freely exposed to sunlight, wind and rain without any protection. After five months, the samples were tested for phosphine retention as mentioned before. The average loss of phosphine in 24 h was determined in each case. The phosphine retention by naturally- or accelerated-aged sheet samples was separately compared with that of the corresponding new sheets by Student's t-test for the difference.

Results and Discussion

Phosphine retention varied over sheet types. As new sheets, carbon impregnated LDPE sheet (225-250 μ) and PVC films, plain or coated, showed the highest retention whilst rubberized fabric was the least retentive (Table 1). Within a type, the phosphine permeability varied with sheet thickness. In multilayered cross-laminated film of 280 μ thickness, phosphine loss of 3.9 per cent/24 h was recorded whereas the lower thickness sheet of 140 μ the loss was high at 6.8 per cent/24 h. Upon accelerated ageing, there was improvement in gas retention in general. In contrast, the films aged naturally by exposure to sunlight, rain and wind in the open for 5 months showed increased permeability to the gas. Naturally aged HDPE films either became brittle and hence suffered physical damage or they retained low amounts of phosphine as reflected by 67 per cent loss/24 h. Similar poor gas retention was also observed in naturally aged LDPE films without carbon impregnation.

As per the BIS standard a fumigation sheet or cover should retain at least 92.5 per cent (or a maximum of 7.5 per cent loss) of applied phosphine. As new sheets, all tested materials, except rubberized fabric, conformed to the BIS standard requirement. The BIS method uses determination of the precipitate formed by the reaction between escaped phosphine and mercuric chloride. It is relatively a less sensitive method when compared with the gas chromatographic method or techniques using specific electrochemical sensors for measuring phosphine. It has been found that the BIS method could not detect phosphine concentrations of 180 ppm (0.25 g/m³) or less (Rajendran & Gunasekaran, unpublished data). Yet the method is widely followed to check whether a given fumigation sheet has sufficient phosphine retention property or not.

Using phosphine-sensitive paper strips, Kashi et al. tested permeability of various films and fabrics. The study revealed that phosphine permeated through a majority of them. It was noted that sheets made of PVC, either plain (unsupported) or coated, were relatively more retentive than others. In a study on gas permeability of different fumigation sheets, carried out earlier in the laboratory, Muthu et al. observed that unsupported PVC followed by LDPE films retained phosphine better than rubberized cloth and fabrics coated with PVC or polyethylene. Later the lab scientists, Rajendran and Narasimhan, conducted a filed study on 135 t wheat stacks in a warehouse in India to compare phosphine retention by covers made of unsupported PVC (150 μ), carbon impregnated LDPE (250 μ) and double texture rubberized fabric (650 μ) following a phosphine dosage of 1.5 g/m² for 7 d. The highest concentration-time (CT) product of 470 g h/m² was estimated in the stack with PVC cover and the CT was much less in the stack with rubberized fabric (275 g h/m²).

Wohlgemuth tested gas-worthiness of certain plastic films and sheets before and after mechanical stress (flex test) using gas chromatographic method to determine phosphine. The study has reported that phosphine retention in films was affected by the
Table 1—Loss of phosphine through new and aged fumigation sheets in 24 h at 27±2°C

<table>
<thead>
<tr>
<th>Sheet type</th>
<th>Thickness, μ</th>
<th>Weight, g/m²</th>
<th>Average loss of phosphine in sheets, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PVC, unsupported</td>
<td>255</td>
<td>390</td>
<td>New sheet: 0.9</td>
</tr>
<tr>
<td>2. PVC coated fabric</td>
<td>335</td>
<td>420</td>
<td>Accelerated aged sheet: 1.4</td>
</tr>
<tr>
<td>3. HDPE woven fabric with LDPE coating</td>
<td>260-330</td>
<td>200-240</td>
<td>Naturally aged sheet: 5.0</td>
</tr>
<tr>
<td>4. Multilayered cross laminated</td>
<td>280</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>5. HDPE film</td>
<td>85</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>6. a. LDPE film, carbon impregnated</td>
<td>225 to 250</td>
<td>210-240</td>
<td></td>
</tr>
<tr>
<td>7. Double-texture rubberized fabric</td>
<td>650</td>
<td>540</td>
<td></td>
</tr>
<tr>
<td>7. b. Without carbon impregnation</td>
<td>140</td>
<td>140</td>
<td></td>
</tr>
</tbody>
</table>

*a Based on 2 to 6 replicates.
*b Significantly different (p < 0.05) when compared with new sheets (t-test).

HDPE - high-density polyethylene; LDPE - low-density polyethylene; PVC - polyvinyl chloride

Source of sheet samples:
1. VPLASt, Pune, Karnataka State Warehousing Corporation, Bangalore (User)
2. Entremonde Polycoaters Ltd., Nashik
3. Texel Industries Ltd, Mumbai, GuiltPack Ltd., Indore, SuryaFlex Poly Tarpaulins, Hyderabad, VPLAST, Pune
4. Siltap Chemicals Ltd., Mumbai
5. ITC Ltd. Guntur (User)
6. a. Food Corporation of India, Mysore (User), Food Corporation of India, Baroda (User), Siltap Chemicals Ltd., Mumbai, and
   b. ITC Ltd. Guntur (User), ITC Ltd. Guntur (User)
7. Food Corporation of India, Mysore (User)

Repeated twisting, which simulated frequent handling of sheets in a practical situation. Conversely, after accelerated ageing, the sheets showed higher phosphine retention over the new ones in the present study (Table 1). This was probably due to changes in the structure of the polymer of the sheets upon exposure to 70°C for 7 d. The accelerated ageing test of BIS is primarily intended to check for changes in terms of physical or mechanical property in the thermoplastics tarpaulins after ageing. In contrast to accelerated aged sheets, the naturally aged samples in the open for 5 months, showed increased permeability to phosphine (Table 1). The UV radiation of sunlight, rain and wind affected sheet quality. Among the sheets tested, carbon impregnated LDPE film and multilayered cross-laminated sheet were the least affected. HDPE sheets were easily damaged or their phosphine retention became very low. Evidently the study shows the importance of phosphine retention test after natural ageing for any gas-proof sheet intended for cover-fumigation of grain stacks held outdoors.

Conclusions

In conclusion, fumigation sheets varied in phosphine retention with type of sheet and, even in the absence of any mechanical stress, the retention property was adversely affected when the sheets were
naturally aged by exposure to sunlight, rain and wind as under cover and plinth (CAP) grain storage conditions. The accelerated ageing, however, further improved the phosphine retention of the tested sheets.

Acknowledgements

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