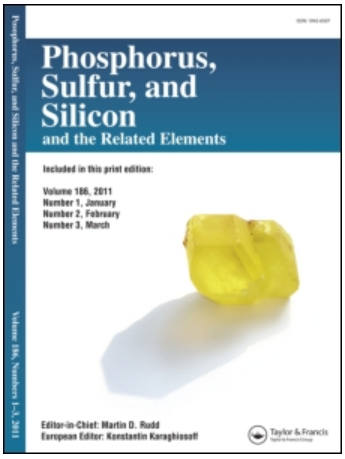

Phosphorus, Sulfur, and Silicon and the Related Elements

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The Use of Phosphine as an Agricultural Fumigant

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THE USE OF PHOSPHINE AS AN AGRICULTURAL FUMIGANT

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Abstract Problems associated with using a phosphine /CO_2 mixture as a fumigant include oxidation and contamination with P_4

Phosphine is an extremely toxic gas and at low concentrations provides an efficient fumigant for stored grain where insect infestations, if unchecked, can cause severe losses. Fumigation has become increasingly important as stricter regulations are placed on pesticide residues in foodstuffs. Phosphine is ultimately converted to environmentally and biologically benign oxidation products and as it is commercially inexpensive, it is an attractive proposition as an industrial chemical. Insects develop resistance to PH_3 but effective control is possible by maintaining a toxic concentration over a lengthy period (1-3 weeks) either in a sealed enclosure or by continuous injection of gas to make up for loss.

Phosphine itself is too dangerous to handle and is replaced by a 2% w/w mixture with CO_2 (Phosfume, USP 4,889,708; GBP 2177004) which is non inflammable. Pure PH_3 is not spontaneously inflammable but it is too expensive. Originally the gas was generated by the slow hydrolysis of crude calcium phosphide

This paper describes difficulties which arose in using the CO_2/PH_3 system in the field, namely fires when dismantling the apparatus and clogging of pipes leading to cessaation of gas flow. The fire problem proved to be due to residual P_4 in the PH_3 and analytical techniques (NMR and GC) were developed to determine it. The clogging, by a yellow-brown solid, apparently a P_nH_x polymer was more difficult to trace and appears due to inadvertent oxidation in the cylinder filling process. Polymer formation can be demonstrated experimentaly. The mechanism is obscure but is presumably a free radical chain reaction The polymeric solid on prolonged exposure to air affords a mixture of phosphonic, phosphinic, and phosphoric acids and an air stable high melting solid which analyses for $CO_2 \cdot P_2H_4$, an apparently unique example of a $PH_3 + CO_2$ reaction.We have been unable to detect P_2H_4 or other spontaneously inflammable higher hydrides unequivocally in either PH_3 or Phosfume