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THE USE OF PHOSPHINE AS AN AGRICULTURAL FUMIGANT

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Abstract Problems associated with using a phosphine /CO₂ mixture as a fumigant include oxidation and contamination with P₄

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 PH₃ 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 CO₂ (Phosfume, USP 4,889,708; GBP 2177004) which is non inflammable. Pure PH₃ 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 CO₂/PH₃ system in the field, namely fires when dismantling the apparatus and clogging of pipes leading to cessation of gas flow. The fire problem proved to be due to residual P₄ in the PH₃ 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 experimentally. 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 CO₂·P₂H₄, an apparently unique example of a PH₃ + CO₂ reaction. We have been unable to detect P₂H₄ or other spontaneously inflammable higher hydrides unequivocally in either PH₃ or Phosfume