Grain protectants: trends and developments

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Abstract

Recent developments in grain protectants are discussed under one heading. These are:

- analytical chemistry;
- efficacy of registered grain protectants;
- efficacy of candidate grain protectants;
- efficacy of insect growth regulators;
- residues of protectants;
- formulations, including impregnated dusts;
- inert dusts considered in another section of this conference;
- structural sprays and space treatments, with reference to trapping;
- efficacy of natural products;
- new trends in regulatory procedures, including implications of the concept of 'maximum theoretical daily intake'.

Some of the many research highlights since the Bordeaux conference include a review paper on analytical chemistry of protectants, a large amount of efficacy data of protectants on tropical crops and on legumes, demonstration that the toxic effect of oils in controlling legumes is almost entirely due to ovicidal action, and demonstration that excellent control of all stored-product pests can be obtained from insect growth regulators. These can be either juvenile-hormone analogues, applied at 8–10 mg/kg, or chitin inhibitors such as the biphenylureas, applied at approximately 1 mg/kg.

The concept of maximum theoretical daily intake is outlined. It is suggested that, if this concept is allowed to become more important than the actual daily intake, one consequence will be no international registration for minor uses, i.e., no registrations to meet the specific needs of poorer countries.

In Section 11 of the paper it is argued that the limiting factor in the use of grain protectants is the cost of registration and of re-registration. Such costs certainly limit the number of grain protectants and it is also possible that some current protectants, especially the inexpensive ones, will not be re-registered. It is also argued that all additives to grain, whether synthetic protectants, fumigants, natural products or inert dusts, are rightly subjected to regulatory constraints. For our work to be 'potentially applicable', it is necessary to consider how it may fit into a regulatory procedure. A schema for registration according to use and type of material is outlined. The implications of possible widespread withdrawal of grain protectants is discussed.

Analytical Chemistry

A pre-requisite for accurate data on the persistence of protectants and their fate during processing is soundly-based analytical chemistry. A review of the analytical chemistry of grain protectants is therefore welcome (Sharp et al. 1988). Two Ph.D. theses discuss analysis of grain protectants by capillary-column gas liquid chromatography (Sharp 1989) and by high-performance liquid chromatography (Brayan 1989). These are important because high-performance liquid chromatography and gas–liquid chromatography are the principal methods used in the analysis of grain protectants and because capillary chromatography enables better resolution of chemicals than can be obtained on packed columns. A number of rapid spot tests have come on the market, but some of these do not use procedures that would extract all pesticide from commodities. However, properly-based ELISA methods of analysis have been published for several protectants (Beasley et al. 1993).

It has been my impression, over the years, that entomologists and engineers in stored products seem to think that chemists produce reliable results, almost by magic. However, this is not true, and even methodologies are often inadequate (cf my conference paper on fumigant analysis and cited references). In my opinion, some analytical chemistry of grain protectants is still based on poor methodologies, though that is now the exception where once it was commonplace. However, some laboratories continue to use non-polar solvents to extract aged residues, despite a large amount of work showing that more-polar solvents are required (e.g. Sharp et al. 1988). In addition to systematic errors, based on poor methodologies, random errors may also occur and many laboratories try to overcome such errors by the type of procedures outlined in my talk on fumigant analysis.

Efficacy of Registered Grain Protectants

'Registered' grain protectants are those approved for postharvest application to grain. Since the last Conference, very useful data have been collected on the efficacy of protectants against a range of pests on a range of cereal grains and legumes (though not oilseeds, with the exception of peanuts). Examples include studies of 14 protectants on *Phaseolus vulgaris* (Daglish et al. 1993a), 13 protectants on peanuts (Daglish et al. 1992), 7 protectants on mungbeans (Daglish et al. 1993b), 5 protectants on paddy (Samson et al. 1989a), and 9 protectants on maize (Samson and Parker 1989a; Giga and Zvontete 1990; Mezule and Oloyede 1991).

Relative efficacies on maize, paddy and wheat have been examined (Samson and Parker 1989b). Efficacies are generally higher on maize than on wheat, and higher on wheat than on paddy.

Mould preservatives such as propionic acid continue to give good results, even under tropical conditions (Kumar et al. 1993).

An increasing number of papers (e.g. Arthur 1992; Samson and Parker 1989a, b) report use of an organophosphorus insecticide to control most species plus a pyrethroid or an insect growth regulator to control bostrychids. In the absence of (resistant) bostrychids, organophosphorous insecticides are usually sufficient for insect control. Deltamethrin is usually used alone, and there is little published on its synergistic effect

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with organophosphorus insecticides (Nicholas et al. 1990), apart from the very recent publication of Arthur (1994b).

Resistance to protectants is covered in several papers (e.g. le Patourel 1992). Perhaps the most disturbing example of resistance is resistance to *Bacillus thuringiensis*, which showed factors of up to 61 in *Plodia interpunctella* (Huebner) (McGaughey and Johnson 1992).

The higher vapour phase activity of methacrifos, relative to some other organophosphorous grain protectants, has been documented (Price et al. 1991). Thus, methacrifos could fill the role of dichlorvos as a chemical with vapour phase activity, at least in some uses.

Higher doses of insecticides are required on legumes than on cereals, with the partial exception of deltamethrin. This is consistent with the more rapid decay of organophosphorus insecticides on at least one legume — peas — relative to paddy or maize (Brayan 1989; Sharp 1989).

In summary, in my opinion, the benefits and limitations of grain protectants on tropical cereal crops and on grain legumes have been clearly established.

Efficacy of Candidate Grain Protectants

Since the last conference, there has been comparatively little work on new candidate protectants. A possible explanation for this is given later in this paper.

A number of papers have appeared on insect growth regulators (IGRs), inert dusts and natural products, and these papers are discussed under those headings. Comparatively few papers have been published on candidate conventional grain protectants. One of these discusses a new 'pyrethroid' (Arthur 1993) and another cyfluthrin (Makundi 1991).

In areas outside of stored products, a large amount of work is being undertaken on viral insecticides. Vail et al. (1991) have established that such viral insecticides have considerable potential in stored products, at least for control of moths.

Efficacy of IGRS

Work in stored products continues to concentrate on two types of IGRs, namely the juvenile hormone analogues, principally methoprene and fenoxycarb, and chitin inhibitors, principally the biphenylureas such as diflubenzuron. Neem, which is also an IGR, is discussed under natural products.

IGRs that have structures similar to juvenile hormone, such as methoprene, hydroprene and fenoxycarb, are less effective against *Sitophilus* species than against many other species. There have been two approaches to this problem. One approach is to use a low dose of an IGR coupled with an organophosphorus insecticide as a '*Sitophilus* killer' (e.g. Samson et al. 1990). The other approach is to apply a larger dose of IGR to control all species and Edwards et al. (1991) obtained good control of four species, including *Sitophilus granarius* (L.), with an application of 8.4 mg/kg fenoxycarb. Eisa and Anmar (1992) also obtained good control of *S. oryzae* (L.) with a similar application of fenoxycarb.

In work on diflubenzuron, it was shown that this chitin inhibitor exerted a delayed effect on adults of *S. oryzae*, with the result that efficacy one week after placing adults on treated grain was much greater than in the first week (Desmarchelier and Allen 1992). Similar effects were observed for other biphenylureas (Elek and Longstaff, 1994).

Excellent results have been obtained from laboratory studies with biphenylureas (Eisa and Ammar 1992; Estal et al. 1993; Elek and Longstaff 1994). Each of four biphenylureas controlled several species of insects, including *Sitophilus* species. Application rates sufficient to give 6–12 months protection are in the range 0.5–1.5mg/kg. Although biphenylureas are not new insecticides, and diflubenzuron has been studied on grain since at least 1975 (Carter 1975), it would appear that these chemicals are able to protect grain against insects for long periods. This is especially the case as their residual efficacy, as well as chemical residues, is persistent (Dhanasekeran et al. 1992).

The biphenylureas show toxicities to insects that are quite different to the juvenile hormone analogues. For example, triflumuron, flufenoxuron, teflubenzuron and chlorfluazuron are, approximately, equitoxic to a range of different species: the juvenile hormone analogues, such as methoprene, are not, however, equitoxic to all species, with *Sitophilus* species being particularly difficult to control, and diflubenzuron controls *Sitophilus* species more easily than several other species, at least in assays that include the delayed effect on adults (Carter 1975; Elek and Longstaff 1994). This raises the possibility of a mixture of diflubenzuron, to control *Sitophilus* species, and methoprene, to control other species, using applications of approximately 1mg/kg for each species.

In summary, the current situation with insect growth regulators is that both their efficacy against stored-product pests and their mammalian toxicity are known. If these insect growth regulators are to be used practically, the most urgent requirement now is work that leads to registration. Such work, of course, requires the cooperation of the chemical companies. The general topic of registration is discussed more fully later in this paper.

Residues of Protectants

Some chemical work on the fate of residues during storage and/or processing has been published (e.g. Brayan 1989; Sharp 1989; Arthur et al. 1992; Papadopoulou-Mourkidou and Tomazou 1991). A large quantity of residue data is, however, not published in the literature but is included in submissions to Codex Alimentarius. Summaries of such data are available from the Food and Agricultural Organisation. As an example of such unpublished data, residue data from two commercial mills are a prerequisite for use of any chemical in Australia, and residues are determined at the Academy of Grain Technology, which is a certified laboratory. Many other countries use similar protocols and it should be noted that data from supervised commercial trials are one of the requirements of Codex Alimentarius for registration (Maybury 1989).

In early work (Desmarchelier 1978), I described loss of protectants in grain in terms of first-order kinetics. This conclusion has been challenged by two Ph.D. studies I cosupervised (Brayan 1989; Sharp 1989). I accept their conclusions that the decay of protectants often 'slows down' as residues become relatively low. A fuller statistical analysis is being prepared for publication.

It is pleasing to note that the combination, over time, of more accurate analytical procedures and more realistic residue data, based on commercial trials, has led to a more reliable estimate of residues of protectants in processed food. As a result, estimates of daily intake of pesticides based on total dietary studies are soundly based.

Formulation, Including Impregnated Dusts

Three types of formulation have been tested: namely dust formulations, slow-release formulations and 'solid' formulations such as wettable powders or suspension concentrates.

Insecticides applied in dusts can be more effective than insecticides applied as sprays (Shawir et al. 1988; Permual and le Patourel 1992). The amounts of carrier, such as amorphous silica, need not be large and amounts of 100g/t suffice (Shawir et al. 1988; Desmarchelier, unpublished). As data presented in the conference session on inert dusts illustrates, such amounts will not cause problems with grain flow.

Slow release formulations have given good results in trials (Grant et al. 1990). The benefit of solid formulations in structural sprays is discussed below.

Dust formulations are often more convenient for small users than sprays though, conversely, the opposite is true for large users, for whom the extra bulk from dust formulations creates logistic problems. Solid formulations sometimes confer benefits in terms of reduced smell (for example, deltamethrin formulated as Cislin® is much less irritating than deltamethrin formulated as Decis®, at least to the author), though, conversely, solid formulations of organophosphorous insecticides may smell more than the emulsifiable concentrates.

Clearly, appreciable benefits have been obtained from work on formulations and further benefits are to be expected from continuing research.

Inert Dusts

Inert dusts are covered in another part of the conference. In this paper I merely note that the range of research since the Bordeaux conference includes activated clays (Permual and le Patourel 1992), wood ash (Wolfson et al. 1991) and amorphous silicas (Aldryhim 1990).

Structural and Space Sprays

A number of papers illustrate the well-known advantages of solid formulations, such as wettable powders or suspension concentrates, for structural treatments (e.g. Giga and Canhao 1991; Claborn et al. 1991; Arthur 1994a). The efficacy of emulsifiable concentrate formulations on concrete, at least for the tested insecticide cyfluthrin, was increased by pre-sealing of the concrete (Arthur 1994a). Toxicity from structural applications is correlated with that from topical application (Arthur and Zettler 1992). Two papers discuss the significance of laboratory tests in evaluation of structural sprays, with emphasis on the time insects in the field are exposed to insecticide (Barson 1991; Desmarchelier et al. 1993). The latter authors emphasise that population monitoring in the field is required for evaluation of structural sprays. This is because extrapolation from laboratory data to the field situation involves arbitrary assumptions about insect behaviour.

Hodges et al. (1992) monitored the efficacy of insecticidal treatments on bagged stacks in storages in Southeast Asia. The conclusion was that spraying bag stacks with chemicals was not justified and was uneconomic. A study (Mohammed and Al-Jabery 1988) compared the efficacy of various insecticides against *Callosobruchus maculatus* (F.) and its parasite *Anisopteromalus calandrae* (How.). Unfortunately, if not unexpectedly, the parasite was more susceptible to the best insecticide — chlorpyrifos ethyl — than was the pest species.

Little work on space sprays has been published since the last conference.

My conclusion is that workers in stored-products have used recent advances in population monitoring to improve the evaluation of insecticidal treatments on structures, such as walls, and on bag stacks. This is a good example of the integrated nature of research in stored products. In some cases, structural treatments have been evaluated as useful (e.g. Desmarchelier et al. 1993) whereas, in other situations, they have been evaluated as uneconomic (e.g. Hodges et al. 1992), but, in each case, improvements in monitoring of insect populations have improved the process of evaluation.

Natural Products

Oils have been widely used on legumes to control bruchids. Recent work (e.g. Don-Pedro 1989a) makes it clear that the toxic effect of oils is almost entirely due to ovicidal activity. Repellency was also observed (Don-Pedro 1989b; Stamopoulos 1991).

Apart from oils on legumes, the toxic effects of a number of natural products have been investigated (e.g. El-Nahal et al. 1989; Weaver et al. 1991; Regnault-Roger and Hambroui, 1993; Schmidt et al. 1991; Makanjoula 1989). Products include extracts of neem (Makanjoula 1989), extracts of *Acorus calamus* (Araceae), an Indian plant (Schmidt et al. 1991), extracts of European herbs and also *Eucalyptus globulus* (Regnault-Roger and Hambroui 1993) and purified linalool, an octadienol found in an African mint, *Ocinum canum* (Lamiaceae) (Weaver et al. 1991). The potential applicability of natural products is discussed, with other items, later in this paper.

Registration of Protectants

There is nothing new in regulatory procedures but a concept called the 'theoretical maximum daily Intake', or TMDI, seems to be growing in importance. Some terms are summarised in Table 1 and a fuller discussion is given by Maybury (1989). The acceptable daily intake (ADI) is the quantity of chemical estimated by the World Health Organisation as being safe to consume. The maximum residue limit (MRL) is the maximum amount allowed on a commodity and the maximum amount that occurs from good agricultural practice. The daily intake of any commodity (e.g. bread or rice) is the average amount of that commodity consumed daily. It varies, of course, between countries. The TMDI is obtaining by multiplying the daily intake of any commodity by the MRL for that commodity, and summing it across all commodities.

Table 1. Some terms used in toxicological studies.

Term	Symbol	Definition
Acceptable daily intake	ADI	The quantity of chemical judged safe to consume every day.
Maximum residue limit	MRL	Upper legal limit on any commodity
Daily intake	–	Amount of commodity eaten daily, according to country, age, etc
Theoretical maximum daily intake	TMDI	(Daily Intake) times (MRL), summed for all uses.
Average daily intake of a pesticide	–	The average amount of a given pesticide consumed

As explained by Maybury (1989), the average daily intake is well below the theoretical maximum daily intake, and this point is well established by total dietary studies on pesticide intake. However, calculations based on the TMDI pose a threat, especially to minor uses. As an example, if the hypothetical country, Ruritania, wanted an international MRL for the hypothetical chemical Protecto, on a commodity (e.g. maize or soybeans), that MRL would become part of a worldwide calculation of the TMDI. Chemical companies may not wish this to occur if it would significantly alter the TMDI and if the TMDI is regarded as important. One consequence is that pesticides will not be registered for minor uses, at least not on commodities where use could significantly increase the TMDI (without, in this instance, any major effect on the actual daily intake). The end result is that specific needs of poorer countries will not be met.

In my opinion, which I cannot support by cited references, calculations based on the theoretical maximum daily intake are currently one factor in the cancellation of certain registered uses and one factor in the non-registration of certain potential grain protectants.

Future Trends in Protectants

Although there are a number of chemicals that would appear to be useful grain protectants, including both synthetic and natural materials, most of these will not be registered. This means that most of these will have little, if any, practical use. The main reason many protectants will not be registered is the cost of registration, but concern about the TMDI is also important. In addition, the cost of re-registration means that, quite possibly, several existing protectants will not be re-registered, but will be withdrawn from use. This probably applies especially to the cheapest chemicals, where the cost of registration may not be able to be recovered from the sale of the chemical. The lack of re-registration of malathion in the USA (Abramson 1991) exemplifies this general point. In the absence of patent protection, no company was prepared to bear the cost of re-registration.

In an excellent review on research in stored-products, McFarlane (1990) suggests that our research should be 'potentially applicable'. This is a nice phrase, as 'potentially applicable' keeps practical usage before our eyes, but without denying the benefits of pure research. Potential application of our work on additives requires some kind of regulatory approval, with the consequence that we need to consider such approvals, if our work is to be potentially applicable.

In my opinion, some publications in stored products give the impression that chemicals can be applied to grain if certain criteria are met, e.g. if the chemicals are natural or if their acute toxicity is low, etc. It is, however, debatable whether such assumptions are true, assuming that I am correct in thinking that such assumptions have been made. I have, therefore, summarised, in Figure 1, possible ways in which chemical uses could, at least conceivably, be approved or otherwise come into use. The schema in Figure 1 will, I hope, focus debate on ways in which research on chemicals can become potentially applicable. Thus the schema is relevant to research in so far as it outlines possible means of taking research from the laboratory into commercial use.

The schema is based on responses (Yes or No) to specific questions. The first question is whether to obtain Codex-type registration or not. 'Codex-type' approvals are of the type described by Maybury (1989) and require toxicological evaluation. The answer to this question can be 'yes' or 'no'.

If one does not seek Codex-type approvals, there are two options. One is to use no chemicals (Option (1)).The approach of 'no chemicals' would allow for the use of cooling or heating and some other procedures, but would exclude the use of chemical additives, whether natural or synthetic and whether fumigant or protectant.

The alternative to 'no chemicals', in the absence of Codex-type approvals, is to use any available chemical (Option (2)). For example, if we lose protectants approved by Codex, or similar bodies, one group of people (the rich) may use chemical-free methods in all situations, whereas the poor will, or may, use any available chemical in at least some situations. Certainly, if protectants fall from registration, the choice will not be between unregistered pirimiphos-methyl and unregistered chlorpyrifos-methyl. It will be a choice between what is available (e.g. lindane) or non-chemical options.

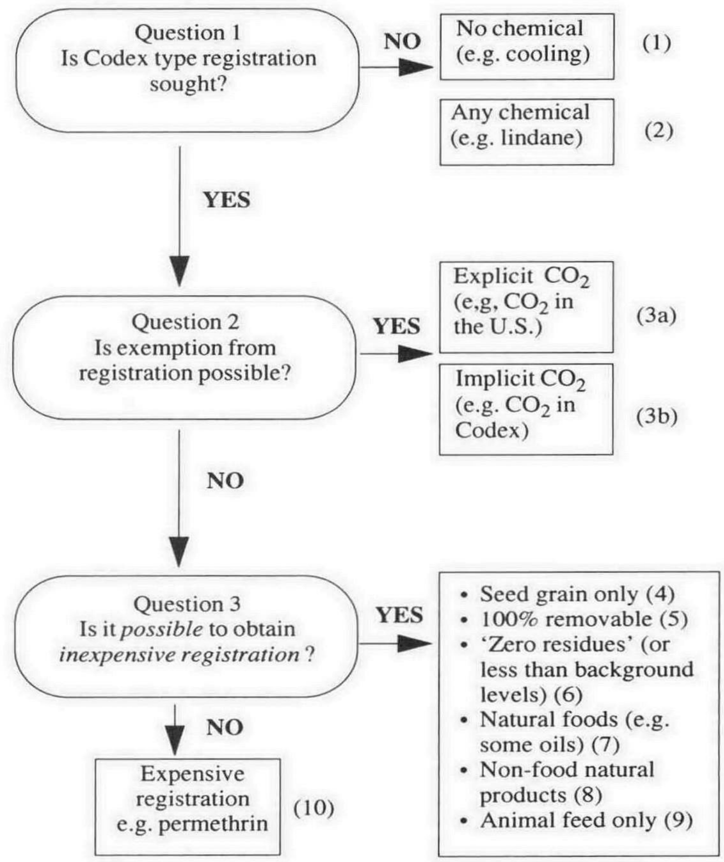

Fig. 1. A schema for pesticide registration

If the answer to seeking Codex-type registration is 'yes', there are two possibilities. One can obtain exemption from MRLs, or one cannot. Exemption (3) in the schema can be either by law (3a), or by tacit acceptance (3b). In this sense, additives such as plant leaves or inert atmospheres are exempt from registration, and there are sound toxicological and practical reasons why this is the case.

If one cannot obtain exemption from MRLs, there are two options. One is Inexpensive Registration, justified on toxicological grounds, and the other is Expensive (full) Registration.

There are, as I see it, six possible ways whereby registration can be inexpensive (schema , 4–9).

One possible form of inexpensive registration is a registration restricted to seed grain (4), schema). This avoids the need for some toxicological data, but seed protectants also require low toxicity, in case of accidental human consumption. Such accidental human consumption led to withdrawal of mercuric fungicides for seed protection and this example illustrates the problems faced by regulatory agencies.

A second possible form of inexpensive registration is registration of dusts that are completely removable, leaving no residues or alteration products (5), schema). In this case, however, it would be an advantage, and probably essential, to have acceptable toxicity data. For example, as amorphous silica is well-known and is present in our diet, it may be easier to register than, e.g. a lead dust.

Chemicals that leave 'zero' residues in food because they degrade rapidly may mean cheaper registration and may even mean tacit exemption from requirements for registration (schema, (6)). There are two possible definitions of 'zero' residues. One is levels that do not exceed levels that occur naturally. It is not possible to enforce regulatory limits that are below the levels that occur naturally, and bromide levels in food illustrate this point. Thus there are feasible uses of , for example, hydrogen cyanide on legumes or methyl isothiocyanate on rapeseed that would leave residues no greater than those that occur naturally. Under such circumstances, registration may be inexpensive, or possibly not required.

A second definition of 'zero' residues is 'below the limit of detection'. This is quite a different definition from that of 'below natural levels' because limits of detection can vary over time. There is also the problem that 'zero residues' can never be proven; one can only show that residues are below a certain defined level.

Natural foods as insecticides could be registered cheaply (or accepted without registration), for example edible vegetable oils on legumes (schema (7)). Even in this case, however, it cannot be assumed that no problems with mammalian toxicity will arise. For example, unsaturated oils mixed with grains may undergo chemical transformations that will be different from, or occur more rapidly than, transformations that occur naturally within the grain, where the oils are protected from ultraviolet radiation.

Plant extracts, other than edible oils, (schema (8)) may be able to be cheaply registered, and that seems to be a presumption in some papers on natural products. However, I very much doubt if any plant extract would be approved solely on the grounds that it is natural. There has certainly been a large amount of work in stored products on plant extracts but there has been very little actual use, with the exception of natural pyrethrins which have undergone a Codex evaluation.

The use of protectants for animal feed only (schema (9)) may result in inexpensive registration. At the very least, it would avoid problems associated with the theoretical maximum daily intake, as all protectants introduced over the last several decades are extensively degraded in mammalian systems. For reasons of possible human consumption, protectants registered for animal feed would require a low mammalian toxicity. Given previous problems with mercuric fungicides on seed grain, it is highly unlikely that a chemical of unacceptable toxicity to humans would be approved for animal feed, even given the unlikely assumption that the chemical was safe to mammals other than humans. However, a chemical company may chose to restrict usage to animal feed to avoid problems with daily human intake, in a similar manner to registration for seed grain only. Such usage already occurs in fact because propionic acid is a protectant that is used predominantly and probably exclusively on animal feed.

In the schema, six options for inexpensive registration are outlined (Schema 4–9). Each of these options is a useful one. Some options, such as edible oils on legumes, may be more useful for poorer than for wealthier countries. The reverse is true, however, for the option of restricting registration to animal food. This is because the proportion of grain consumed by animals to that by humans increases with economic standards, at least up to a certain economic threshold.

Despite these useful options, the use of approved chemical additives to control pests in food still remains a very useful option. In stored-products, as McFarlane (1990) has pointed out, there is no 'single best option', but a range of options that are each best for given situations. Stable food protectants are one such best option in some situations. This usage requires expensive registration (schema (10)). This is the usage which has major potential benefits especially for poorer countries and it is precisely this usage which is most threatened by the large, and increasing, cost of registration and of re-registration.

As you are all aware, the use of synthetic chemicals is widely attacked in the general media and many articles in stored products attack grain protectants, even in cases when the alternative natural product promoted may be considerably more toxic than the synthetic material attacked. As one who has worked on grain protectants, I welcome any method for safe storage of grain that is better or cheaper than ones I have helped to evaluate. However, for reasons well summarised by McFarlane (1990), such alternatives are never universally better, but rather better in particular circumstances. Thus fumigation or cooling may be better in some situations and grain protectants in other situations, and a choice between methods is the best of all options. This is for reasons of economics and for reasons of management of resistance.

In summary, registration is a very complex issue, but some form of registration, whether implicit or explicit, is required if research work on additives is to find practical application. This, I believe, applies to all additives, including natural products and inert dusts, as well as to synthetic chemicals. The cost of registration is currently a major constraint on the commercial use of new protectants, and will continue to be a major constraint because the legitimate concerns of food regulators have to be met.

There is no magic solution to these problems but only the solution of excellent research and development.

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