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CONTROLLING THE PERSISTENCE OF INSECTICIDES WITH SPECIAL REFERENCE TO MICROENCAPSULATION

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Introduction This paper considers only deposits of insecticides on plant surfaces. Further complications are encountered with soil-applied insecticides which are systemic in plants.

In considering the fate of residual deposits, the persistence of the insecticide as a chemical in the given environment should be distinguished from the persistence of its biological activity, which we may term its toxicological persistence. This relates to the 'availance' $\int_0^\infty C\,dt$ (Hartley, 1963, 1966). There are many reasons why biological activity may be less than expected because the chemical is prevented from exerting its full toxic effect. Generally, both chemical persistence and biological activity will be governed not only by properties of the insecticide such as its volatility, solubility or dispersion in rain, or stability to U-V radiation in sunlight, but also by the properties of any other components of the insecticidal formulation or by the nature of the substrate. There are well-known instances where the effectiveness of the toxicant is enhanced by the presence of other compounds (synergism), but generally other compounds present have a diluent effect and sometimes a masking effect on toxicity. Processes such as sorption or solution depress the volatility of the insecticide, thus increasing its chemical persistence but not necessarily the persistence of its biological activity. In this connection it may be noted that considerable amounts of lipophilic non-systemic insecticides can dissolve in waxes on plant surfaces and enter into internal tissues, thus increasing the chemical persistence and possibly creating residue problems on harvested crops, but decreasing the persistence of activity against insect pests on the plant surfaces.

Attempts may be made to control the persistence of an insecticide by modifying its chemical structure, although this usually also alters toxicity. Thus, this approach is limited. However, it has been used successfully, for example, to extend persistence of synthetic pyrethroids (Elliott et al., 1973).

The other principal method of controlling persistence (with which this paper is concerned) is to modify the formulation. Marrs & Middleton (1973) commented that the replacement of persistent pesticides with more toxic but short-lived compounds has resulted in the introduction of more sophisticated formulations. Such formulations give reduced handling hazards, greater control of placement and persistence, and greater specificity towards the insect pest. They require lower application rates and less critical timing than conventional sprays. Examples of these formulations will now be considered in relation to some of these potential advantages.

Controlling persistence by preventing rainwashing losses

Losses of material from the treated area by rainwashing is an important aspect of the effects of weathering on persistence. In attempts to increase rainfastness, stickers such as polyisobutene are sometimes added to emulsifiable

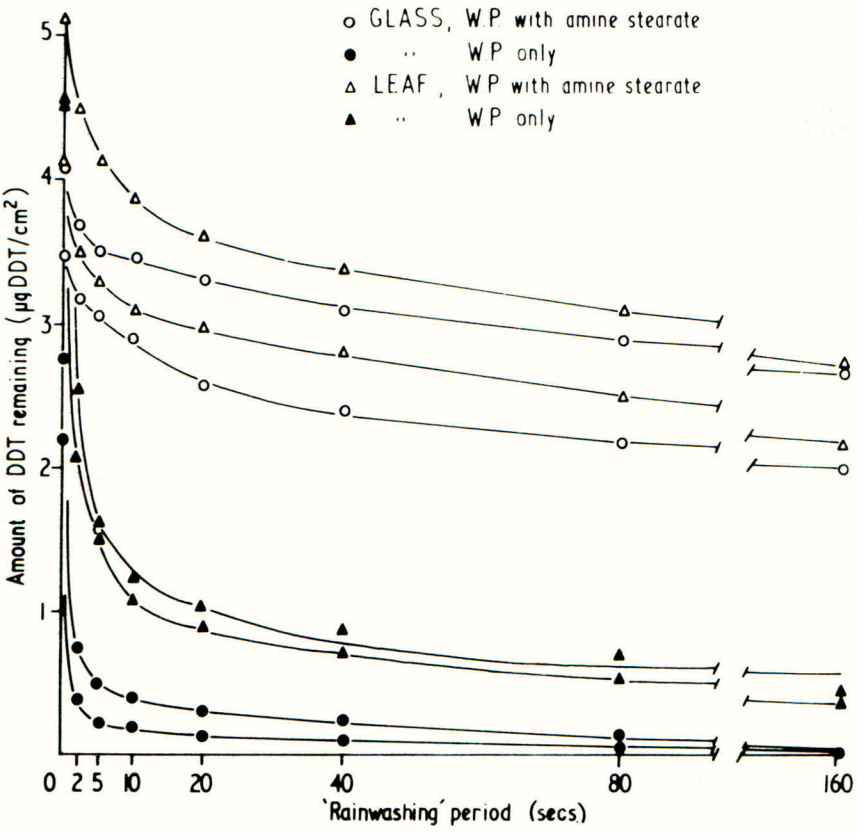


Fig. 1. Effects of 'rainwashing' wettable powder deposits on glass and cotton leaf surfaces (each experiment is duplicated). The rates of loss are exponential.

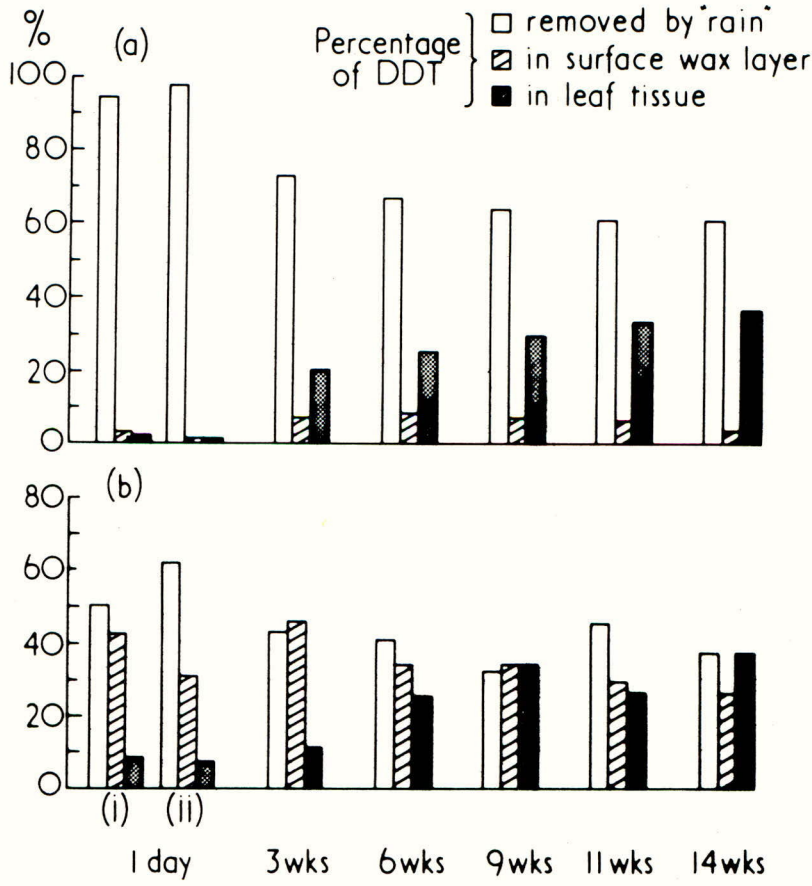


Fig. 2. Effects of 160 seconds 'rainwashing' of 2-5 μg DDT/cm^2 deposits on cotton leaves aged for 1 day - 14 weeks and formed from:
(a) wettable powder suspension
(b) wettable powder suspension with 5% v/v amine stearate solution.

oils. Suspensions of solid particles such as those given by wettable powder formulations, which consist of insecticide sorbed on clays, are particularly susceptible to rainwashing after deposition on surfaces, and stickers (often oils or gums) have proved effective as additives in the spray to improve retention (Hoskins, 1962). Other polymeric substances used include an acrylic adhesive for retention of Sevin wettable powder (Pielou & Williams, 1962), and a polybutyl acrylate (Phillips & Gillham, 1973) to retain microcapsules on leaves.

An interesting formulant developed by Fisons Ltd. to increase the persistence of wettable powders to rainwashing consisted of amine stearates (such as trimethyl and methyldibutyl ammonium stearates) added to the spray. On drying, very hydrophobic and tenacious deposits composed of a mixture of stearic acid with the wettable powder formed on plant surfaces. The stearic acid apparently forms an open lattice with the wettable powder and the following effects were noted on comparing DDT wettable powders with and without amine stearates (Phillips & Gillham, 1966, 1971):-

(i) With 5% v/v amine stearates dissolved in the aqueous spray, the amounts of deposit retained on surfaces after stringent testing by rainwashing were greatly increased (Fig. 1).

(ii) The presence of stearic acid in the deposits had little apparent effect on DDT losses by volatilisation. Furthermore, although adding amine stearates to the sprays initially caused faster penetration of DDT into the leaves, they did not affect the final concentration of DDT found in the leaf tissues. (Fig. 2).

(iii) The toxicity of the deposits to insects walking on the surfaces depended on the amounts of stearic acid present. Increasing the percentage of stearic acid in deposits containing equal amounts of DDT decreased the toxicity (Table 1).

TABLE 1. Median lethal concentrations of DDT wettable powder deposits to houseflies

FORMULATION	LC_{50} value (μg DDT/cm^2)	
	GLASS	COTTON LEAF
"Standard" wettable powder (W.P.) suspension W.P. suspension + 2½% v/v amine stearate solution	1.2	2.4
" " + 5% " " " "	3.7	7.4
" " + 10% " " " "	8.7	*

* LC_{50} value not attainable; LC_{10} value = 8 (approx.)

By choosing the optimum concentration of amine stearates in the spray solution (circa 5% v/v) the persistence of the wettable powder deposit under heavy rainfall conditions was greatly increased at small expense in terms of reduced contact toxicity.

Controlling persistence by modifying volatilisation using controlled release mechanisms

There are many reports in the literature describing incorporation of materials such as heavy (chlorinated) oils, natural and synthetic waxes, glues, gelatins and polymer substances generally, into pesticide formulations in

attempts to prevent rapid dissipation of the active ingredient and maintain toxicity at the treated surface. These agents control the release of the toxicant by various mechanisms affecting volatilisation, penetration and diffusion into the substrate, and thus the availability of the toxicant (which in some circumstances may be further affected by humidity changes such as those noted by Barlow & Hadaway, 1968). For example, the presence of different concentrations of a coumarone resin in a DDT oil spray regulated both the persistence and toxicity of the formulation (van Tiel, 1952). The slow release of pesticides from polymer matrices and from chemical combinations with wood waste materials is described by Allan et al. (1971a, 1971b) and Neogi & Allan (1974), whilst Beasley & Collins (1970) indicate how any pesticide with a carboxylic group can be formed into a polymer which will slowly release the active monomer in the presence of water. Neogi and Allan (1974) using Fick's Law of Diffusion as a basis, showed that theoretically the quantity of pesticide diffusing from a polymer matrix should be proportional to the square root of time. They verified this experimentally using a water soluble pesticide combined with a series of polyamides having different molecular weights. When these were formed into blocks with one face of each block exposed to water, the pesticide was released into water at rates which agreed very well with the theoretical prediction. By such methods it is hoped that useful controlled release formulations can be developed having a predicted persistence. Rubber latex and gelatins have also found use as agents for controlling release. Stephenson (1972) described the slow release of a molluscicide under the action of water from gelatins crosslinked ('tanned' or hardened) to different degrees by formaldehyde; the more hardened the gelatin, the slower the rate of release of molluscicide. Similar effects of crosslinking on diffusion rates were demonstrated earlier by Barrer and Skirrow (1948) who measured diffusion of nitrogen through rubbers which had been progressively crosslinked by sulphur (vulcanised); the matrix diffusion coefficient decreased exponentially with the degree of crosslinking. Generally, with synthetic plastic materials diffusion rates increase with increase in the percentage of plasticiser present because this reduces the crosslinking (Flynn, 1974).

All these methods for controlling persistence have in common that the material controlling the release of toxicant in the surface deposit acts as a network or lattice in which the toxicant is entrapped physically (sometimes irregularly) or bonded chemically throughout the matrix. Pesticide molecules are generally large, and, if at the centres of such matrix particles, can only diffuse out of the material with difficulty. Hence the degree of control possible is dependent not only on the natures of the insecticide and the matrix but also on the geometry and size of the matrix particles; in some circumstances problems could arise because of insecticide residues.

This concept can be taken one stage further by enclosing the toxicant in many small reservoirs with thin walls which allow the active ingredient to escape very slowly. This is the principle of microencapsulation.

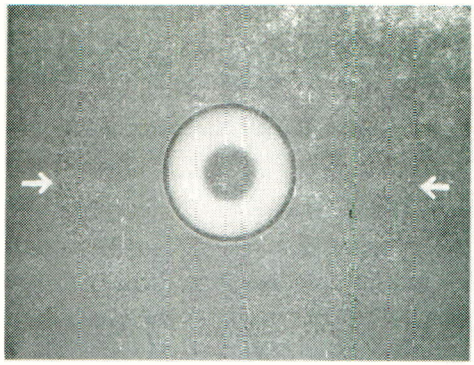
Controlling persistence and other properties by microencapsulation

A microcapsule comprises a wall material or envelope enclosing an internal phase consisting of a liquid droplet (or sometimes a solid particle) which contains the active ingredient. There are mechanical, chemical and physical methods of preparing microcapsules and examples of all methods are described by Vandegaer (1974).

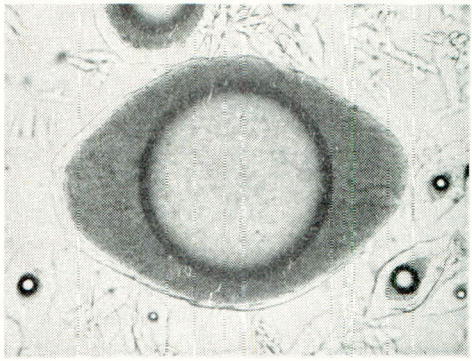
Mechanical methods have the disadvantage of requiring sophisticated apparatus and also are not suitable for preparing microcapsules with diameters below about 350 microns.

The chemical method involves interfacial condensation polymerisation, in

(a) Coacervation of first wall (gelatin/ carragheenan). Phase contrast microscopy showing boundary of oil droplet (dark ring) and boundary of coacervate wall (arrowed). Oil droplet diameter = 150 μm



(b) Coacervation of second wall (gelatin/gum acacia). Bright field microscopy, showing second wall (translucent layer) forming on first wall. Large oil droplet diameter (centre) = 500 μm.



(c) Drying of microcapsules in air. Bright field microscopy, showing wall shrinkage as water is lost. Microcapsule diameter = 400 μm.

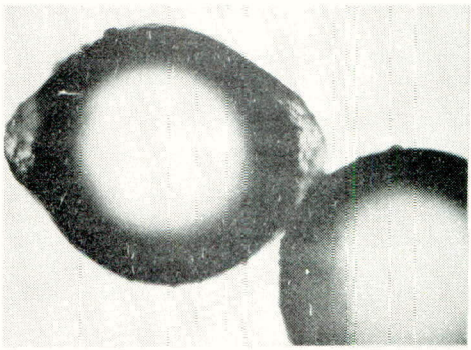


Fig. 3. Formation of double walled microcapsules. (Photomicrographs by G.E. Gregory, Rothamsted).

which a substance dissolved in one phase (oil) condenses with another substance in another phase (water) at their interface and further polymerisation may occur by crosslinking of the polymer. These microcapsules can be of the type described by Chang et al. (1966) where, after the initial dispersion of an aqueous phase as droplets in an oil phase, microcapsules with thin semipermeable nylon walls are produced. Alternatively, they can be of the type (claimed to have many uses in pesticide applications) where an oil phase containing the pesticide is dispersed in an aqueous phase, and the resulting microcapsule wall consists of a choice of polymers such as polyamides, polyesters, polyureas, or polycarbonates (DeSavigny and Ivy, 1974).

The physical method employs the process of coacervation, whereby changes of the conditions in a solution such as alteration of pH, removal of associated water molecules from colloids, or lowering of temperature, cause colloidal substances of opposite charge to become more hydrophobic and form a coacervate around, for example, droplets consisting of a pesticide dissolved in oil and dispersed in water. This is the method used by the National Cash Register Co. (NCR) in encapsulating leuco dyes for their carbonless copying paper. Using the NCR method we have developed a technique at Rothamsted whereby double walls are formed around the oil droplets in one process, so that thicker and less permeable walls are produced in order to decrease leakage. The first wall is of gelatin/carragheenan and the second of gelatin/gum acacia. The gelatin is then crosslinked (hardened) with glutaraldehyde. Because water (or a high humidity) increases the leakage rates of the contents, these microcapsules are filtered from the aqueous phase in which they are prepared and dried to give a flowable powder which may be resuspended in water before use. Fig. 3 shows photomicrographs of this coacervation process (with double walls) using permethrin dissolved in soya oil as the encapsulated insecticide.

Some examples where control of persistence has been achieved by encapsulation will now be considered, although there are few quantitative experimental measurements of the rates at which different microcapsules release their various contents under the different environmental conditions in the field.

G.S. Hartley (personal communication) estimated the effect of encapsulating a 1 mm diameter toluene drop in a gelatin/gum acacia wall with a 9:1 ratio of internal phase to wall material. The unprotected toluene drop would evaporate in about 3 minutes at normal temperatures in still air. If enclosed in a wall material having the same solvent power and same permeability as water has for toluene, the initial rate of loss of toluene through the wall by diffusion would be approximately 1% per minute. However, toluene is lost through a well-made gelatin/gum acacia wall at a rate of about 1% in 10^5 minutes (or 70 days). Therefore, the permeability of this wall material for toluene is as little as 10^{-5} times that of water forming a shell of equal thickness around the toluene drop. Hartley points out that intensive drying of the capsule wall would be expected to produce micro-cracks which would increase permeability. A small amount of water in the wall would probably decrease the permeability, although larger amounts with the attendant swelling effects would certainly have the opposite effect. The National Cash Register Co. finds that there is no significant loss of internal phase on storage at a moisture content of less than 3% in the walls. The extent of swelling of the wall material (and hence, rate of leakage) can be controlled to some degree by the amount of crosslinking or hardening of the gelatin by glutaraldehyde during the manufacturing process.

The same factor operates in the microcapsules produced by interfacial condensation polymerisation as illustrated by Marrs & Middleton (1973) in their accelerated tests in the laboratory by elution with methanol. By increasing the percentage of a polyacid chloride crosslinking agent in polyurea microcapsules, the rate of release by elution of the liquid organophosphorus insecticide pirimiphos-ethyl through the walls was greatly reduced. Their

graph showing rates of release apparently displays some exponential features, becoming sigmoid (logistic) with increasing crosslinking due to the initial delay in penetration of the walls by the eluting solvent.

The effect of moisture on single wall gelatin/gum acacia microcapsules of 500 micron diameter, prepared at Rothamsted, is shown in Table 2.

TABLE 2. Leakage of DDT from microcapsules: amounts found in hexane washings

Period (days)	Environment 1: µg DDT	Environment 2: µg DDT
0-2	1.3	1.6
2-5	1.0	1.6
5-9	1.2	2.2
9-14	1.3	2.8
14-21	1.3	2.9

Environment 1: 28°C (day)/20°C (night), 55% R.H.
Environment 2: 28°C (day)/20°C (night), 95% R.H.

The results show that a 0.1% DDT solution in toluene enclosed in hardened walls (with a nominal 5:1 ratio of internal phase to wall material) was released at twice the rate when the humidity was greatly increased. These microcapsules were also compared with a more conventional formulation (a DDT wettable powder) and the increased persistence obtained is demonstrated in Table 3 where the percentage of DDT lost by volatilisation and by penetration into the substrate (cotton leaf surfaces) from the microcapsules was less than half that from the wettable powder (Phillips, 1974).

TABLE 3. Persistance of DDT in two formulations on cotton leaf surfaces under constant cyclic conditions

TIME (weeks)	WETTABLE POWDER % DDT REMAINING	MICROCAPSULES % DDT INSIDE CAPSULES	MICROCAPSULES % DDT OUTSIDE CAPSULES*
0	100	100	0
1	44	87	3
2	40	84	3
3	37	80	4
4	35	78	4
5	34	76	5

* Removed by quick washing with hexane

Conditions: 28°C (day)/20°C (night), 10 h daylight, 55% R.H.

Phillips & Etheridge (unpublished data) observed that under very adverse conditions, namely wet soil, an insecticide in well-made double walled microcapsules can persist for several months and control a pest as well as a granule formulation. This was shown by comparing the two formulations of the systemic insecticide disyston over a six month period as soil treatments for controlling aphids on field beans in glasshouse pot tests. The two formulations were distributed as uniform thin layers in the soil beneath the roots of growing bean plants and their efficacy tested by bioassay using aphids caged on the

leaves. In both cases, mortality was about 75% in the first month, rising to 95% in the second and third months, before falling to 50% in the fourth and fifth months. It should be emphasised that these pot tests do not necessarily simulate large scale field trials, but are useful for preliminary comparison of different formulations. Although the two formulations gave similar results in these pot tests, it should be considered that different soil water tensions caused by a wide variability in soil porosity and moisture content, in addition to leaching by rain, could influence the release of active ingredient to different extents, leading to differences in efficacy.

The lack of quantitative measurements of release rates of microencapsulated insecticides and so-called 'release profiles' of the type exemplified by Madan, Price and Luzzi (1974) in their in vitro studies of drug release from microcapsules has not prevented the practical use of microencapsulated products in situations where an extended life of the active ingredient is required. Encapsulated methyl parathion was used by Ivy (1972) for controlling such diverse pests as mites, beetles and moth larvae. The encapsulated insecticide showed no phytotoxicity, unlike emulsion formulations, on some plants. Insect pathogens (e.g.) a bacterium (Raun & Jackson, 1966) and a virus (Ignoffo & Batzer, 1971) have been encapsulated in efforts to improve their stability. The persistence of a soya oil solution of mirex was successfully prolonged by encapsulation for treatments which eradicated the fire ant by aerial application (Markin & Hill, 1971).

In addition to controlling persistence, microcapsules have other advantages. Microencapsulated solutions of pirimiphos-methyl and permethrin in soya oil were used with some success in experimental poison baits to destroy large nests of leaf-cutting ants in Brazil, the purpose of the encapsulation being to prevent immediate contact action and hence delay the toxic effects of these quick-acting poisons (Phillips, Etheridge & Scott, 1976). Microencapsulated fonofos (Stauffer Chemicals "Dyfonate") seed treatments successfully controlled wheat bulb fly (ADAS, Eastern Region Report for 1974) where both the increased persistence given to the insecticide and the suppression of its phytotoxicity brought about by microencapsulation helped to improve performance and hence increase crop yields. The selectivity of such a formulation which can control pests and at the same time leave beneficial insects unharmed leads to the feasibility of using similar microencapsulated formulations against, for example, weevils on oil seed rape during flowering when bees are present.

In summary, the advantages of microencapsulation may be enumerated:-

(i) Microcapsules reduce the need to introduce large amounts of pesticides in the environment. Instead of the wasteful dissipation by weathering of large amounts of unprotected insecticide deposits on plant surfaces, the slow release rates from microcapsules prolong the persistence and improve the 'availance' $\int_0^\infty C\,dt$ of the toxic compound against appropriate insects, hence making the insecticide more efficient. One application may be sufficient for control, where otherwise repeated applications would be necessary.

(ii) The risk of insect resistance to insecticides may be decreased by the judicious use of microencapsulated insecticides; the build-up of resistance to a particular insecticide which can occur after repeated blanket sprayings of large areas using high concentrations of insecticide may be avoided.

(iii) Transitory pesticides may be used in place of intrinsically persistent ones such as the organochlorines which can cause environmental problems by incorporation into the food chain. Microcapsules afford

considerable protection from weathering, including the effects of U-V light if a light-filtering dye is incorporated.

(iv) The specificity of the insecticide to a particular pest may be enhanced. For example, almost all contact toxicity may be eliminated or it may be considerably lowered so that only stomach poisoning will be effective, provided the microcapsules are small enough (5 microns diameter) to be ingested by leaf-eating pests. Effects on predators or other beneficial insects would be very small.

(v) Microencapsulation offers the possibility of delaying the toxic action until required. For example, a microcapsule may be prepared so that it releases its contents only under certain conditions such as a high temperature or humidity or mechanical pressure causing rupture. This is exemplified by the incorporation of encapsulated permethrin (a very rapid acting insecticide) into baits for leaf-cutting ants, where a delayed toxic action is necessary for success. The bait must be retrieved and disseminated by ants within the many hundreds of chambers forming their very large nests before moisture or any chewing action by the ants causes release of toxicant.

(vi) Repellency effects may be greatly reduced. Often a bait or other formulation is not effective because of a repellent or irritant effect of a high concentration of the pesticide, and microencapsulation would mask this effect.

(vii) Phytotoxicity may be avoided. The damage to plant tissues, caused by high concentrations of some pesticide formulations, can be prevented by microencapsulation.

(viii) Handling hazards to operators may be eliminated or reduced very considerably, thus obviating the need to use protective clothing (which is particularly advantageous in tropical countries).

In considering the problems of environmental pollution by insecticides there is no doubt that microcapsules used in appropriate situations score heavily over those more conventional pesticide sprays which produce toxic surface deposits. Only tiny fractions of the massive doses applied in these sprays are actually used in killing the pest (Neogi and Allan, 1974; Graham-Bryce, 1975). The only disadvantages in the production of the novel microencapsulated formulations appear to be, first, the extra care necessary in quality control to obtain reproducible batches - poorly made microcapsules would be both wasteful and ineffective - and secondly, the cost of producing such sophisticated formulations. The first problem can be solved by improvements in technique and experience. The second problem is controversial and may depend on which is regarded as more important, the long-term aim of good pesticide practice involving little chance of future pollution, or the shorter term concern for bigger profits. However, microcapsules used in suitable situations would reap profits in more senses than one.

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