3

Formulation of pesticides

Pesticides are biologically active in extremely small quantities, and this has been accentuated by the development of the pyrethroid insecticides and other more active pesticides, so the chemical has to be prepared in a form that is convenient to use and to distribute evenly over large areas. The preparation of the active ingredient in a form suitable for use is referred to as 'formulation'. Manufacturers have their own particular skills in formulation, details of which are a closely guarded secret because of competition from rival companies. Knowles (1998) and Van Valkenburg *et al.* (1998) give general information on the principles of formulation. In the first of these books, De Raat *et al.* (1998) and Wagner (1998) describe the regulatory requirements for the European Union and the USA, respectively.

Most pesticides are formulated for dilution in water, and as the measuring of the product and transfer to the sprayer brings the user into the closest contact with the active ingredient, recent changes have aimed at reducing the risk of spillage and operator contamination. This has included developments of new types of formulation as well as improvements in packaging, including the use of water-soluble plastic containers. Changes in equipment have also made it easier to load spray liquids into the tank, by using closed filling systems or providing low level mixing facilities. Some formulations can be applied directly without dilution at ultralow volumes, but toxicological, technical and economic considerations limit the number of chemicals which can be used in this way. Most pesticides were formulated as emulsifiable concentrates, but concern about exposure of the environment to organic solvents has led to greater emphasis on particulate formulations. Where pesticides were marketed as wettable powders owing to the high cost of suitable solvents for the active ingredient, concern about the risk of inhalation hazards has also led to new formulations using dispersible granules (Bell, 1998) or suspension concentrates (Mulqueen *et al.*, 1990; Seaman 1990).

Types of formulation

A range of different formulations is usually available for each active ingredient to suit individual crop-pest and regional marketing requirements. These are now designated by a two-letter code (Table 3.1). Differences between formulated products of one manufacturer may be due to the availability of solvents, emulsifiers or other ingredients at a particular formulation plant. Registration requirements also influence the availability of certain formulations.

Table 3.1 Codes for pesticide formulations[a]

DP	Dust	EC	Emulsifiable concentrate
GR	Granule	UL	Ultralow volume
MG	Microgranule	OF	Oil-miscible flowable
BR	Briquette	TK	Technical concentrate
SC	Suspension concentrate	CS	Capsule suspension
SP	Water soluble powder	EW	Oil-in-water emulsion
WP	Wettable powder	GL	Gel
WG	Water-dispersible granule		

[a] Full list is available from the Global Crop Protection Federation (GCPF, formerly GIFAP), Brussels – Technical Bulletin No. 2 (1989).

Formulations for application as sprays

A few pesticides dissolve readily in water and can be applied as solutions. Examples are the sodium, potassium or amine salts of MCPA and 2,4-D. Owing to insolubility in water, many require formulating with surface-active agents or special solvents.

Wettable powders (WP)

These formulations, sometimes called dispersible or sprayable powders, consist of finely divided pesticide particles, together with surface-active agents that enable the powder to be mixed with water to form a stable homogeneous suspension. Wettable powders frequently contain 50 per cent active ingredient, but some contain higher concentrations. The upper limit is usually determined by the amount of inert material such as synthetic silica (HiSil) required to prevent particles of the active ingredient fusing together during processing in a hammer or fluid energy mill ('micronizer'). This is influenced by the melting point of the active ingredient, but an inert filler is also needed to prevent the formulated product from caking or aggregating during storage. The amount of synthetic silica needs to be kept to a minimum as this material is very abrasive. Apart from wear on the formulating plant, the nozzle orifice on sprayers is liable to erosion, thus increasing application rates.

Wettable powders have a high proportion of particles less than 5 μm, and all the particles should pass a 44 μm screen. Ideally, the amount of surface-active agents should be sufficient to allow the spray droplets to wet and spread over the target surface, but the particles should not be easily washed off by rain.

Wettable powders should flow easily to facilitate measuring into the mixing container. Like dusts, they have some extremely small particles, so care must be taken to avoid the powder concentrate puffing up into the spray operator's face. Most wettable powders are white, so to avoid the risk of confusing powder from partly opened containers with foods such as sugar or flour, small packs containing sufficient formulation for one knapsack sprayer load have been used in some developing countries (Gower and Matthews, 1971). Water-soluble plastic sachets of some products have now superseded this type of packaging, so the whole package is added to the spray tank.

The wettable powder should disperse and wet easily when mixed with water and not form lumps. To ensure good mixing, some pesticides should be pre-mixed with about 5% of the final volume of water and creamed to a thin paste. When added to the remaining water the pre-mix should disperse easily with stirring and remain suspended for a reasonable period. The surface-active or dispersing agent should prevent the particles from aggregating and settling out in the application tank. The rate of sedimentation in the spray tank is directly proportional to the size and density of the particles (see p. 78). Suspensibility is particularly important when wettable powders are used in equipment without proper agitation; for example, many knapsack sprayers have no agitator. Suspensibility of a wettable powder suspension is checked by keeping a sample of the suspension in an undisturbed graduated cylinder at a controlled temperature (WHO, 1973). After 30 min a sample is withdrawn halfway down the cylinder and analysed. The sample should contain at least 50 per cent of the pesticide.

Polon (1973) has described methods of preparing wettable powder formulations. Some wettable powders contain too much surface-active agent and foam when air is mixed in the spray liquid. Foam within the spray rig may cause intermittent application, and is prevented by keeping air out of the spray system. No more than 10 ml of foam should remain in a 100 ml graduated cylinder 5 min after mixing a sample of spray at field strength. Foam can be dispersed by silicones such as Silcolapse.

Wettable powders should retain their fluidity, dispersibility and suspensibility, even after prolonged storage. Containers should be designed to that even if wettable powder is stored in stacks, the particles are not affected by pressure and excessive heat, which may cause agglomeration. The World Health Organization requires tests for dispersibility and suspensibility after the wettable powder concentrate has been exposed to tropical storage conditions. Poor quality wettable powders are difficult to mix and readily clog filters in the spray equipment.

Normally, wettable powder formulations are not compatible with other types of formulation, although some have been specially formulated to mix with emulsions. Mixing wettable powders with an emulsion frequently causes flocculation or sedimentation, owing to a reaction with the surface-active agents in the emulsifiable concentrate formulation. Sometimes a small quantity of an emulsifiable concentrate can be added to a wettable powder already diluted to field strength, but compatibility should always be checked before mixing in the field.

Water dispersible granules (WG)

To overcome the problems associated with wettable powders, the powder can be granulated with a highly water soluble or water absorbing material and binding agent to form dispersible granules (Fig. 3.1) (Wright and Ibrahim, 1984) (Table 3.2). These granules disintegrate rapidly when mixed with water and essentially form a particulate suspension similar to that of a wettable powder. Bell (1989) and Woodford (1998) describe various techniques for producing water-dispersible granules including pan granulation, fluid bed granulation and spray drying.

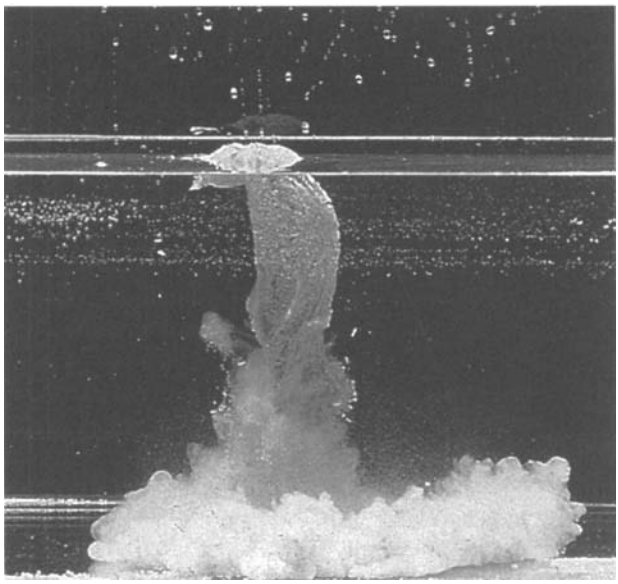

Fig. 3.1 Dispersible granule formulation on mixing with water (courtesy Giba-Geigy, now Novartis).

Suspension concentrates (SC)

Farmers generally prefer to use a liquid formulation, as it is easier to measure out small quantities for use in closed systems. Furthermore, some environmental authorities have restricted the use of certain solvents and surfactants. These factors have led to more interest in suspension concentrates in which a particulate is pre-mixed with a liquid. With an aqueous base they are less hazardous to use. Initially these colloidal suspensions had a short shelf life, as

Table 3.2 Example of a wettable powder formulation

75% Wettable powder	(wt %)
Technical	76.5
Inert filler: HiSil 233 (hydrated silicon dioxide)	21.0
Wetting agent, e.g. Igepon T.77	1.5
Dispersing agent, e.g. Marasperse N	1.0
	100.0

the pesticides sedimented to form a clay deposit which was not easily resuspended. Advances in milling of particles (Dombrowski and Schieritz, 1984) and improved dispersing agents (Heath *et al.*, 1984; Tadros, 1989) have significantly enhanced the shelf life of aqueous based suspension concentrates, which are often referred to as 'flowables' (Fraley, 1984). Mixtures of two pesticides, which are not easily co-formulated in an EC, can be formulated as an SC. Following rain, deposits of an SC formulation were retained better than an EC or WG formulation on cotton leaves (Pedibhotla *et al.*, 1999).

Where possible, the agrochemical industry is replacing emulsifiable concentrates with suspension concentrates. Tadros (1998) gives a detailed account of suspension concentrates.

Emulsifiable concentrates (EC)

An important component in these formulations is the surfactant emulsifier, a surface-active agent, which is partly hydrophilic and partly lipophilic. There are four types of surfactants, namely anionic (negatively charged hydrophilic group), cationic (positively charged hydrophilic group), non-ionic (uncharged) and amphoteric (with both positive and negatively charged hydrophilic groups). A pesticide dissolved in a suitable organic solvent such as xylene or cyclohexanone cannot be mixed with water, because the two liquids form separate layers. The addition of an emulsifier enables the formation of a homogeneous and stable dispersion of small globules, usually less than 10 µm in size, of the solvent in water. The small globules of suspended liquid are referred to as the disperse phase, and the liquid in which they are suspended is the continuous phase. The concentration of many emulsifiable concentrate formulations is usually 25% w/v active ingredient. One of the lowest concentrations available commercially is 8% w/v tetradifon, but manufacturers prefer to use the highest concentration possible, depending on the solubility of the pesticide in a particular solvent. Some pesticides, such as carbaryl, cannot be formulated economically as an emulsifiable concentrate because the solvents in which the active ingredient is soluble are too expensive for field use.

Van Valkenburg (1973) discussed the factors which affect the stability of an emulsion which involves a complex dynamic equilibrium in the disperse phase–interface–continuous phase system. The stability of an emulsion is improved by a mixture of surfactants as the anionics increase in solubility at higher temperatures, whereas the reverse is true of non-ionic surfactants (Van Valkenburg, 1973). Becher (1973) lists a number of emulsifiers, together with a numerical value for the hydrophile–lipophile balance (HLB). An unstable emulsion 'breaks' if the disperse phase separates and forms a 'cream' on the surface, or the globules coalesce to form a separate layer. Creaming is due to differences in specific gravity between the two phases, and can cause uneven application.

Agitation of the spray mix normally prevents creaming. Breaking of an emulsion after the spray droplets reach a target is partly due to evaporation of the continuous phase (usually water) and leaves the pesticide in a film which may readily penetrate the surface of the target. The stability of emulsions is affected by the hardness and pH of water used when mixing for spraying and also conditions under which the concentrate is stored. High temperatures and frost can adversely affect a formulation.

Choice of solvent may also be influenced by its flashpoint so as to reduce possible risks of fire during transportation and use, especially with aerial application. For example, naphthenes are too inflammable for use as insecticide solvents. Emulsifiable concentrates have been applied without mixing in water, but their use as a ULV formulation is not advisable owing to the high volatility of the solvent.

Emulsions pre-mixed with a small quantity of water to form a mayonnaise-type formulation deteriorate in storage, so are not used. Miscible oil formulations are similar to emulsifiable concentrates, but contain oil in place of, or in addition to, the organic solvent. These products are less volatile and more suitable for applications in hot, dry climates.

Invert emulsions

Use of a viscous invert (water-in-oil) emulsion has been considered for aerial application of herbicides to minimize spray drift (Pearson and Masheder, 1969) but has not been accepted because of the need for specially designed equipment. Invert suspensions have been used as drift control agents (Hall *et al.*, 1998).

Encapsulated pesticides

Microencapsulated formulations have been developed primarily for volatile chemicals, e.g. pheromones (Fig. 3.2) (Hall and Marr, 1989) and for controlled release of the pesticide. There are three basic processes:

(1) a physical method of covering a core with a wall material
(2) a phase separation in which microcapsules are formed by emulsifying or dispersing the core material in an immiscible continuous phase, or
(3) by using the second process followed by an interfacial polymerization reaction at the surface of the core.

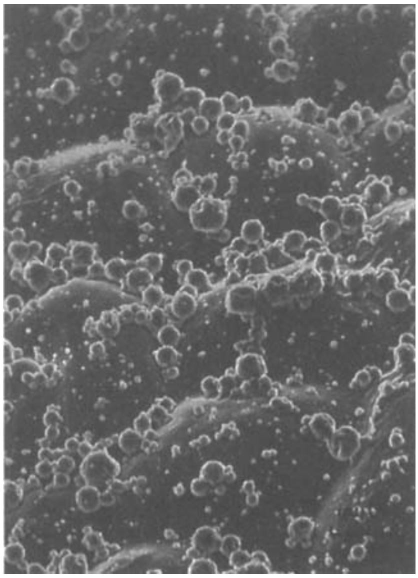

Fig. 3.2 A microencapsulated formulation of a pheromone on the adaxial surface of a cotton leaf (photo: ICA Agrochemicals, now Zeneca).

These processes are discussed in detail by Marrs and Scher (1990) and Tsuji (1990, 1993), Scher *et al.* (1998) and Perrin *et al.* (1998). The persistence of a deposit can be controlled by varying the wall thickness and type of polymer as well as the size of the microcapsule. Special materials to screen the effect of UV light can be incorporated in the capsules. Microcapsules of less than 10 μm diameter have been sprayed very effectively, but the wall thickness relative to the actual capsule size needs to be optimized for specific pesticides and their intended use. Beneficial insects are less exposed (Dahl and Lowell, 1984), although it has been argued that bees can collect capsules because their size is similar to pollen grains. An insecticide can be targeted at foliar feeding lepidoptera when the capsule wall is ruptured only when it reaches the alkaline gut (Perrin, 2000). Specificity can be increased, especially if a suitable attractant is used with a stomach poison, for example in leaf-cutting ant control (Markin *et al.*, 1972). Retention of microcapsules applied in suspension in water with stickers such as Acronal 4D is good on foliage, even after rain (Phillips and Gillham, 1973). In practice slow-release characteristics of microcapsules are particularly useful for application of chemicals which affect the behaviour of insects (Campion, 1976). Application of the pheromone disparlure was reported by Beroza *et al.* (1974), dicastalure by Marks (1976) and gossyplure by Campion *et al.* (1989). Evans (1984) has described a soluble acrylic system for applying the pheromone gossyplure.

Some surfactants solubilised in the aqueous phase of an insecticide microcapsule dispersion can provide a second barrier to the microcapsule wall. This enables the dermal toxicity of a product to be reduced without affecting the release rate of insecticide to such an extent that its activity is reduced to an unacceptable level. A micro-encapsulated formulation of fenitrothion was as effective as the UL formulation against grasshoppers, with some aggregation of capsules in large droplets (Holland and Jepson, 1996).

Ultralow volume formulations

When small spray droplets are used to achieve effective coverage, the evaporation of the droplets needs to be minimized. The decrease in size of droplets between the nozzle and the target as a result of evaporation is discussed in relation to meteorological factors in Chapter 4. A few insecticides such as malathion can be applied as the technical material without any formulation, although there is no need for such high concentrations of active ingredients. The number of such pesticides is very restricted, but it has been possible to formulate a biopesticide with lipophilic spores in a UL formulation. In many cases the viscosity has to be adjusted with a suitable solvent which is normally used to dissolve chemical pesticides. Barlow and Hadaway (1974) investigated a number of solvents to determine which were sufficiently non-volatile for a spray deposit to remain liquid for days or weeks rather than minutes or hours (Table 3.3). Although meteorological factors considerably influence rates of evaporation, they concluded that a suitable solvent should have a boiling point of at least 300°C at atmospheric pressure.

Table 3.3 Volatility of single compounds from cellulose papers at 25°C (from Barlow and Hadaway, 1974)

Compound	Boiling point at 760 mmHg (°C)	Volatility (g/m^2 per day)
n-Decane	174	2030
Isophorone	215	290
n-Hexadecane	287	2.7
Dibutyl phthalate	340	0.05

In addition to low volatility, a solvent suitable for ULV application should have a low viscosity index, i.e. the same viscosity at different temperatures, should be compatible with a range of chemicals and not be phytotoxic. The specific gravity should be high to increase the terminal velocity of small droplets, and pesticides should readily dissolve in it. Viscosity is particularly important in relation to flow rate of liquid to the nozzle. The risk of phytotoxicity is reduced with small droplets. Solvents with all these characteristics are not available (Table 3.4), so a mixture of solvents may be used which overcomes the problem to some extent and is a compromise between persistence and the need for the spray droplet to spread and penetrate an insect

Table 3.4 Physical properties of solvents (from Maas, 1971) (italic type signifies undesirable characteristics)

		Dissolving power	Volatility	Viscosity	Phytotoxicity
I	Low boiling aromatic hydrocarbons, e.g. xylene and solvent naphtha	Good	*High*	Low	Low
II	High boiling aromatic hydrocarbons, e.g. Iranolin, KEB	Good	Low	Low	*High*
III	Aliphatic hydrocarbons, e.g. white spirit kerosene	*Poor*	*Medium*	Low	Low
IV	High boiling alcohols, e.g. nonanol	*Medium*	Low	Low	*High*
V	Ketones, e.g. cyclohexanone	Good	*High*	Low	*Medium*
VI	Special solvents, e.g. pine oil and tetralin	Good	Low	Low	*High*
VII	Vegetable oils, e.g. cottonseed oil and castor oil	*Poor*	Low	*High*	Low
VIII	Glycolethers and glycols	*Medium*	Low	Low	Low
Ideal	ULV solvent	Good	Low	Low	Low

cuticle or plant surface. If droplet size is increased to allow for the volatility of one component of a mixture, fewer droplets can be sprayed from a given volume, reducing the coverage of the target, for example because of the cube relationship between diameter and volume of a droplet, doubling the diameter from 75 to 150 μm reduces the number of droplets to one-eighth. Data on the volatility of certain commercial formulations used in aerial spraying of cotton in Swaziland are given by Johnstone and Johnstone (1977). Solvents used in ULV formulations should have no detrimental effects on the application equipment and fabric of aircraft.

Several different mixtures of a low volatility oil and a more volatile solvent have been tried (Johnstone and Watts, 1966; Coutts and Parish, 1967). Vegetable oils such as cotton seed and soyabean oil have been in some ULV formulations (Scher, 1984). Special solution formulations of carbaryl, DDT and dimethoate (Maas, 1971) were applied successfully on cotton at 2.5 litres/ha, using a sprayer with a spinning disc nozzle (Matthews, 1973) and also with aerial application (Mowlam, 1974), but phytotoxicity was evident on foliage if droplets were too large. The high cost of these special formulations has limited their use, so products diluted in water have been used at 10–15 litres/ha, i.e. very low volume (VLV) on narrow swaths with the spinning disc held close to the crop (Mowlam *et al.*, 1975; Nyirenda, 1991; Cauquil and Vaissayre, 1995). In some areas, molasses has been added as an anti-evaporant and the volume of water reduced to 5 litres/ha (Gledhill, 1975).

Farmers using these VLV techniques still have to prepare the spray as with conventional hydraulic spraying, but are using a more concentrated spray. While this is suitable for some pesticides, the original concept of using ULV treatments was to eliminate mixing on the farm. In some situations pre-packaged products are available to fit directly on the sprayer without any further mixing. Progress in this direction requires closer collaboration between the equipment and chemical manufacturers to match the pesticide product with the sprayer. Products suitable for electrostatic spraying are referred to in Chapter 9. Other products, including several herbicides, are marketed for spinning disc sprayers. These products usually contain either a vegetable oil or refined mineral oil. The latter are selected with a minimum of unsulfonated residue (UR) of 92% to reduce phytotoxicity. A light mineral oil alone or with a fungicide is used at very low volume (VLV) 10–30 litres/ha to arrest development of banana leaf spot 'Sigatoka' (*Mycosphaerella musicola*) (Klein, 1961). Copper fungicide in a heavy alkylate oil was more resistant to field weathering when applied to control angular leaf spot of cucumber (Mabbett and Phelps, 1976). Superior deposition was achieved with ULV copper sprays for control of early blight of tomato (Mabbett and Phelps, 1974). Carbendazin fungicide mixed with a high-grade paraffinic oil was successfully applied to groundnuts for *Cercospora* control (Mercer, 1976). In general, ULV formulations should be checked for phytotoxicity at the proposed field application rate and also at double the rate, using the correct droplet size. Multiple applications may be required to detect any undesirable symptoms which do not show after a single application. Ideally, studies on phytotoxicity should include measurements of photosynthesis and respiration in the crop. Excessive rates of application or too large a droplet are likely to have an adverse effect on plants. The lower surface tension of oils allows greater penetration through stomata of certain leaves, and also through lipoidal leaf cuticles. As these oils are such poor solvents, a suitable solvent and cosolvent to dissolve sufficient active ingredient may have to be added. An advantage of mineral oils is that spraying equipment is not corroded or otherwise affected.

Specially formulated oils such as rapeseed oil plus emulsifier may be added to other formulations mixed with water, specially for controlled droplet application (Barnett, 1990). The proportion of oil in the final spray will depend on the volume applied; usually only 1–2 litres of oil per hectare can be used economically. Further evaluation of this type of carrier is needed with a range of chemicals on different crops to establish optimum concentrations and application rates. Less active ingredient may be required against some pests or weeds when formulations based on oils are used, because the chemical is spread more effectively on the target and is less likely to be washed off plant surfaces.

Uptake of the active ingredient may be reduced if high concentrations of active ingredient are applied in minimal volumes when users attempt to apply the same dose per unit areas as used in HV sprays. This may be caused by localized toxic effects preventing further absorption of the active ingredient.

Fog formulations

In thermal fogging machines, an oil solution of insecticide is normally used. Kerosene or diesel oil is a suitable solvent, provided the solution is clear and no sludge is formed. If a sludge is present a cosolvent, such as heavy aromatic naphtha (HAN) or other aromatic solvent, with a flash point in excess of 65°C should be used. Consideration of flash point is particularly important to avoid the hot gases igniting the fog. Wettable powder formulations have been used, but are normally mixed with a suitable carrier. Certain carriers are based on methylene chloride and a mixture containing methanol. Pre-mixing the powder with some water is advisable, especially with certain wettable powder formulations, so that a clod-free suspension is added to the carrier. Care must be taken to ensure that the viscosity of the fogging solution allows an even flow, and that powder formulations remain in suspension, as the spray tank on fogging machines is not equipped with an agitator. Pesticides such as pirimiphos methyl which have a fumigant effect are ideally applied as an aerosol spray or fog, provided the appropriate concentration is retained for a sufficient time.

Smokes

The pesticide is mixed with an oxidant and combustible material which generates a large amount of hot gas. Water vapour with carbon dioxide and a small quantity of carbon monoxide is produced when a mixture of sodium chlorate and a solid carbohydrate (e.g. sucrose) is used with a retarding agent such as ammonium chloride. The pesticide is not oxidized, as sugars are very reactive with chlorate. Care has to be taken in the design and filling of smoke generators to avoid an explosion and to control the rate of burning. The high velocity of the hot gas emitted from the generator causes the pesticide to be mixed with air, before condensation produces a fine smoke. The period of high temperature is so short that breakdown of the active ingredient is minimal. Smokes have been used in glasshouses and in warehouses and ships' holds. Care must be taken to avoid the smoke diffusing into nearby offices or living quarters, which should be evacuated during treatment.

A special form of smoke generator is the mosquito coil. The coils are made from an extruded ribbon of wood dust, starch and various other additives and colouring matter, often green, together with natural pyrethrins or allethrin. MacIver (1963, 1964a,b) gives a general description of the coils and their biological activity. Each coil is usually at least 12 g in weight and should burn continuously in a room without draughts for not less than 7.5 hours. Chadwick (1975) suggested that the sequence of effects of smoke from a coil on a mosquito entering a room is deterrence, expulsion, interference with host finding, bite inhibition, knockdown and eventually death. The coils provide a relatively cheap way of alleviating the nuisance from mosquitoes during the night.

Dry formulations

Dust

Dust is a general term applied to fine dry particles usually less than 30 µm diameter. Most dust formulations contain between 0.5 and 10 per cent of active ingredient. Transport of large quantities of inert filler is expensive, so a manufacturer may ship more concentrated dusts that are diluted before use in the country importing them. Sulphur dust is applied against some pathogens without dilution.

The concentrate is prepared by impregnating or coating highly sorptive particles with a solution of the pesticide. Alternatively, it may be made by mixing and grinding together the pesticide and a diluent in a suitable mill. The concentrate is then mixed, usually with the same diluent, to the strength required in the field (Table 3.5). Diluent fillers with high surface acidity or alkalinity, or a high oil absorption index, need to be avoided as the formulation would be unstable. Suitable materials for the diluent or carrier are various clay minerals such as attapulgite, often referred to as fuller's earth, montmorillonite or kaolinite (Watkins and Norton, 1955). Forms of silica or almost pure silica such as diatomite, perlite, pumice or talc are also used. Diatomite is composed of the skeletons of diatoms and, like all the other materials mentioned above except talc, it is highly abrasive to the insect cuticle, and can have an insecticidal effect (David and Gardiner, 1950). In the tropics, road dust drifting into hedges and fields is often very noticeable and can upset the balance of insect pests and their natural enemies. Dusts have been used to protect stored grain without an insecticide, but mortality is less as the moisture content is increased (Le Patourel, 1986).

Apart from sulphur dust used mainly as a fungicide, dusts are no longer used as much as the extremely small particles are prone to drift downwind, and winnowing of independent particles of active ingredient and diluent can also

Table 3.5 Examples of dust formulations

Component	Content (%)
(*a*) Dust concentrate	
50% Sevin (carbaryl) dust concentrate	
Technical carbaryl	50.5
a Montmorillonite clay, e.g. Peak clay	49.5
	100.0
(*b*) Field strength dust (by dillution)	
5% Sevin dust	
50% dust concentrate	10.2
a Montmorillonite clay, e.g. Pikes Peak clay	9.8
a Kaolinite clay, e.g. Barden A.G. clay	80.0
	100.0

occur (Ripper, 1955; Eaton, 1959). Often only 10–20% or less of a dust is deposited on the target (Courshee, 1960), so most dusts are now used to treat seeds, to protect horticultural crops grown in long narrow polythene tunnels where the water in sprays can exacerbate fungal diseases, and in farm stores. Seed can be treated centrally by seed merchants, but the product used in the treatment should contain a warning colour and bitter ingredient to prevent such seeds being eaten by humans, birds or farm animals.

Most dust is removed from foliage by rain, although the very small particles can adhere very effectively to plant surfaces. In some cases redistribution by rain can be advantageous; thus dusts applied to the 'funnel' of maize plants may be washed to where stalk-borer larvae penetrate the stem. However, most farmers now prefer to use larger microgranules to control this pest. Dusts with a low content of active ingredient (0.5% a.i.) with a short persistence such as malathion and pirimiphos methyl, have been mixed with grain (Hall, 1970), but there is concern about residues, even though surface deposits are removed by washing before the grain is ground into flour and cooked.

Granules

Large, discrete dry particles or granules are used to overcome the problem of drift, although care is essential during application to avoid fracture or grinding of the granules to a fine dust, which could be dangerous if inhaled or touched. This is particularly important, because pesticides, which are too hazardous to apply as sprays, such as aldicarb, are formulated as granules. These granules may be coated with a polymer and graphite to improve the flow characteristics and reduce the risk of operator contamination. Granules are prepared by dissolving the pesticide in a suitable solvent and impregnating this onto a carrier which is similar to those used in dust formulations, namely attapulgite or kaolin. Other materials that have been used include vermiculite, coal dust, coarse sand and lignin (Allen *et al.*, 1973; Wilkins, 1990; Humphrey, 1998). Sometimes a powder is made and the granule formed by aggregation (Whitehead, 1976). Goss *et al.* (1996) provide a recent review of granule formulation.

The choice of the inert carrier will depend on the sorptivity of the material, its hardness and bulk density (Table 3.6) (Elvy, 1976). Bulk density is especially important in relation to the volume of the product that has to be transported. Like dusts, the concentration of active ingredient is usually less than 15%, so transport costs per unit of active ingredient are high. The rate of release of a pesticide from the granules will depend on the properties of the pesticide, solvent and carrier, but the period of effectiveness is often longer than that obtained with a single spray application. The coating of a granule and the thickness of it can be selected to control the rate of release to increase persistence.

When an infestation can be predicted, a prophylactic application of granules may be more effective than a spray, especially if weather conditions prevent sprays being applied at the most appropriate time. Uptake of a pesticide by a

Table 3.6 Properties of dust diluents and granule carriers

	Bulk density (g/dm^3)	Specific gravity	pH
Oxides	144–176	2.0–2.3	5–8
Silicon			
Diatomite			
Graded sands			
Calcium	448–512	2.1–2.2	12–13
Hydrated lime			
Sulphates	784–913	2.3	7–8
Gypsum			
Carbonates	769–1073	2.7	8–9
Calcite			
Silicates	480–833	2.7–2.8	6–10
Talc	448	2.7–2.9	6–7
Pyrophyllite	608–705	2.2–2.8	6–10
Clays	480–561	2.6	5–6
Montmorillonite	432–496	2.6	7
Kaolinite			
Attapulgite			

plant may be negligible if the soil is dry and movement of chemical to the roots is limited, so granules of certain pesticides are more suitable on irrigated land where soil moisture can be guaranteed. Conversely, there may be phytotoxicity under very wet conditions. Granules have been used extensively in rice cultivation where they are broadcast, but the main advantage of granules is that they can be placed very precisely, so less active ingredient may be required and there is less hazard to beneficial insects. They are often placed alongside seeds or seedlings at planting, but spot treatment of individual plants is possible later in the season. In Africa, control of the stalk-borer of maize has been achieved with a 'pinch' of granules dropped down each maize 'funnel' (Walker, 1976). Banana plants may be treated with granules to control burrowing nematodes. Granules are often applied by hand, but this should be discouraged even if the person wears gloves. Simple equipment with an accurate metering device is available for both placement and broadcast treatments (see Chapter 12). With more precise placement, there is also less hazard to beneficial insects.

Despite the advantage of not mixing the pesticide on the farm, there has been a rather slow acceptance of granule application. One main drawback is that equipment required for granule application is more specialised than a sprayer and, with a smaller range of products available in granule form, farmers are reluctant to purchase a machine with a limited use. Granules are often applied at sowing, in which case the applicator has to be designed to operate in conjunction with a seed-drill or planter. Secondly, development of suitable equipment has been hampered by a lack of research to determine the best means of distributing granules to maximise their effectiveness, especially with herbicides where uniform distribution is essential. Variation in the quality of granules has also caused difficulties in calibrating equipment. Granules have been categorised by mesh size, the numbers indicating the coarsest sieve through which all the granules pass, and on which the granules are retained (Table 3.7), but similar samples may have quite different particle size spectra (Table 3.8) (Whitehead, 1976). The Agriculture (Poisonous Substance) Regulations in the UK require that not more than 4% by weight shall pass a 250 μm sieve, and 1% by weight through a 150 μm sieve when the more toxic pesticides are formulated as granules (Crozier, 1976). The size range affects the number of particles per unit area of target (Table 3.8).

Table 3.7 Sieve analysis of two samples described as 8/22 mesh granules

Pass mesh no.	Retained by mesh no.	Percentage of granules in sample	
8	12	2	10
12	16	36	60
16	22	42	30

Table 3.8 Estimated number of attapulgite granules per unit area

Mesh size	Particle size (μm)	Calculated no. of particles/m[a] applying 1 kg/ha
8/15	2360–1080	32
15/30	1080–540	253
20/40	830–400	817
30/60	540–246	2712
80/120 (microgranule)	200–80	78125

[a] The number of granules per kg will depend on whether dried or calcined granules of attapulgite are used; number of granules per plant can be calculated knowing the plant density.

Larger granules (8/15 mesh) which fall easily, even through foliage, are used principally for application in the soil or to water surfaces, for example to control mosquito larvae or aquatic weeds. Granules, including soft ones such as bentonite which release the toxicant quickly, have been widely used to control various pests in paddy fields where they can be broadcast by hand. Movement of insecticide is partly by systemic action, but also some chemical is carried by capillary action between stems and the leaf bases. With some pesticides, there may also be a localised fumigant effect. Chemical is lost if granules are carried out of the fields in irrigation water, so smaller microgranules (80–250 μm particle size) which adhere to foliage are used for application to rice plants. Size 30/60 mesh granules are normally used for stalk-borer control on maize.

Impregnating fertiliser granules with pesticides has been considered to eliminate the cost of an inert carrier and save time and labour during application. Apart from the possible breakdown of the pesticides when combined with fertiliser, there may be different requirements for timing and placement of toxicants and nutrients, although a broadcast application of certain herbicides plus fertiliser ('herbiliser') has been used with success (Ogborn, 1977). Walker (1971) reviewed the subject of residues following the application of granules.

Dry baits

Pesticides are sometimes mixed with edible products or sometimes with inert materials, usually to form dry pellets, or briquettes, which are attractive to pests. Using bran as a bait has controlled cutworms and locust hoppers, and banana bait has been used in cockroach control. Baits have also been used to control leaf-cutting ants (Lewis, 1972; Phillips and Lewis, 1973) and slugs. Maize and rodenticides have been mixed in wax blocks for rat control in palm plantations. Peregrine (1973) reviewed the use of toxic baits. A major problem with pelleted baits is that domesticated animals can eat them, and they disintegrate readily in wet weather and are then ignored by the pests. Non-pelleted baits go mouldy very rapidly, but a silicone waterproofing agent can be added to delay mould development. For invertebrate pests such as ants, the bait can be dispersed in the infested area, but mammalian pests may develop 'bait shyness' especially if dead animals are left near a bait station. Pre-baiting or a mixture of poisoned and unpoisoned baits reduces this.

Dry fumigants

Aluminium phosphide compressed in small, hard tablets with ammonium carbonate, on exposure to moisture releases the fumigant phosphine, together with aluminium hydroxide, ammonia and carbon dioxide. The tablets can be distributed evenly throughout a mass of grain in stores. Normally, no appreciable evolution of the fumigant occurs immediately, and respirators are not required if application is completed in less than one hour. The exposure period for treatment is usually three days or longer, so precautions must be taken to avoid personnel becoming affected. Other fumigants such as methyl bromide are supplied as liquefied gases under pressure in special containers, and their use is described in Chapter 14.

Other formulations

Pressure packs

The pesticide active ingredient is dissolved in a suitable solvent and propellent, and packaged under pressure in a 'pressure pack', commonly referred to as an aerosol can. Apart from pesticides, these are used to dispense a wide range of products such as hair lacquers, paints and deodorants. The pressure pack is a convenient but expensive means of producing aerosol droplets, and is used as a replacement for the 'Flit gun' (Fig. 3.3), which is less expensive, but requires manual effort to force air through a nozzle to which the insecticide is sucked by a venturi action. Propellants such as butane, carbon dioxide and nitrogen are now more commonly used, as fluorinated hydrocarbon use has been discontinued.. Because the propellant is confined at a temperature above its boiling point, opening of the valve on the top of the container (Fig. 3.4)

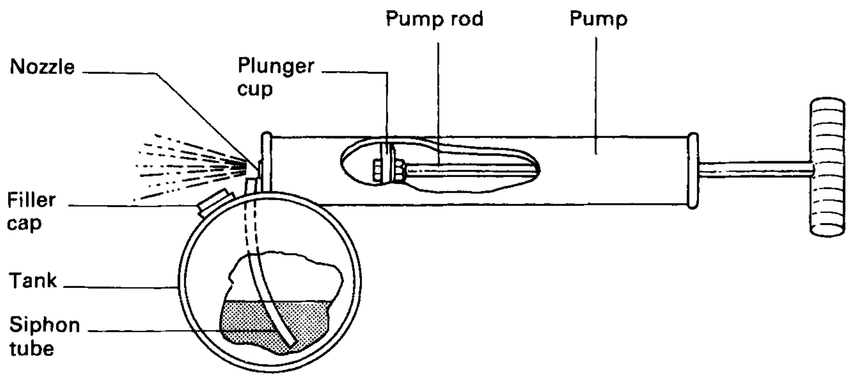

Fig. 3.3 Flit gun.

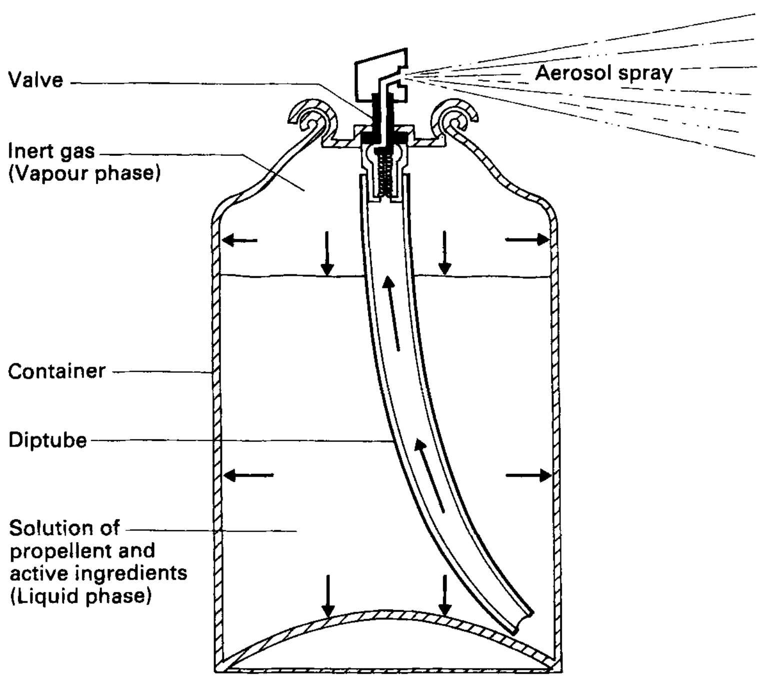

Fig. 3.4 Cross section of typical pressure pack.

allows the pressure inside the container to force the contents up a dip tube and through the valve, which is essentially a pressure nozzle. However, as the propellant reaches the atmosphere, some of it flashes from a liquid to a gas and causes the solution of active ingredient to break up into droplets. Further evaporation of the propellant and solvent causes a reduction in droplet size between the nozzle and target; hence the pressure pack should not be held too close to the target otherwise an uneven deposit will be obtained.

Typical valves continue to operate while the valve is depressed, but others incorporate a metering chamber, so that the quantity of product discharged can be controlled. The standard orifice is usually about 0.43 mm. When a coarse spray is required, the amount of propellant is reduced, and the valve may incorporate a swirl chamber as on cone nozzles. Finer sprays in a wider cone are obtained when the orifice in the valve has a reverse taper. The problem for some of the alternative propellants such as compressed carbon dioxide is that the pressure decreases as the pressure pack empties. The pressure increases with temperature when a liquefied compressed gas is used. Droplet size decreases rapidly after formation of droplets at the nozzle when a very volatile solvent such as xylene is used.

Tar distillates

These contain a mixture of aromatic compounds such as benzene, naphthalene and anthracene, tar bases such as pyridine and tar acids including phenol and cresol. This mixture starts to boil at 210°C, but less than 65 per cent of the volume has boiled at 350°C. Tar distillates have been used as dormant sprays.

Solubilised formulation

Solubilisation refers to the mixing of a water-soluble pesticide with oil by using suitable surfactants as cosolvents. The aim is to produce a formulation which increases penetration of the bark or leaf cuticle, but permits translocation of the active ingredient in the plant. The technique has been tried with some herbicides (Turner and Loader, 1974). The effect of leaf-applied glyphosate was improved compared with an aqueous spray, but the cost of oil and solvents was too great.

Banding materials

Localized application of pesticide to the trunk of trees can be achieved by banding. Grease bands have been used to trap insects climbing trees.

Plastic strips

Some volatile insecticides such as dichlorvos have been impregnated onto plastic strips. When hung in a closed room or room with minimal ventilation, the concentration of vapour released from the strip is sufficient to control some insects. This type of formulation is also used to dispense pheromones.

Paints and gels

Some insecticides have been incorporated into paints applied to surfaces where insects such as cockroaches may walk. Experiments have also included a systemic insecticide with a latex paint applied to the inside of pots to protect young seedlings from aphids and other sucking pests (Pasian *et al.*, 2000). Dispersion of herbicides makes it difficult to control aquatic weeds, so slow release formulations (e.g. gels) have been used (Barrett, 1978; Barrett and Logan, 1982; Barrett and Murphy, 1982).

Adjuvants

A wide range of non-pesticidal products has now been marketed as adjuvants (Fig. 3.5) (Hall *et al.*, 1993; Thomson, 1998). Manufacturers of these products claim that their use will enhance the performance of a pesticide and in some cases reduce the amount of active ingredient that needs to be applied. Many agrochemical companies believed that mixing an adjuvant with their pesticide was unnecessary due to their precise formulation, but with the extensive range of targets for a pesticide, it has become increasingly recognised that an adjuvant may be required in certain situations. Indeed, some agrochemical

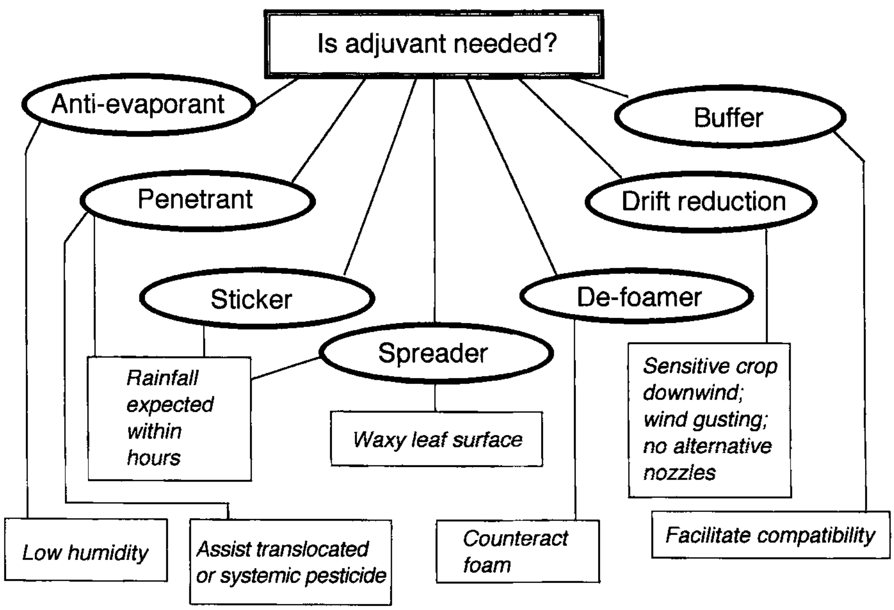

Fig. 3.5 Chart to show different types of adjuvants.

companies have marketed specific adjuvants for tank mixing with their pesticide. Although not pesticides, adjuvants do require registration as they affect the performance of pesticides (Chapman and Mason, 1993; Chapman *et al.*, 1998).

Adjuvants can be divided into several distinctly different types, although some will act in more than one way (Fig. 3.5). Adding a surfactant to a spray may improve the spread of a droplet across a hydrophobic surface, such as a waxy leaf. A surfactant can also improve penetration of the spray deposit through the leaf cuticle and thus reduce losses if rain occurs soon after application. Addition of an oil with emulsifier can reduce the proportion of small droplets in a spray and also decrease the effect of evaporation on droplet size, thus enhancing deposition with less drift (Western *et al.*, 1999).

Refined white oils have also been added to emulsifiable concentrate sprays applied at HV to improve penetration of the toxicant where the cuticle is particularly resistant to uptake of water-based sprays. Control of scale insects on citrus and other crops is a good example of this, where the addition of a suitable oil improves the effectiveness of an insecticide.

Reduction but not elimination of drift, particularly with aerial application, is assisted by adjuvants containing thickening agents, such as polysaccharide gum with thixotropic properties, alginate derivatives, hydroxethyl cellulose and various polymers. Using bioassays, Thacker *et al.* (1994) demonstrated that a polymeric adjuvant significantly reduced the amount of drift of an organophosphate insecticide. In the USA, Hewitt *et al.* (1999a) provide a review of drift control agents as a background to future guidelines on assessing their impact in minimising drift. These adjuvants can affect spray distribution, although such effects are less important with translocated herbicides than with a contact chemical (Downer *et al.*, 1998a). Sanderson *et al.* (1994) reported that agitation affected the polymer structure, and the addition of some of these has created mixing problems and increased costs. Some of the polymers used in drift retardant adjuvants lose their effectiveness after being re-circulated through the pump (Zhu *et al.*, 1997). In many cases changing the spray nozzles to provide a coarser spray, preferably with a narrow range of droplet sizes, or applying granules has more effectively reduced drift.

The persistence of a formulation can be improved by adding 'stickers', but care must be taken to avoid protecting the deposit so much that the availability of it to a pest is reduced. Persistence to rain-washing was improved by formulating wettable powders with amine stearate (Phillips and Gillham, 1971). Such formulations were effective on foliage that was difficult to wet, for example cabbage leaves (Amsden, 1962), and were also useful where new growth was insufficient to justify repeat applications. The addition of a surfactant to increase penetration of glyphosate has been used in tropical areas (Turner, 1985), but rain within one hour can remove 75 per cent of a herbicide deposit (Reddy and Locke, 1996). Apart from the use of various additives (including oils), improved rain-fastness can also be achieved with fine particles, which are not readily washed off by rain. Even a tropical thunderstorm fails to remove all the dust from surfaces, as electrostatic forces hold the particles to a surface. Advantages of small size and slow release of a pesticide are combined with microencapsulated formulations.

The addition of an adjuvant may affect the droplet spectrum of a nozzle due to changes in dynamic surface tension and viscosity. Butler Ellis and Tuck (1999, 2000) give data on the effects of adjuvants on fan nozzles. Changes in temperature can also influence spray droplet formation; thus the VMD decreased with increasing temperature (10–50°C) when the drift retardant Nalcatrol II was added, but droplet size increased with an organo-silicone surfactant (Downer *et al.*, 1998b). Adjuvants may also affect the distribution across the spray swath (Chapple *et al.*, 1993a; Hall *et al.*, 1993). The addition of a surfactant should also be checked to ensure that no phytotoxicity occurs at the concentration used. Some surfactants can interact with the epicuticular wax on leaves depending on the oxyethylene chain length (Knoche *et al.*, 1992). Regular conferences report effects of adjuvant use with different pesticides (e.g. Foy, 1992; Foy and Pritchard, 1996).

Choice of formulation

Formulations have usually been selected on the basis of convenience to the user. Farmers who have large tractor-mounted sprayers fitted with hydraulic agitation prefer liquid concentrates which can be poured into the tank or transferred straight from the container, as a volume of concentrate is much easier to measure than to weigh out a powder. Nevertheless, in many parts of the world, the less expensive wettable powder or granule is used extensively. Pre-packaging selected weights of dry particulate formulations facilitates having the correct dosage for knapsack or tractor equipment, by eliminating the need to weigh them on the farm. When these dry formulations are packaged in a sachet made from a water soluble polymer, the whole sachet can be placed in the spray tank or induction hopper (Fig. 3.1). Particular care is needed to avoid touching the surface of these sachets with wet hands/gloves and keeping them protected in a dry container until needed. The water soluble polymer may be slow to dissolve at low temperatures. Wettable powders have a rather better shelf life than emulsifiable concentrates, an important factor when it is difficult to forecast requirements accurately.

Barlow and Hadaway (1947) showed that a particulate deposit was more readily available to larvae walking on sprayed leaves than an emulsifiable concentrate, perhaps because the leaf absorbed the emulsion more readily. Large-scale trials on cotton confirmed that by using a wettable powder instead of an emulsifiable concentrate formulation against bollworm, farmers obtained a higher yield at less cost (Matthews and Tunstall, 1966). Similarly, DDT wettable powder was recommended for residual deposits on walls of dwellings for mosquito control. With powder formulations, particle size is important, especially with some pesticides such as insect growth regulators. In general, micronization of a formulation provides finer particles which are more effective for contact pesticides than when coarse particles are present.

When stomach poisons are applied, surface deposits are effective against leaf-chewing insects, but less so against borers which often do not ingest their first few bites of plant tissue. The effectiveness of stomach poison can be improved by the addition of a feeding stimulant, such as molasses, to these sprays. Carbaryl wettable powder is relatively ineffective against the noctuid *Helicoverpa armigera*, but up to 20 per cent molasses added to the spray gave improved larval mortality and also considerable mortality of moths feeding on the first three nights following application.

Choice of formulation has often been dictated by the availability of equipment in developing countries. Low percentage concentration dusts and granules can often be applied by hand or shaken from a tin with a few holes punched in it, when a sprayer is not available. On the other hand, farmers may be reluctant to use granules where neither labour nor specialised equipment is readily available. Shortage of water in many areas has dictated the use of dusts or granules, but high transport costs have favoured the use of highly concentrated formulations as these are less bulky.

Phytotoxicity is another factor in determining the choice of formulation, as some plants, or indeed individual varieties, are susceptible to certain solvents and other ingredients, such as impurities due to the use of cheap solvents. Phytotoxic effects may be caused by chemical burning, physically by droplets on the plant surface acting as lenses which focus the sun's rays on the plant tissue, or by subsequent effects on plant growth.

The use of formulations of low concentration reduces the toxic hazard when measuring and mixing the concentrate material with diluent or applying it undiluted. This hazard can be reduced by properly designed and standardised containers, which allow the concentrate to be either poured easily or pumped directly into the spray tank. The greatest danger occurs when the spray operator does not wear protective clothing, especially when only a small quantity is required from a large container. Spillage may occur over the operator's hands or feet, or a splash may contaminate the eyes or skin. Water-soluble plastic sachets eliminate handling of concentrate formulations, but strong outer packaging is needed to keep the sachets dry until required. Some liquid products are now packed in containers which incorporate a measure (Fig. 3.6).

Usually, what is readily available and the price decide the choice of formulation. In general, the cheapest in terms of active ingredient are wettable powder formulations and those with the highest amount of active ingredient per unit weight of formulation. When assessing costs, the whole application technique needs to be considered, since the use of a particular formulation may affect the labour required, the equipment and spraying time. Whichever formulation is chosen, users must read the instructions with great care before opening the container. Manufacturers attempt to provide clear instructions on the label of each container, but limitations of pack size may restrict information on the label, in which case an information leaflet is usually attached to the container. Care must be taken to avoid premature loss of labels, and important information can also be easily obliterated by damage under field

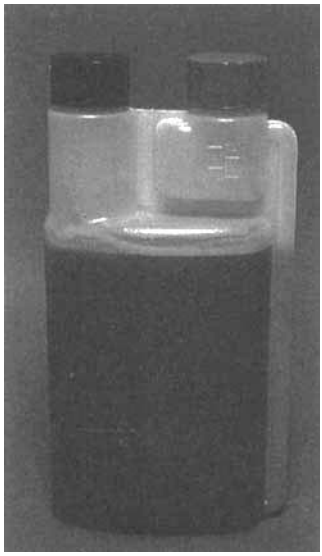

Fig. 3.6 Litre container incorporating measure to dispense small volumes of liquid pesticide formulations.

conditions. If in doubt about the correct dosage rate and method of use, alternative sources of information, such as the appropriate pesticide manual or crop pest handbook, should always be checked before starting a pesticide application programme.