

THE FORMULATION AND MANUFACTURE OF GRANULAR PESTICIDES

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Summary Granular pesticides are now an accepted part of agriculture. This paper covers the formulation and manufacturing techniques used in preparing granular products.

INTRODUCTION

It is essential to understand that in any discussions on the formulation and manufacture of granular pesticides there are two major types of granules. For convenience I shall call the two types of granules

- A. Core Granules
- B. Compounded Granules

With core granules the starting point is a granular inert carrier base of the required particle size. The fundamental manufacturing step involves the impregnation into or the coating onto the granule, of the active pesticide. Compounded granules differ in that the fundamental manufacturing step is the creation of granules from raw materials of smaller particle size than the finished product. This paper discusses the formulation and manufacture of these two fundamentally different types of granule.

FORMULATION CONSIDERATIONS IN GRANULE MANUFACTURE

The formulation Chemist must aim to fulfill the following objectives in producing a granular pesticide:

- (i) A biologically satisfactory granule
- (ii) A chemically stable granule
- (iii) A free-flowing granule
- (iv) A non-caking granule
- (v) A dust-free granule
- (vi) A granule strong enough to travel without breaking down

The decision as to whether a core granule or a compounded granule will be made is greatly influenced by the answers to the following questions:

- (a) The physical and chemical properties of the active ingredient.
- (b) What concentration of active ingredient is required.
- (c) In what form the technical material is available.
- (d) What particle size is desirable for the end product.
- (e) What shape of granule is required.
- (f) What particular method of application will be used.
- (g) What special features of the granule are required, e.g. slow release, delayed release etc.

- (h) What can the crop afford in the way of a granular product. Can it afford an expensive formulation or is a cheap formulation required.

### IMPORTANT GRANULE CHARACTERISTICS

#### Particle Size Classification

Granules are classified in terms of size by reference to the mesh size. For example, granules are called:

- 8 - 22 mesh or 8/22 mesh i.e. 2mm to 0.7mm sized particles
- 22 - 44 mesh or 22/44 mesh i.e. 0.7mm to 0.35mm sized particles
- 15 - 30 mesh or 15/30 mesh i.e. 1.2mm to 0.5mm sized particles
- 30 - 60 mesh or 30/60 mesh i.e. 0.5mm to 0.2mm sized particles

This means that in any mesh grading the particles will pass through a sieve having a mesh size of the first number and will be retained on a sieve having a mesh size corresponding to the second number. For example, granules designated 8/22 mesh will pass through an 8 mesh sieve and be retained on a 22 mesh sieve. In practice the specification may allow a small percentage to be retained on the 8 mesh sieve and also permit a small percentage to pass the 22 mesh sieve. The bulk of the granules should however fall between 8 mesh and 22 mesh. A typical specification might be for 8 - 22 mesh granules.

Retained on 5 mesh	Nil
Passing 5 mesh retained on 8 mesh	2% max.
Passing 8 mesh retained on 22 mesh	96%
Passing 22 mesh	2% max.

Similar specifications exist for the other classifications. Usually the type of sieve standard is specified, e.g. B.S.S. 8 mesh or U.S. 8 mesh etc. These sieve fractions are fairly wide so two samples designated the same sieve size will not be necessarily identical in particle size spectrum. The sieve analysis on two samples both described as 8/22 mesh granules might well have the following compositions,

	Sample A	Sample B
Passing 8 mesh		
Retained on 12 mesh	2%	10%
Passing 12 mesh		
Retained on 16 mesh	36%	60%
Passing 16 mesh		
Retained on 22 mesh	42%	30%

Particle size is very important when formulating very toxic materials and under The Precaution Scheme, the following Specification must be met:

Not more than 4% shall pass a 60 mesh B.S.S. screen and not more than 1% shall pass a 100 mesh B.S.S. screen.

This Specification, usually known as the Dust Specification, protects those applying granular pesticides from contamination risks due to airborne toxic dust. In practice, a more rigorous specification is used to allow for any breakdown of granules during transit from factory to field. It is interesting to note that these 60 to 100 mesh and finer than 100 mesh particles have been regarded hitherto as dust. We now have the advent of the microgranule where smaller particle sizes are being investigated as granules but which under existing legislation should be classified as dust. There is also some confusion at the moment as to what exactly constitutes a microgranule. In some cases a 30 - 60 mesh granule is called a microgranule. In general the 80 - 120 mesh size range seems to be the popular concept of a micro-granule.



### Particles per Pound of Granules

The number of particles per pound of granules varies enormously in the different gradings of granules available, as the following table shows:

<u>Mesh Sizing</u>	<u>No. of Particles per lb of Granules</u>
8/16 mesh	170,000
16/30 mesh	1,300,000
18/35 mesh	3,250,000
25/50 mesh	8,700,000
30/60 mesh	13,600,000

In some cases biological efficiency of a granular pesticide is very largely governed by the number of particles per pound, so field trials with different mesh grades of granules are essential to determine the importance of this with a given pesticide. A close Specification for the granules is needed if a pesticide is influenced by the number of particles per pound.

### Granule Hardness

The granule must be hard enough to stand up to rigours of transportation, and also be hard enough to pass through application equipment without undue breakdown. Attrition tests on granules usually consist of placing granules and small steel balls in a jar and rotating the jar for a given time. At the end of the rolling time the steel balls are removed and a sieve analysis performed on the granules. The amount of dust produced is used as a measure of the granule strength.

### Compatibility of the Active Ingredient with the Granular Carrier or the Components of a Compounded Granule

The shelf life of a granule should be at least two years. Studies to check chemical stability of the product show that several causes of degradation of the active component take place either on or within the granule.

### Degradation by Hydrolysis

Many organophosphorous compounds are easily decomposed by water. Tests must be made to measure the water content of granules which can be quite high in impregnated granules where an absorbent carrier is used. Care must be taken in these tests to be quite sure that the water is in fact causing hydrolysis. There are cases where small percentage of water added to the concentrated pesticide will promote decomposition but the same percentage of water in the granule will not cause decomposition because the water appears to be very strongly absorbed by the carrier. In other cases the very presence of water is sufficient to produce decomposition, so each case must be studied individually. With non absorbent granules water may be present very much as free water. In the case of compounded granules it may be featured in the actual manufacturing process or released from raw materials in the process.

### Acid or Alkaline Degradation

The surface of carrier granules may be sufficiently acidic or alkaline to cause decomposition of the pesticide. In compounded granules pH of the component raw material might be the cause of the trouble.

### Catalytic Decomposition

When active sites on the granular carrier or in the raw materials used promote decomposition, action must be taken to prevent this happening. The carrier granule or the offending raw material may be changed, but in attempting to overcome instability in this way, other desirable properties of the granule might also be affected. For example, a carrier granule might be very hard, giving a dust free product but an alternative granule without degradation problems might be softer and not dust free.

Instead the carrier or raw material can be treated in some way to eliminate the problem. For example, treatment of the carrier with glycols, alkanolamines and in some cases sodium hydroxide has been found to substantially reduce decomposition of chlorinated hydrocarbons on acidic carriers. Inhibition of decomposition of organo-phosphorous compounds which are more prone to alkaline decomposition is reduced with alcohols, ketones, glycols and ethers. Carbamates are best formulated on neutral or acidic carriers.

#### Flowability of Granules

Granules must travel and store without caking or fusing together to form large agglomerates and must flow well through applicators. Any agglomeration however small might block or even jam the applicator, so that granules are not applied evenly or at the correct application rate.

### RAW MATERIALS, METHODS AND EQUIPMENT USED IN GRANULE MANUFACTURE

These are considered in the following categories:

- A. Core granules based on impregnated or absorption techniques.
- B. Core granules based on non-absorption techniques.
- C. Compounded granules.

#### A. Impregnated Granules

These granules are made by dissolving the active ingredient in suitable solvent, selecting a carrier granule and spraying the solution onto the granular carrier.

#### Granular Carriers

The most commonly used carrier granules are naturally occurring minerals.

- (a) Attapulgites
- (b) Montmorillonites
- (c) Sepiolites
- (d) Pumices
- (e) Bentonites

All are characterized by having porous molecular structures which can absorb liquids. They are obtained by mining, crushing, drying and sieving to the required size. Some granules are hardened to increase resistance to breakdown in water by calcining at high temperatures of around 450°C; in which case two grades are available. The ordinary dried grade is usually designated Regular Volatile Material Grade (R.V.M.) or the calcined grade known as Low Volatile Material Grade (L.V.M.). With Attapulgites, a further stage may consist of adding water and pug-milling followed by extrusion prior to drying or calcining. These two grades are designated AA RVM for the pugged, extruded dried grade and AA LVM for the pugged, extruded calcined grades. The pugging and extrusion operation increases the absorptive capacity of the granules. Thus, granules which release active ingredients at different rates are produced by careful choice of carrier.

#### Impregnation of the Carrier Granule

The physical and chemical properties of the active ingredient determine the manner in which the impregnation is carried out. When the active ingredient is a liquid under normal conditions, it is simply sprayed onto the granules with or without the addition of a deactivating agent. If low concentrations are required a solvent may be added to facilitate even coverage of the granules. Some pesticides, solids at normal temperatures, can be liquified by melting and again with or without deactivators sprayed on the granules. Solid pesticides which cannot easily be melted are dissolved in a suitable solvent, and sprayed onto the granules. The granules are dried or subjected to some form of solvent removal process.



The solvent should ideally:

- (a) Dissolve reasonable quantities of pesticide.
- (b) Be fairly volatile to assist its subsequent removal.

When large quantities of poor solvents have to be used, subsequent removal of the solvent is more difficult. Volatile solvents may cause crystallisation problems in spray lines and nozzles, but if too involatile removal will also be difficult. The deactivator may have to be sprayed onto the granules before the active ingredient.

#### Equipment Used

The plant used for production of granules is outlined schematically in Fig.1 and consists of:

1. A mixing vessel for the preparation of the spray liquid.
2. Measuring device for controlling volume/weight of liquid sprayed.
3. Pump or pressure pot and spray lines to convey liquid to blender.
4. Spray nozzles in blender to give uniform distribution of liquid.
5. Blender with or without solvent removal/recovery.
6. Granule feed to blender, often via screening plant.
7. Dump tank from blender.
8. Screening and bagging unit for finished product.
9. Fume and dust extraction to all parts of plant.

The most important piece of equipment is the blender. The rest of the equipment is conventional and needs no special discussion here. Several different kinds of blender are available. The following blenders are the most commonly used:

- |                                   |         |
|-----------------------------------|---------|
| (a) Ribbon Blenders               | Fig. 2a |
| (b) Drum Blenders                 | Fig. 2b |
| (c) Cone and Double Cone Blenders | Fig. 2c |
| (d) Pan Blenders                  | Fig. 2d |

Ribbon Blenders Care must be taken to ensure adequate clearance between the end of the blender arms and the walls of the mixing vessel. If the clearance is only small then the mixing action can cause breakdown of the granules creating dust problems. Ribbon blenders can easily be totally enclosed and also heated. This makes the removal of solvent a fairly easy task.

Drum Blenders These are fitted with internal flights or baffles. Rotation of the drum lifts the granules giving a very thorough mixing action. The spray inlet is arranged as near to the centre of the drum as possible so that granules are constantly exposed to the spray solution. Drum blenders are usually totally enclosed and can be heated thus facilitating solvent removal.

Conical and Double Cone Blenders are very efficient mixers. The tumbling granules are separated into two fractions continuously by coming into contact with the rotating V shaped wall surface. They are also easily heated and totally enclosed, aiding solvent removal.

Pan Blenders are open inclined cylindrical pans. There is less protection for the operator and solvent removal and recovery in the pan is hazardous or impossible because of the essential open nature of the pan. Very often agglomeration of granules occurs so over-sized particles have to be removed.

Drum and cone blenders are the most commonly used for impregnated granules.

#### B. Non Absorbent or Coated Granules

These granules differ from the impregnated granules in that there is little or no absorption and the active ingredient remains on the surface of the granule. A film of liquid is put around each granule and then the granule is rendered dry and

free flowing by treatment with powdered material. Two variations of this technique are available. The first one involves spraying the liquid active ingredient onto the granule followed by drying with inert powdered material. The second method involves spraying some inert liquid onto the granule and then using the powdered solid active ingredient to effect drying. The second variation is extremely useful for active ingredients which are very insoluble solid materials, but require an inert powder as well.

#### Granular Carriers Used

The most commonly used are:

- (a) Limestones
- (b) Sands
- (c) Granites

#### Equipment Used

Any of the blenders described and illustrated in Fig.2 for impregnated granules can be used, although the most favoured types are Drum and Cone blenders. The rest of the plant is also very similar.

#### Inert Liquid Used

The following liquids are found to have most use:

- (a) Polyhydric Alcohols
- (b) Poly Ether Compounds
- (c) Glues
- (d) Molasses

#### Inert Powdered Compounds Used

- (a) Talcs
- (b) China Clays
- (c) Silicates

Drying with the powders must be very carefully controlled. If too little, granules may not flow properly: if too much, the finished granule may be dusty. As with impregnated granules particles must be screened prior to packaging.

#### C. Compounded Granules

Production of compounded granules is different from the other types of granules considered so far, particularly the granule formation stage. The basic manufacturing procedure involves the following steps and is illustrated schematically in Fig.3.

1. A blend is made of all the components of the formulation. This will include:
  - (a) Active ingredients
  - (b) Inert diluents, solids
  - (c) Binding agents
  - (d) Liquids
2. The blend is granulated,
3. The granules are dried if necessary.
4. The granules are screened and the under and over sized particles re-worked if possible.
5. The finished product is bagged.

#### Equipment

##### Blending, Screening and Drying

Several methods of granulation are available.



### Granulation by Compaction and Crushing

After blending the powder mix is subjected to compaction under very high pressure. This is usually achieved by passing the powder between two rotating rollers set very close to each other, Fig.4. The powder passing through the narrow gap is subjected to tremendous pressure: it is compacted and emerges as a very thin flat sheet. The flat sheet is then broken up into small particles by conventional crushing equipment or a further set of rollers may be used. One of the rollers has indentations in the surface which produces granules. The blend consists of active ingredients, inert diluents such as talc and china clay, and binding agents such as molasses or sulphite lyes. The granules produced are irregular in shape and there may well be a high proportion of under and over sized particles. The capital costs of such equipment are high.

### Extrusion Granulation

In this process pressure is used to squeeze the powder blend through holes in a rotating cylindrical die. The powder is converted into cylindrical threads by the compaction. These threads are cut to size by meeting knife blades set at the appropriate distance on emergence from the die.

Two systems are illustrated. In one (Fig.5) the powder blend is squeezed between two rollers, one of which is solid but the other one is perforated. The cylindrical threads of granules are squeezed into the centre of the perforated die and cut to length with the knife blade. In the other system (Fig.6) the powder is fed into the centre of the die and is squeezed from the inside to the outside by a pair of rollers situated inside the die itself and rotating close to the wall of the die. The knife blade is arranged externally to the die. Cylindrical granules are produced by both methods. Larger granules, about 4mm and from 6-9mm in length are produced with the first method. In the second method granules of up to 2mm diameter and 3-4mm length approximately are produced. The still damp extruded cylinders maybe converted into spheres by further rotary action. The extrusion process can produce a high percentage of on size granules, but screening to remove under and over sized particles is still necessary. Capital and energy costs are high and the dies and rollers need frequent replacement.

### Pan Granulation

The powdered mix is placed in an inclined rotating pan (Fig.2d). A fine spray of liquid, usually water, is then directed onto the tumbling powder. The rolling action produced in the powder together with the liquid droplets produces by a snowballing action a spherical granule. Great care has to be taken with this technique because a wide range of particle sizes can be created. Very large agglomerates can be produced with this method. The equipment is relatively cheap to purchase and to run, but the operator is exposed to the powdered product because of the open nature of the pan.

### Ribbon Blender or Z Blade Mixer Granulation

A variation on Pan granulation can be achieved by using Ribbon blenders or Z Blade mixers. Again, a fine spray of liquid is directed onto the mixing powders. This technique can also be used for granulation, starting with a granular core and adding a saturated liquid or a suspension to the mixing core. This is extensively used in the production of fertilizers on a very large scale.

### Fluid Bed Granulation

In another variation of the basic technique of agitating a powder blend and spraying a fine spray of liquid onto the powder, agitation is achieved by means of air passing via porous plate into the body of the powder. The powder becomes airborne and collision between particles and liquid droplets causes granulation.

### Granulation by Prilling

This is a basically simple technique, but it is dependant upon achieving very special conditions. These are the production of a molten mix of components or the formation of hot highly concentrated liquid systems. The molten liquids or solutions must crystallize to give a hard product on cooling. The granulation is achieved by pumping the liquid onto a rapidly rotating disc or perforated cup. The centrifugal action of the disc produces small very spherical droplets. These droplets must now be cooled to produce solid granules. Air cooling is commonly used in the preparation of fertilizer prills, but to obtain the required residence time for cooling, very tall prilling towers are needed. Air is blown up the tower to retard the fall of droplets. This plant is extremely expensive and can only be used for production with very high sales potential. Alternately droplets are cooled in a liquid, provided the materials being prilled do not react or dissolve in the cooling fluid. A smaller plant can be used but economically large tonnages of product are required to make these systems viable. With most pesticides the special conditions required for these methods are difficult to achieve.

### Comparisons of Core Granules against Compounded Granules

Core Granules, Impregnated or Coated have the following advantages:

1. The particle size can be carefully controlled. The carrier granule is purchased against rigid specification. This does not usually change much in manufacture.
2. By careful choice of carrier the granules physical properties can be closely controlled.
3. The plant required to produce the granules is relatively simple and not expensive to install.
4. The manufacturing process is fairly simple.

Core Granules have the following disadvantages:

1. There is a limit to the amount of active ingredient which may be impregnated or coated. For impregnated granules the percentage concentration is 10% w/w. In the case of coated granules the maximum concentration is around 5% w/w.
2. The active ingredient is not homogenously distributed over each granule. In any mesh grading, smaller particle sized fractions contain a higher percentage of active ingredient than the larger particle sized fractions. Overall, the average analysis is satisfactory.

Compounded Granules have the following advantages:

1. Much greater concentrations of active ingredient are possible.
2. The mixing of two or more active ingredients is easier to achieve.
3. The granules are more homogenous.

Compounded Granules Have the following disadvantages:

1. The plant is usually more complicated and more expensive to install and man.
2. Much more sieving is required which could lead to more recycling of material.
3. The granules may breakdown more easily in transit.



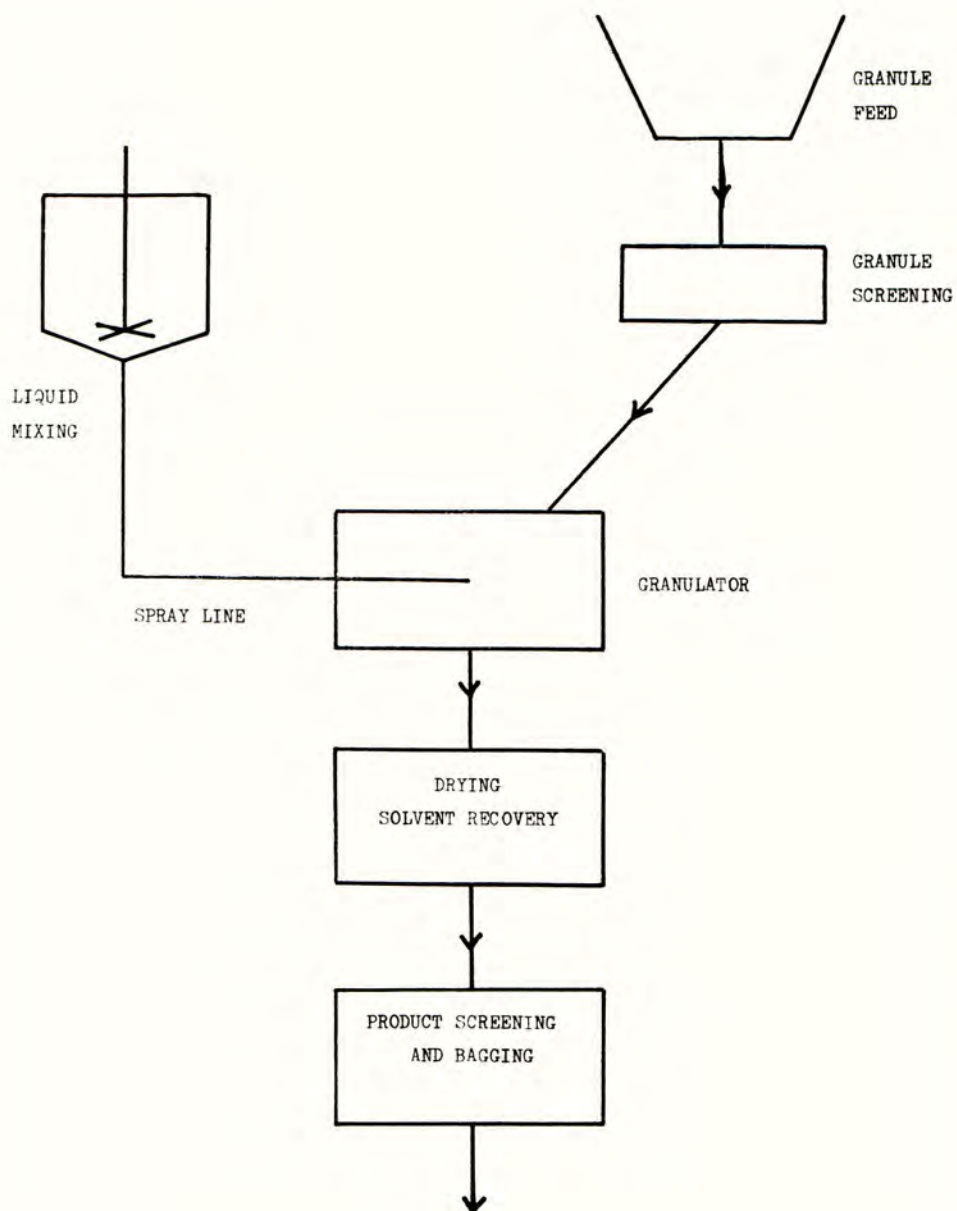
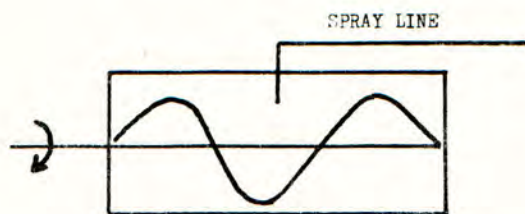
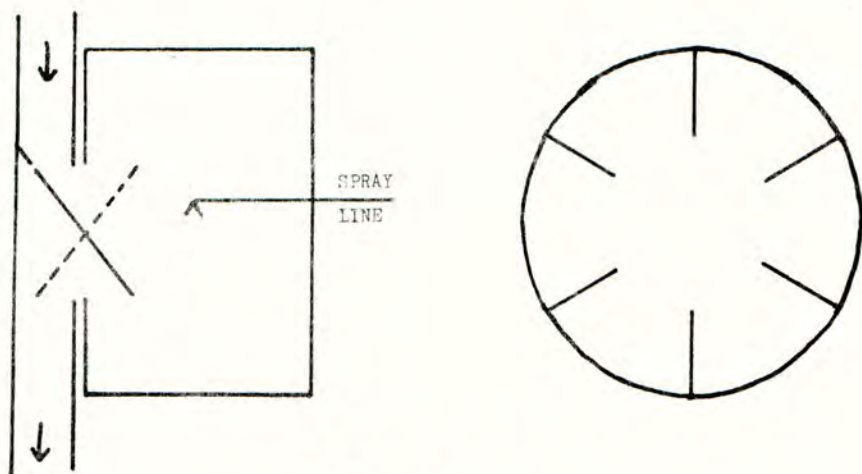


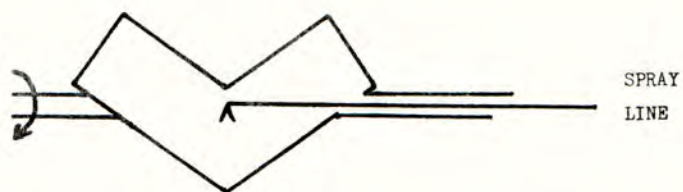
FIG. 1 .



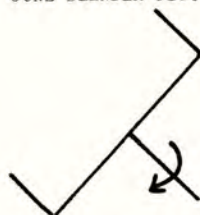
RIBBON BLENDER FIG. 2A



DRUM BLENDER FIG. 2B



CONE BLENDER FIG. 2C



PAN GRANULATOR FIG. 2D



RAW MATERIALS

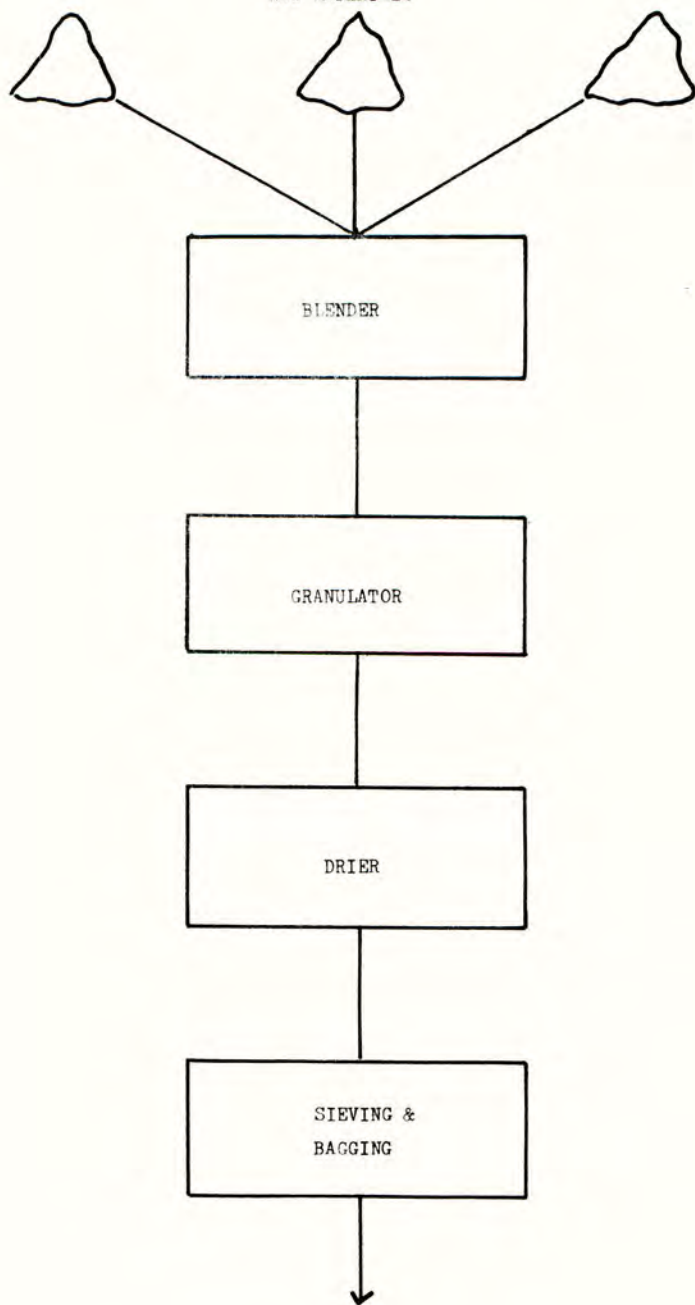
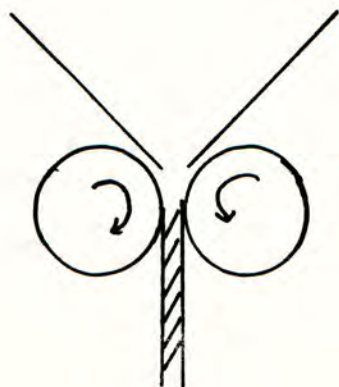
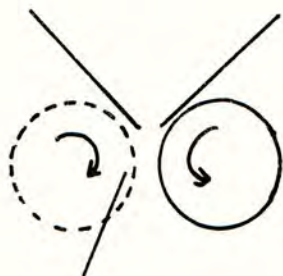


FIG. 3



COMPACTION GRANULATION

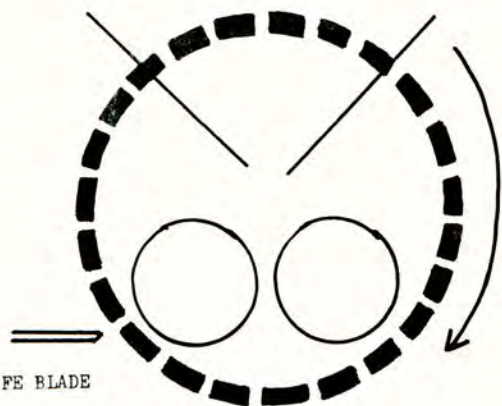
FIG. 4



EXTRUSION  
COMPACTION GRANULATION

FIG. 5

KNIFE BLADE



EXTRUSION  
COMPACTION GRANULATION

FIG. 6

KNIFE BLADE



GRANULES AND THEIR APPLICATION

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Summary With the discovery of certain pesticides which were either highly toxic to mammals or highly volatile and which, therefore, could not be sprayed in the conventional manner a whole new approach to application was needed. Thus granules were born, and my personal involvement with them began when they were first introduced in the U.K. in 1959/60. This paper is a summary of my views on the design of granule applicators and it is based on over 15 years of constant development work, which began with the simple gravity models, still virtually unchanged today, and progressed as granules came along which required broadcasting to the air-assisted models and, over the years various pedestrian models, either back-pack or hand-held, have been added to the range. It will be noted that such reference is made to the granules themselves, rather than their application, and this is done to highlight my personal belief that a designer's knowledge should go beyond engineering principles.

INTRODUCTION

Common to all applicators is the need for calibration. If this is inaccurate, there can be serious losses, either through excess cost of granules - quite substantial in many cases - or loss of crop, due to over-application. Under-application, of course, means an under-protected crop, which, in itself, can be quite serious. Unfortunately, granules vary in their volume/weight ratios and flowability characteristics and, therefore, the methods of calibration used with liquids are not applicable. Neither is it safe to rely on the farmer entirely, as so few farmers are equipped with the necessary calibration equipment, and, even if they were, they would find the task time-consuming and difficult to work in a farming environment. It is essential that the farmer is given the maximum amount of help at this vital stage and this can only be done by processing granules, preferably at the point of manufacture of the applicator, and supplying accurate information to the farmer upon which he can base his calculations. This, in most cases, reduces the farmer's share of the task of calibration to a mere check.

Moving on from calibration, though the two are usually related, it should be appreciated that an application rate is not merely an amount of granule per acre/hectare, but also a given amount of material in a given target area. It is no use having an exact output per acre if this is not accurately distributed in the row, as is the case with a number of designs. For instance, when using positive displacement calibration, the displacement pockets should be as small as possible, thus creating the largest number of deposits in a given distance. The problem is to ensure that capacity is not lost through cavitation of the displacement pockets. It is in lateral distribution that the controlled flow type of calibration used in some designs scores, but, unfortunately, these advantages do not cancel out the problems experienced with controlling the flow under varying speeds and conditions.

Initial calibration is not an end in itself - it must be maintained. Now that we are seeing more granules based on sand and other abrasive materials, more care is needed in the design of the calibrating unit to ensure that excess application does not occur due to wear. A rate that deviates by 10% may not damage the crop, but it will certainly upset the economics.



## GRANULES - THEIR DISADVANTAGES AND ADVANTAGES

It is the fact that granule bases change from country to country and sometimes in the same country, using the same product, in successive years, that presents the problems of how the farmer should receive his instructions for setting his machine. For instance, if the applicator settings are supplied when the machine is purchased and, subsequently, the granule bases change, though the chemicals' names remain the same, the farmer needs new calibration information. Even if it were technically possible, the applicator manufacturer cannot keep supplying up to date information to all his customers over the many years during which they may use the same machine. It is therefore essential that this information comes to the farmer from his chemical supplier. The possibility of drafting out standard settings has been discussed many times over the years without much success and such an endeavour will require close co-operation between chemical and machinery manufacturers, so that the former quotes the weight/volume ratio of his granule whilst the latter supplies volumetric information on the machine's output. Unfortunately, the longer we delay in doing this, the more machinery and granule manufacturers will enter the field, and the more difficult it will become to achieve this type of co-operation.

One can have much sympathy with Amsden (1970) who suggested that the bulk density and flow rate of all granules should be published on their containers and accompanying literature to assist in calibration, but, unfortunately, manufacturer's tolerances could not be maintained with sufficient accuracy for this to be of any use to the farmer and, in any case, many of our designs do not rely on flow characteristics. Today, in fact, most of the newer models rely on positive displacement for calibration. Many other people ask that we should have a standard granule, but this is not possible either, as the granule is not just a diluent and carrier, but also part of the biological process of killing the pest or weed. The rate of release of the chemical can, in many cases, be controlled by the base carrier and attention must also be paid to the question of compatibility of chemical with base. It is these constant changes in formulation which demand that the applicator manufacturers must have a constant on-going programme to check out the compatibility of the granules with the machines and their calibration settings.

With these points in mind, let us look at the question of what a granule actually is. It is a particle, normally of inert material, carrying a predetermined amount of active chemical, releasing it into the soil, water, atmosphere, or plant at a given rate. A variety of materials are chosen, depending upon availability and individual characteristics. In most cases, the granule is accurately sized during manufacture, so that the liquid droplet's equivalent is already formed during manufacture. Granules require no dilution on site and the bulk to be applied is infinitely less than with liquid sprayers, so the effective payload of the applicator is increased. Granules, obviously, are also more tangible and more easily observed on the target. The different characteristics of granules allow them to either lock-in or expose the chemical, as required, and their controlled particle size means that there need be no airborne dust to put the operator at risk through inhalation. Because they do not have the wetting characteristics of liquids, safety precautions are much easier to adhere to, so that much higher toxic loadings can be used without risk to the operator.

How can we justify the use of granules when water is readily available as a carrier and costs virtually nothing? Granule bases are comparatively expensive and there is also much more bulk to cause transport and storage problems and, hence, more expense. The cost differential must, however, be eroded by one or more of the following advantages.

1. Operator risks are reduced because the active ingredient is locked into a solid particle and not atomised into the air.



2. Highly volatile chemicals can be more progressively released.
3. Solid particles can be placed with greater accuracy on the soil or foliage.
4. Distribution can be much more accurate, particularly as the particle size is also more accurately controlled.
5. There is less risk of drift.
6. Certain formulation problems can be overcome.
7. The application work rate is much higher due to reduced bulk and the fact that there is no need for on site dilution.
8. Calibration is easier and more accurate.
9. A range of granule bases are available to the formulator, who can exploit their various characteristics to enhance the efficacy of his active ingredient and, in some cases, to make it physically possible to apply them at all. For instance, due to solvency problems, granules have been developed on sand bases. Sand can be used where a readily available, cheap carrier is required, but the absorbent carrier must, however, remain as first choice, whenever it is technically suitable and its cost is justified.

#### MICROGRANULES

Microgranules, that is particles falling in the 150 - 300 micron range, are the 'nobody's child' in the field of pest control. Whilst they are nearest to the suspension used in liquid application, they are, nevertheless, a dry application and use the same equipment as is used for granule application. Perhaps this accounts for some of the reluctance within many companies to enter the field of microgranules. Admittedly, certain trials have not been very successful, but, on the other hand, others have been highly successful. My own personal observations are that the real reluctance to use microgranules stems from the problems associated with their production. To produce a small batch for initial field trials is a difficult process and certainly much more difficult than producing small trial batches for liquid application trials. On the other hand, those on the commercial side of the chemical companies are reluctant to push their colleagues on the production side to produce microgranules, because they would merely act as replacements for liquids, which are already selling well.

We are now, however, seeing a change of heart on the part of the sales staff of the chemical companies, in as much as they see the potential in the under-developed countries, which could be increased immeasurably by the use of dry application, as water is obviously not available to the same extent as it is in Europe. Many have argued that lack of water will effect the efficacy of the chemical, but it is now generally accepted that one night's dew will apply more water than a conventional spray of 50-60 gallons/acre.

I have spent almost a decade of my life, and no small amount of my resources, in developing equipment for microgranule application and I am now convinced that other than commercial implications within the chemical companies there is no reason why microgranules should not capture a substantial part of the liquid market. Now that we are learning how to calibrate and tolerate a wider range of particle sizes, we may well see production costs falling below those of conventional liquid formulations. When operator hazards, such as those which have to be avoided with organo-phosphorous and other compounds, are not present, insecticides in microgranule form offer tremendous increases in work rate and possibly a drop in production costs also. Ironically, there now seems to be a change of thought within our formulating companies regarding microgranules at a time when I have turned much of my attention to controlled droplet application. Fortunately, though not obviously, they have much in common, and, therefore, I hope to continue to work successfully with each in parallel.



## BROADCASTING

Another slow starter in the field of granule application has been the broadcasting of granules. It has always been a widely held belief that absorbent granules are too expensive to broadcast, but now that people are looking at granules, not just as a diluent, but also as a part of the biological process, they are appreciating the improved performance and work rate of broadcast granules, this method is being much more widely used. Broadcasting by full width calibration machines presents a problem, due to the extremely low flow rates involved, which exclude the lowest rates of application and of course the width of cover is limited. Fertiliser distributors, such as the spinner, have been used, but one has only to refer to fertiliser distribution pattern graphs to see that they cannot optimise the performance of the chemical.

Inevitably, this leads us to pneumatic distribution, where kinetic energy is applied by an air compressor to carry the granules to the distribution nozzle. It is imperative with these designs that:

1. The amount of energy is equal at all distribution points.
2. The amount of granule is equal at all distribution points.
3. The nozzle pattern is accurate.

In the case of the latter, the radial pattern is out, because of its inherent inaccuracies, so this leaves us with the impact nozzle. Those of you who play golf or other ball games will know very well how swirl and minute changes in impact effect the chosen path. I have spent years investigating this phenomenon and now know all too well the extremely small margins in manufacturing error which are tolerable at this point. The real limiting factor with accuracy is the granule itself, but with high quality granules we have achieved rates of 5 lbs/acre (lower rates are possible) accurate within  $\pm 2\%$  and distribution, whilst often as low as  $\pm 5\%$  in still air, is usually around our target of 10%. Because of wide variations in particle size, the cheaper of the sand granules cannot achieve this, but around  $\pm 20\%$  is achieved, which is still better than with conventional spraying. Now that we seem to be able to apply low grade granules - those with a wide variation in particle size - it has opened up the possibility of using much cheaper granule bases and therefore making granules still more competitive for broadcasting. These techniques will however remain confined to chemicals with low toxicity ratings.

## PEDESTRIAN EQUIPMENT

Even when capital is available, a very large proportion of the world's agriculture is not equipped with tractors and, therefore, for various reasons, granules must be applied on foot. These applications fall into the following categories:

1. Small spots for the treatment of brassica, etc.
2. Larger spots for the treatment of banana trees, etc.
3. In furrow band treatment at seeding.
4. Broad bands for the application of herbicides in forests or nematicides in greenhouses, etc.

Simple and relatively inexpensive equipment is now available for all these purposes and no one need be deterred by the cost and availability of a suitable applicator.

## ANCILLARY EQUIPMENT

So far, this paper has been confined to means of despatching the granule, but a range of ancillary equipment is necessary to complement the larger equipment. Whilst none of these are of much technical interest, the following items are, undoubtedly, important as part of the total system of granule application.



1. A coultter which we developed in conjunction with ADAS at Leeds gives a vertical band of granules in the soil, which coincides with the path of the pupae, thus controlling cabbage root fly.
2. Gravity broadcasters are available, either to fit on cereal seed drills or on the front of the tractor for simultaneous seeding or incorporation.
3. Sub-surface broadcasting of granules is now possible, thanks to one of our new developments.
4. Granule application is not confined to planting or during the growth stage, as equipment is now available for putting granular material into crops such as maize silage during harvesting.

#### THE FUTURE

In terms of machinery, this is difficult to predict, as, though new granules are still coming along, they do not require new machines for their application. Although by no means a new idea, one can see an increasing tendency to incorporate the granule applicator into the original planter or seed drill specification. The possibility of all manufacturers doing the necessary testing is extremely unlikely and it would be far better if specialist companies were to supply components for incorporation on other manufacturer's equipment.

The situation is different with formulated chemicals in granular form. If CDA liquid application fails to catch on for the herbicide market, then this means that the case for microgranules will be greatly strengthened and the formulator must meet this challenge. The coated sand granule must have the ability to open up new fields, as it is readily available, low in cost, and has great potential for local production. Our existing nematicides must extend their range of crops because of the demand for increasing yields. Equipping a farm for a great variety of crops is becoming prohibitive and therefore the farmer will tend to grow crops on an ever-reducing cycle, with the eventual possibility, in many cases, of monoculture and it is to the nematicides that we look to make this technically possible. In the field of cereal growing, we may one day see nematicides used to maintain yields under continuous cereal growing, but, on the other hand, so much of the world potential remains unexplored that the need for new products is not as great as the need for wider application of those that do exist.

The fact that the scope for granules is only partly explored is indisputable, but, unfortunately, this rests with the chemical companies who are reluctant to leave liquid formulation until market demand compels them to do so. It is a matter of great concern to me that, in Europe granules have achieved such a small fraction of their real potential and that, eventually, we may see market demand becoming greater in what we class as the under-developed countries, moving the centre of this technology away from our shores. We have seen this happen with the motor car and electronics industries, will this be yet another example of how we fail to exploit that which we have been instrumental in initiating? I certainly hope not. We have inherited from our forebears the ability for great technological achievement - are we going to abandon it in this, the field of granule application?

SPECIFICATIONS FOR GRANULES

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Summary General requirements for pesticides specifications are discussed with special reference to specifications for granular pesticides.

The necessity for specifications, both national and international, for pesticides formulations can hardly be disputed since, when correctly used, they serve the interests both of the user and of the reputable manufacturer. The wide-spread adoption of WHO and FAO specifications for public health and agricultural purposes is evidence of this need. (FAO, 1971; WHO, 1973).

Among the purposes of specifications we can include:

1. They are used as a basis for buying and selling between manufacturer and formulator and between manufacturer and user and serve as a yardstick for comparing the excellence of various samples. They also protect the buyer and reputable vendors by establishing common standards of quality and discourage inferior products.
2. They are used as a basis for official approval.
3. They provide information for safety measures by indicating desirable and undesirable features, both from the view of mammalian toxicity and phytotoxicity.
4. They can provide a basis for ensuring biological efficacy.

In order to cover adequately these objectives a specification may include some or all of the following clauses:

1. Description This can include the physical nature of the material and may indicate undesirable features. The description should not be too restrictive, for example, in specifying too rigidly the colour of the product.
2. Active ingredient This cannot specify the nominal content in a general specification but the permitted limits of variation should be given and the parameter determined by the specified method should be defined. This clause will also include an identification requirement, preferably using more than one criterion.
3. Impurities Specifications must for most products include limits on the likely impurities but it is important that production costs are not forced up by unnecessary refining. Known contaminants should be given together with reasons



for the objections to their presence; but only rarely is there experimental evidence to fix their necessary limits. Until these can be agreed, limits should cover the variations normally found in commercial products, reducing the limits just to make the specification look better is not recommended.

4. Physical Properties The physical properties to be specified will depend on the nature of the formulation, but will include properties specified to ensure that the formulation is not hazardous and that it can be applied efficiently and correctly.
5. Storage Stability Clauses specifying the conditions of storage tests, both at low temperature and at elevated temperature may be required. Manufacturers often produce formulations at various strengths for different markets according to climate and difficulties will arise if an attempt is made to compile complete specifications for world-wide application. The specification should indicate the general method of test but the actual temperature and duration of the test should be related to the eventual destination and use of the product.
6. Containers The choice of materials and methods of package must not be too rigidly defined by the specification. The manufacturer should use the most effective way to pack his product adequately, always remembering that it may be necessary to comply with pertinent national or international transport and safety regulations. The manufacturer could be required to state the storage life of the product in the original containers when stored under stated conditions but the purchaser is always at liberty to specify his packaging requirements in the contract.
7. Biological Properties The biological properties that can be specified with certainty are very few in number and clauses under this heading may be required for information only.

Considering granular pesticides certain parameters or properties may need defining or limiting to some degree.

Regarding the description, some uncertainty exists about the size range applicable to 'a granule' and subdivisions into microgranules, fine granules and macrogranules have been suggested (Goehlich, 1970; GIFAP, 1975). If fertiliser granules are included in a general definition, the range to be covered is approximately 100  $\mu$ m to 6 000  $\mu$ m although most pesticide granules would fall in the range 250  $\mu$ m to 2 500  $\mu$ m. It would seem to be useful if an agreed size range could be decided so that a specification for a granular pesticide would mean the same to all those likely to use the specification. Failing this the size range can be declared in a later clause of the specification.

The active ingredient content shall be declared and when determined by the specified method of analysis the content shall not differ from that declared by more than  $\pm$  x% of the declared content. The limits of variation will depend on the actual content of active ingredient; as a rough guide  $\pm$  5% of the nominal content is generally satisfactory with some widening at low contents and a reduction at higher levels. The limits will also be influenced by the following three considerations:

- (a) the 'between laboratory variability' of the method of analysis
- (b) the 'sampling error' of the product
- (c) the demands of the purchaser



The 'between laboratory variability' can be derived from the collaborative work used to agree the method of analysis and will depend on a number of factors inherent in all inter-laboratory determinations. The 'sampling error' for granular samples can be very high as with all coarse materials, and it would be useful if an agreed sampling procedure for granular products could be defined. The 'demands of the purchaser' is a parameter which is difficult to evaluate but will include an element based on financial interest and the precision required in the use he is to make of the product. The method of analysis will have a defined standard deviation associated with it and confidence limits at the recommended significance level will have to be taken into account in deciding whether the material complies with this particular clause of the specification.

Identity tests required in this clause, for example, gas or thin layer chromatography, infra-red analysis, usually involve an element of judgement and the criteria for acceptance of agreement between the sample and a standard material should be laid down.

Impurities may need specifying, and a method of analysis for their determination provided. Apart from those contaminants associated with the active ingredient or its method of preparation, granular pesticides may need limits for wetting and dispersing agents, the de-activator, binder and unevaporated solvent. If the usual impurities are listed and reasons given for their limitation, then the buyer may make a judgement on the suitability of the material for his particular purpose.

There are a number of physical properties particularly relevant to granular pesticides which may be used in specifications but at the moment there are few methods which have been collaboratively tested and approved as suitable for inclusion in a specification. The main property which does have an agreed method is the particle size distribution. The Agriculture (Poisonous Substances) Regulations 1965 require that the more toxic pesticides in granular form shall have no more than four per cent by weight (cumulative percentage) passing a 250  $\mu\text{m}$  sieve, and no more than one per cent passing a 150  $\mu\text{m}$  sieve, to allow some relaxation in the protective clothing requirements. The Benelux specifications are similar and in the United States the limit is a maximum of five per cent through a 250  $\mu\text{m}$  sieve. This is a sieve test based on the product as received but there is probably a need for a sieve test of some sort to be carried out on the product after it has undergone standard breakdown tests both in the dry state and under aqueous conditions.

The rate of release of the active ingredient from the formulation depends on a number of factors and is a property which may need to be considered when specifications are drawn up. The carrier used and the method of formulation will affect this property and it must be borne in mind that some granular formulations are designed to disintegrate in contact with moist soil whereas others release the active ingredient from intact granules. The chemical will be released by volatilisation, leaching action of rain and by molecular diffusion in water films (Graham-Bryce, 1972). The prime determining factor is the physical properties of the active ingredient and materials with a low water solubility and vapour pressure are likely to have a low release rate (Seaman and Warrington, 1972).

Other physical properties of interest include bulk density - useful information from the point of view of packaging and application; angle of repose and flowability which may affect the distribution of the product; and hardness, which is of importance in predicting the abrasion likely to occur to the application equipment, particularly the metering system, and also affects the attrition of the product during handling and storage. Accurate application is of great importance with granular pesticides but in view of the wide range of application equipment it will not be possible to specify this in anything but general terms. Uneven distribution is probably the most common cause of excessive residues and phytotoxicity if the



toxicant dosage is too high, and lack of effect if it is too low. A property which can be measured and which will have an influence on the uniformity of application is the number of particles per unit weight. Although specified limits could be laid down for this property it is probably more suitable that this should be an information clause.

The Granules Group of the Pesticides Analysis Advisory Committee is at present collaboratively testing a number of these methods but until they have been tested and agreed, specifications for granular pesticides can only be worded in general terms.

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THE LABORATORY EVALUATION OF POTENTIAL GRANULAR CARRIERS

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Summary The quantity of pesticides applied in the form of granular products has increased considerably in recent years. Although attapulgitic, montmorillonitic and bentonitic are frequently used, the formulation chemist is often asked to examine either a completely new granule carrier or a material similar to a known one from an alternative source, with a view to producing a commercial product. There is no single test which can be used to determine the suitability of granule carriers and the final decision on this, and the formula for the eventual product, results from the overall conclusion drawn from a series of physical and chemical tests. The majority of these tests are carried out in the laboratories, and have been developed to simulate handling, storage, and application conditions normally encountered in commercial practice.

INTRODUCTION

In the selection of granular materials as potential substrates for pesticide products there is considerable divergence between what is desired and what has to be used.

The ideal granular carrier is one which has the following physical chemical properties:

1. Is inert and completely compatible with the pesticide.
2. Has sufficient capacity to fully absorb the pesticide to be incorporated.
3. Is sufficiently hard to withstand attrition and wear during transport.
4. Will not cause wear to manufacturing or application equipment.
5. Has a uniform particle size with no dust (ideally to be all the same size).
6. Be cheap and readily available.

Also in theory, the formulation chemist should be able to say to the manufacturing/sales departments "This is the best carrier for X; go and use".



In the cold world of reality, almost the exact opposite happens. A small bag (anything from 5g to several Kg) is presented to him with the well known instructions "This is available in ..... quantities at a cost of a few pence per ton. Please make it into a marketable product containing 10% of compound X which has a shelf life of an indefinite duration at an unknown temperature". The bag could contain anything from a fine dust to particles several inches in diameter or any variation/combination in between. The practising formulation chemists will be only too aware of the above and also, in some cases, the final discovery that this cheap excellent material has inexplicably disappeared after one has completed several months of work.

In order to attempt to rationalise the ideal and the practicable, the formulation chemist has to devise a number of laboratory tests to simulate handling, storage and use of the product under typical commercial conditions. It is obviously not practical to make several tons of the product straight away and launch it into the agricultural arena only to discover it does not meet the requirements envisaged.

This paper outlines a number of typical tests which are carried out in formulation and analytical laboratories engaged in the development of granular products. The purpose is to provide a general picture and the series of tests described are not claimed to be complete or exhaustive. Particular laboratories will have additional tests of their own or variations on those described.

Essentially the tests may be divided into two main categories:

- Evaluation of physical properties
- Evaluation of chemical properties

#### EVALUATION OF PHYSICAL PROPERTIES

The typical physical properties which are evaluated in the laboratory are as follows:

1. Absorptive capacity
  2. Hardness
  3. Attrition
  4. Particle size distribution
  5. Density
1. Absorptive Capacity

A large number of the available pesticides, particularly the organo-phosphorus type are liquid and hence this becomes one of the most important tests. The substrate must absorb sufficient of the pesticide, together with the deactivator if this is required, to produce a dry free flowing product. A good idea of the suitability of the carrier can be obtained from the following simple test (quantities are for a 10G formulation).

Place 5 g ( $\pm$  0.5 g) dedusted (ie 100 mesh material removed) granules in a 20 ml glass bottle fitted with a screw cap. Add exactly 1 ml ethylene glycol. Replace the cap and shake by hand to ensure even mixing and, with a spatula release any isolated "pockets" of sticky granules from the inside edges and sides.

Shake the bottle rapidly on a flask shaking machine for 45 minutes. Examine the contents of the bottle periodically and release any isolated pockets of sticky granules from the inside edges.

Although this simple test quickly rejects unsuitable granules, confirmatory tests are always carried out on the apparently acceptable ones in laboratory spray impregnation equipment and on the pilot plant scale. Alternatively, a "maximum" absorptive capacity can be estimated by a relatively simple modification of the above test.

## 2. Hardness

This characteristic is relevant both to the physical strength of the granules and, in conjunction with their surface form, to the abrasiveness to manufacturing and application equipment. Hard, rough surfaced or angular carriers will cause more wear than smooth ones.

A quantity of the carrier is sieved to remove the material finer than BS 60 mesh and 50 grams is placed in the receiving pan of an 8 inch standard sieve set. Ten x 13 mm steel balls are put into the pan and the lid is inserted. The assembly is placed on a mechanical sieve shaker and is rotated for 30 minutes. The material is then resieved and the quantity passing through the BS 60 mesh is estimated. The amount of new "fines" produced is a measure of the granules hardness.

## 3. Attrition

This test is used to give an indication of the potential breakdown of the products under transport conditions.

A quantity of the carrier is sieved to remove the material finer than BS 60 mesh and a known weight (usually 80-100 g) is placed in a 2.5 litre ball mill pot. This is then placed on a barrel roller and rolled for 16 hours at 30 rpm. The carrier is then resieved and the percentage of generated fines smaller than 60 mesh is calculated.

## 4. Particle size distribution

This test essentially consists of fractionating the sample into a series of size ranges using a set of standard sieves. The basic test is fully described in the CIPAC Handbook (method MT 58.3)<sup>1</sup>. Individual organisations vary the sieves used to suit their own particular product and/or local legal requirements.

## 5. Density

The purpose of this test is to give guidance on the size and general properties of the containers in which the final product is to be packed or sold. Also if the product is for aerial application, a low density could lead to misplacement and drift problems.



Here again, the basic test is fully described in the CIPAC Handbook (method MT 58.4)<sup>2</sup> and is based on British Standard Method 1460:1967. It essentially consists of placing a known weight of the granules in a graduated measuring cylinder and measuring the volume after it has been dropped from a fixed height for a specified number of times.

#### EVALUATION OF CHEMICAL PROPERTIES

The purpose of these tests is to give an idea of the chemical compatibility of the active ingredient and the granule carrier in order to ensure that the product has an adequate shelf life under commercial conditions. Two main types of test are carried out.

1. Inertness
  - a) pH
  - b) pKa
2. Storage stability

##### 1a) Inertness pH

A good idea of the compatibility of the active ingredient and the carrier can be obtained by measuring the pH of a 10% slurry of the carrier in freshly distilled water. Products giving an alkaline pH would obviously be unsuitable, without deactivation, for many of the organophosphorus compounds.

##### 1b) Inertness pKa 3 and 4

For some highly sorbtive materials such as attapulgite and montmorillonite, pH is not necessarily an indication of intrinsic acidity and a measure of surface acidity expressed as pKa, is needed. For example DILUEX has an aqueous pH of 9.2 but has a surface pKa equivalent in strength to that of 70% sulphuric acid. One explanation for this anomaly is that water neutralises the acidic sites on the clay surface through hydrogen bonding and hence does not give a true indication of intrinsic acidity.

The following is an outline of the pKa test :

pKa - Transfer 200 mg of test substance to a test tube of 10-15 ml capacity and with a glass stirring rod mix well with a 2-3 ml dry benzene. Add 2-3 drops of a 0.1% dry benzene solution of test indicator, swirl the tube contents gently but thoroughly for 10-15 seconds and record the colour reaction on the surface of the substance.

The indicators and corresponding pKa and acid strength are shown below.

<u>INDICATOR</u>	<u>Basic Colour</u>	<u>Acid Colour</u>	<u>pKa</u>	<u>H<sub>2</sub>SO<sub>4</sub> Equiv. % by weight</u>
Phenylazonaphthylamine	Yellow	Red	+4.0	5 x 10 <sup>-5</sup>
p-dimethylaminoazobenzene (E.K. 338)	Yellow	Red	+3.3	3 x 10 <sup>-4</sup>

<u>INDICATOR</u>	<u>Basic Colour</u>	<u>Acid Colour</u>	<u>pKa</u>	<u>H<sub>2</sub>SO<sub>4</sub> Equiv. % by weight</u>
Benzeneazodiphenylamine (EK 1714)	Yellow	Purple	+1.5	0.02
Dicinnamalacetone	Yellow	Red	-3.0	48
Benzalacetophenone	Colourless	Yellow	-5.6	71
Anthraquinone	Colourless	Yellow	-8.2	90

## 2. Storage Stability

Apart from pH and surface pKa, a number of other factors can affect the chemical stability of a given pesticide on a particular carrier substrate. These include moisture level, iron and other natural contaminants in the clay and the presence of organic solvents (necessary where granules are prepared by spray impregnation when using a solid pesticide). The influence of these can only be really tested by storing the product for a known length of time under known conditions.

Since it is impractical to wait for two years, possibly only to discover towards the end of the period that the stability is not quite good enough, accelerated storage conditions are used. These entail storage of the product at a number of storage temperatures for several weeks or months. A typical format may be

Assay on storage at 50°C for 4, 8, 12 weeks

35°C for 4, 8, 12, 18 weeks

25°C for 8, 12, 18, 26 weeks.

A shelf life and/or quantity of active ingredient (including overages) necessary to maintain label claim for a fixed period can then be estimated. If the degradation follows first order kinetics, the estimates can be made using the Arrhenius relations

$$\log k = \frac{1}{T}$$

since a rate constant can easily be obtained for each temperature either by calculation or graphical means. If degradation is not first order, the calculations are much more complicated and one usually resorts to one of the computer programmes which are now fairly readily available.

In this series of tests, potential stabilising agents will be evaluated (when these are necessary) and the concentration needed for optimum shelf life will be determined.



## DISCUSSION

There are a variety of delivery systems available for the application of pesticide products and the increasing popularity of granules in particular is due to a number of factors which include:

1. Less subject to drift than sprays in windy conditions.
2. Increased safety with highly toxic materials
3. Release rate and other properties can be controlled.
4. Ready for use without prior reconstitution on the farm.
5. Superior foliar penetration.

A considerable gap exists between the ideal granule carrier and those carriers which are actually available. A number of tests have been described which are applicable to most products but particular additional tests may be carried out when a specific end use is envisaged. This category of tests (not dealt with above) would include release rate in soil, release into static or flowing water, delayed release and rate of disintegration in water.

Substances which could be used as substrates for granular pesticides are relatively unrestricted. Those in use most commonly today are of the mineral type and the final selection is dictated by some compromise between

- a) Availability
- b) Cost
- c) Shelf life
- d) Overage requirements if some inherent instability
- e) Effect on equipment
- f) Acceptable biological performance
- g) Safety to the operator
- h) Physical properties

This paper has deliberately avoided dealing with any one specific substrate but those in common use in the industry include :

Attapulgate	Pumice
Montmorillonite	Sized brick
Sepiolite	Sized sand
Diatomite	Gypsum
Bentonite	Calcite
Kaolin.	

Some natural products such as corn-cob grits, olive kernal and apple pomace are also used.

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CHLORMEPHOS: MUTUAL ADAPTATION OF THE FORMULATION AND  
THE EQUIPMENT USED FOR ITS APPLICATION

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Summary Attapulgit was chosen as a formulation base for chlormephos granules on the basis of industrial, chemical and commercial criteria. This formulation has been used successfully in a wide range of granule applicators. The interaction of certain features of these applicators with the formulation are discussed. The need for cooperation between manufacturers of application equipment and granular formulations is emphasised.

INTRODUCTION

Chlormephos has been formulated to take account of existing equipment for granule application to the crops. Granule bases selected for biological and commercial reasons were tested in different applicators. Finally a formulation with attapulgit as the base was chosen according to certain physical criteria. These were:-

1. Good flow throughout the metering and distribution system of the applicator.
2. Least friability and least abrasiveness.
3. Optimum density to facilitate adjustment of metering systems thus allowing the correct dose of insecticide to be applied using existing equipment.
4. Uniform size grading (more than 90% of the granules between 250  $\mu$ m and 800  $\mu$ m in diameter. Granules in this size range may also be referred to as microgranules).
5. Least hygroscopicity and greatest resistance to generation of static electricity due to friction.

The ideal granular base does not exist but attapulgit has provided a good compromise of these requirements. The design of granule applicators in relation to the use of chlormephos granules is discussed. So far no modifications have been required on a wide range of equipment.

DEVELOPMENT

When choosing a granule base, it is worth examining certain parts of the applicator:-

1. The Hopper. The shape of the hopper is important to facilitate delivery of the product either directly through the metering and distribution system or indirectly via a 'constant level' device, (BENAC Micro, HERRIAU Granyl). This

'constant level' device allows gentle refilling of the metering system without putting pressure on the hopper contents. This principle is mainly of interest with a slightly friable base such as attapulgit.

From this point of view the more common pyramidal or conical shaped hoppers, are better than those with almost parallel sides, (INTERNATIONAL HARVESTER, OLT etc.). The design of the bottom or "bowl" of the hopper, where the metering and distribution system is connected, is especially important for even delivery of the product. Various machines have a smooth surface, or deflectors, or an agitator which may be capable of being disconnected (SMC, Bimigrasol Multiproduits) or not (RIBOULEAU).

A sieve (NOUDET-GOUGIS, SMC Bimigrasol Multiproduits, etc.) incorporated in the hopper not only allows elimination of foreign matter, but also accidental aggregates. The cover should have an air-tight fit particularly when using granules like attapulgit which are slightly hygroscopic. A complete cover (SEGUIP MICROSEGUIP, SEFEBA), a screw-tightened lid (NIBE-VERKEN Nibex, SCHMOTZER, TROSTER Hassia) or a rubber lid with a joint at the lip (MARCHETTI Mark 4 or 6) are probably more efficient than one with overlapped rim (usual) which is not airtight despite means for holding it in place, such as internal spring clips (EVRARD DLM, GASPARDO, HORSTINE FARMERY Microband, RIBOULEAU Microsem) or bolts (GANDY, GARAVINI, HORSTINE FARMERY Microband).

## 2. The metering system

- (a) Applicators with a moving floor. Metering is by adjustment of the cross section area of a chute by means of a lever or micrometer. Granules drop on to belts carried on pulleys (SMC Migrasol, Bimigrasol and Bimigrasol Multiproduits) or by rotation of a drum (NIBE-VERKEN Nibex, SCHMOTLER, TROSTER Hassia).
- (b) Gravity-fed applicators. In this type of equipment a helical rotor, (FONTANI M-75), a grooved rotor (DAKOVIC, GANDY, GARAVINI, INTERNATIONAL HARVESTER, JOHN DEERE, OLT, TANK Super, etc.) or one with cavities (old TANK) feeds the product regularly through one or several holes, the size of which can be regulated.
- (c) Volumetric applicators. Various forms of rotor distribute, on each revolution, the required volume of product, which is more or less constant. This is the most common category and can be subdivided by the method used to regulate the delivery:
  - (i) - machines with fixed rotors and variable speed of rotation: for example the HERRIAU Granyl with a cavity rotor or the DELFOSSE and RIBOULEAU Microsem with a continuous screw, for which adjustment of delivery is obtained by choice of rotation speed of the distributor.
  - (ii) - machines with fixed rotation speed and variable rotor capacity; these are granule applicators with sliding grooves (CARRARO, GASPARDO, SEGUIP Microseguip and SEFEBA), variable, masked grooves (ZORKA D<sub>1</sub>) or with a non-adjustable continuous screw (ZORKA D<sub>2</sub>).
  - (iii) - machines with adjustable rotation speed and rotor capacity: examples are the BENAC Micro, EVRARD DLM, HORSTINE FARMERY Microband, MARCHETTI Mark 4 or 6 and NOUDET-GOUGIS. Interchangeable rotors are available for each product, or alternatively feed rate can be adjusted by varying



the position of a valve (NOUDET-GOUGIS).

The design, and operation of the metering system effects different granule bases according to:-

- (i) - speed of rotation of the metering device. This influences the extent of flattening or crushing of the product. With attapulgit, this speed is low because of the density of the product (0.7) and because the application rate of chlormephos is not very high, (in France, 31-36 g/100m on sugar-beet, and 50 g/100m on maize).
- (ii) - clearance between moving parts and their housing. This also affects breakdown of the product. Attapulgit is somewhat friable, so applicators with a cavity rotor, charged by "constant level" (BENAC Micro, HERRIAU Granyl) machines with a smooth moving floor (SMC Bimigrasol Multiproduits, TROSTER Hassia, etc.) are best. Alternatively machines with a continuous screw (Microsen Ribouleau) in which the granule is not "forced" between two close surfaces, can be used. In the grooved, completely volumetric system, wear of the product, is surprisingly limited (1-2%\*). This is mainly due to the action of scraper knife-edges (HORSTINE FARMERY Microband, SEGUIP Microseguip, SEPEBA) at the bottom of the hopper, so that the contents of each groove remain almost intact. The gravity-fed machines are likely to present most problems, either because most of the product, caught between two rotor paddles does not pass through the exit openings, and is recycled (GANDY, new TANK with grooved rotor), or because the product is constantly flattened between the rotor and the bottom of the tank (for example the old TANK with cavity-spools).
- (iii) - their ability to deliver precisely the required dose of product. All machines, including the oldest, are well adapted to apply attapulgit granules because of the density and the small quantity of granules to be distributed. An interesting point with chlormephos on attapulgit is that the recommended dose is well below the average delivery possible with most machines. It is therefore convenient to choose a slow rotation speed (e.g. for volumetric machines which are the most frequent in France), at a large groove width. For example, the range of deliveries with products based on attapulgit can be from:  
  
2.7 - 28.7 kg/ha with the RIBOULEAU Microsem  
3.3 - 16 kg/ha with the EVRARD DLMC on a NOUDET-GOUGIS drill.  
3 - 20 kg/ha with the SMC Bimigrasol Multiproduits.  
  
Note that the old HERRIAU granule applicator could only be used to distribute attapulgit granules.
- (iv) - method of adjusting delivery. Some granule applicators with sliding, grooved rotors should be adjusted from the minimum to the maximum and not vice-versa. When using attapulgit this will lead to jamming of the product by restriction of the useful width of the groove, thus reducing the applied dose.

\* % reduction in particles of 400  $\mu$ m diameter.

3. The delivery system. An applicator can be adapted to the formulation of chlormephos by the choice and arrangement of the delivery tubes. Attapulgit granules, because of their relatively low density are less easily discharged and more susceptible to movement by wind in the seed drills, than a siliceous base. In addition, attapulgit is hygroscopic and subject to static charges. Good discharge of attapulgit to the drills requires that discharge tubes be of sufficiently large internal diameter (20 mm), which is uniform along the whole length. The tube should be kept in a vertical position, but if tubes must be curved it is essential to have a large radius of curvature. This depends on the position of the hopper with respect to the components of the drill, the angle of the outlets in relation to the longitudinal vertical plane and the design of the drill.

It is necessary to fix the position of the drills by means of metal guides. The choice of materials in the delivery system must be made carefully. Metal tubes are useful because they avoid accentuated curves and bends and are less subject to static electricity. On the other hand, plastic tubes are less liable to condensation and if transparent, they show any blockages.

Some rare cases of clogging of the delivery tubes using chlormephos on attapulgit have been reported in France and have been attributed to static electricity, possibly caused by certain weather conditions (e.g. dry air, etc.) types of subsoil, or the proximity of H.T. lines, all of which can cause the same effect as friction. This type of nuisance can be remedied by using antistatic tubes such as those proposed in the USA by GANDY and JOHN DEERE. The particular case of air assisted transport of microgranules in the NOUDET-GOUGIS completely eliminates these problems.

Efforts must be made to prevent chlormephos granules drifting due to the wind after leaving the delivery tubes. When the delivery tubes (TANK SSEC, TROSTER Exakta or Exaktamat, etc.), emerge from the back of the coulter, the gap between the tube and the soil should be small. Thus a gap of 1-3 cm is sufficient to obtain a distribution of granules with a band width of ~3 cm. Similar remarks apply in the case of air assisted applicators.

Finally, the user also has a part to play in integrating the product and equipment, particularly by cleaning and maintaining the equipment. When using chlormephos granules, it is necessary to:

- (i) - ensure the absence of condensation or traces of oil in the hoppers before filling.
- (ii) - completely empty the equipment at the end of the day, especially in damp environments.
- (iii) - if possible, block off the ends of the delivery tubes over-night.

#### CONCLUSION

Of all the different types of agrochemical formulations, granular products require the most effective integration of application equipment and product formulation.

Difficulties with some commercial granules in the last three or four years in France and other European countries (Belgium, Italy, Greece, Yugoslavia) necessitated so many modifications of existing equipment, that new models have been developed. This demonstrates the need for collaboration between the agrochemical industry and the makers of application equipment.



When a company first produces a granular formulation it must take into account the performance of existing commercial equipment. It is also necessary at the outset to foresee the type of equipment likely to be encountered during commercial use of the product. Considerable modifications of the product have often been required of the manufacturers of granular formulations although the range of granular bases is limited by the need to maintain a high level of biological activity in the product, consistent with an acceptable cost and storage stability.





PESTICIDE GRANULES: DEVELOPMENTS OVERSEAS, AND OPPORTUNITIES

FOR THE FUTURE

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Summary The properties of granules which are of value overseas are given; they fall where wanted, release of toxicant is controlled, no water is needed, they are safer for humans and beneficial insects, and of value in integrated control. Less toxicant is used. A good applicator is discussed, and a summary of methods and uses overseas given: on maize, sorghum, rice, fruit, bananas, tree crops; with pheromones, fungicides, molluscicides, nematocides etc. The main factors limiting development overseas; cost, application, moisture, trials and specifications, are reviewed.

It is traditional for those who predict the future to be brief and enigmatic. Perhaps I can be brief without being obscure. I propose to run through the properties of granules and their particular uses overseas, and then discuss selected points which you can develop in discussion into practical ideas for the future.

THE PROPERTIES OF GRANULES

Granules have a number of properties which make them preferable to dusts, sprays or seed dressings overseas.

- a) they are discrete particles which fall through vegetation to the site of action, either on soil, water or plants. They can be selectively placed, and do not drift.
- b) they roll or are shaken into positions, such as leaf axils or whorls, where the toxicant is released, and can act by vapour, contact or systemic action.
- c) the rate of breakdown or release of toxicant can be controlled, either by treatment during formulation, or by the addition of binding agents or inhibitors or choice of solvent. Plastic based and encapsulated granules are a valuable recent development. In the soil, slow release of toxicant may avoid loss of activity due to sorption in the soil or evaporation, and toxic chemicals with short persistence can be made effective for longer. Plant roots grow out to granules to give a longer period of effect of systemic pesticides. Intermittent rain, dew or flooding continues to release toxicant, e.g. in maize funnels or rice paddy water or soil.
- d) granules are dry, and water is not needed for dispersion or application.

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Transport and distribution may be a problem, but the granules are ready for use. e) they are safer to handle and apply than liquids and dusts; no splash, or contact with concentrates, no dilution, less danger from toxic dusts. This is important overseas, where there may be less supervision and training, and user conditions can be more uncomfortable.

f) they are less hazardous to beneficial insects, being placed where they are wanted, there is no overall spread of toxicant, and toxicant release is controlled. Granules are rated much safer to bees than sprays in East Africa, and have also been found less toxic to moth parasites in India.

g) in application, although sometimes applied by expensive, accurate, specially designed equipment, one can take advantage of their benefits without special equipment, sprinkling by hand or from a simple container, for instance on maize, rice or bananas. When used, equipment can easily be attached to seed drills or cultivation machinery, and used without extra field operations.

h) often less toxicant is needed because of the precise, controlled nature of granule application, with obvious environmental advantages. In Kenya we have obtained complete control of maize stem borer for a season with a pinch of about 128 mg, 0.3 kg/h endosulfan, to plants, compared with a usual three applications of 1 to 2 kg/h DDT.

i) to look forward, when integrated control calls for a combination of technically advanced, expensive treatments such as insecticide plus pheromone plus a pathogen, this could be done centrally, leaving cheap, simple application of a combi-granule to the unskilled farmer.

#### REQUIREMENTS OF A GOOD APPLICATOR

Granules are expensive and need to be applied accurately. There is a need for the development of applicators with the following attributes:

- a) if delivery is intermittent, accurate delivery of the amount calibrated.
- b) accurate repetition or replication of the delivery each time.
- c) in continuous, spreading delivery, both evenness and the form of distribution are important, and how the form of distribution affects overlapping runs.
- d) absence of damage to granules by grinding or impaction in the machine. This will depend on type and size of granule.
- e) adequate mixing, feeding and flow in the applicator.
- f) ease of use, repair and replacement of gears, cut-off baffles etc. The use of standard bicycle or auto parts, bolts, wing nuts etc. might be considered.
- g) lightness and comfort when carried in the hand or on the back. The centre of gravity may be a deciding factor between two machines.
- h) robustness to withstand more than average misuse; sitting on the hopper, dropping from transport, etc.
- i) corrosion proof, perhaps to withstand moist materials left in the machine, or the machine being left in the rain.
- j) cheapness.

There must obviously be a compromise between robustness and weight, corrosion proofing and cost, but weakness in one factor may make a machine completely unacceptable to buyer or user, or lead to its abandonment for something cheaper or easier to use or maintain.

#### METHODS OF GRANULE USE OVERSEAS

As in temperate countries, granules can be applied in four ways, depending



on the type of crop and the type and biology of the pest in relation to the crop.

a) drilled in the seed furrow, below or alongside the seed, not in contact with it for phytotoxic reasons, or in a bow-wave of soil produced by the drill coulter, leaving the seeds surrounded by granules. The applicator can be attached to a hand seed drill for experimental work or on smallholdings, or to a tractor-powered drill, with hoppers mounted on a variety of planters, hoes or tool-bars, with special coulters delivering to the required position near the seed.

b) continuous soil surface or plant top-dressing in bands, over or alongside the plants. Machines are usually knapsack, or hand or tractor propelled wheeled applicators, although small hand-held blower machines exist. For soil sterilization and nematicides, application may be followed by rotavation or incorporation in the soil.

c) intermittent soil or plant top-dressing. Some hand-held applicators exist, for example two-handed rotary blowers, or one-handed applicators with a lever-grip, or a gravity-weight flip-over action, or activation by an arm on the ground. Some have the advantage of ground level delivery without stooping. However granules are often applied by hand with a plastic measure, or simply a pinch of the fingers. The amount of a pinch can vary from 6 to 355 mg, but great repetitive accuracy can be obtained. Rubber gloves are recommended, but tend to be ignored in hot or humid climates.

d) broadcasting. A spinner may be used, as with fertilizers, with a throw of several metres, or air may be used to transport granules in the machine, or from machine to target. Some of the difficulties found with air-flow machines, such as uneven air volume and speed, have been discussed by Farmery (1970). Both air-flow and spiral feeds have been used to transport granules to outlets in aircraft, with a spinner or feed into the airstream for final distribution. Johnstone (1963) discussed the distribution of granules from a helicopter.

Accurate metering into the gravity or airflow system of the machine is essential, and the ability to control from a land wheel is an advantage of granule application. Amsden (1970) and Goehlich (1970) have examined metering.

#### INDIVIDUAL USES AND PROBLEMS OVERSEAS

Many temperate crops are grown in the tropics, and uses of granules similar to those in temperate areas are increasing. For instance granules are used on potatoes against aphids and wireworms, and on sugarbeet against aphids, with retention of granules in leaf-axils (Stiemerling 1966). On brassicas, similar granule treatments are used against cabbage root fly and aphids. On maize, many insecticides such as carbofuran and phorate are used against rootworm, and furrow treatment to last throughout the stem borer season is claimed for carbofuran, perhaps with a side-band top-up later. On pastures, granular organophosphates are extensively used in New Zealand, and experimental rapid break-down formulations are on trial for grass grub control where rainfall is low. On wheat and barley, fonofos and phorate have been found effective against Hessian Fly in Cyprus, and fonofos and carbofuran against Barley Fly in Kenya, others for wireworm and Sunn pest, *Eurygaster*, control. In general, economics are against granules for small grain cereal treatment overseas, except perhaps in difficult to reach terrain.

On maize and sorghum against stem borers, a variety of insecticides have become standard control as granules, endrin being replaced by carbaryl,



endosulfan, diazinon, trichlorphon, carbofuran and tetrachlorvinphos, while DDT is still widely used. Granules are funnelled into the whorl of leaves, where moisture from rain or dew accumulates. Insecticide forms a contact barrier against migrating larvae, and a systemic concentration in the plant. By tracing with radioactive insecticide, a greater concentration is found in the whorl and leaves after top dressing than after furrow treatment, in which a lower concentration but for a longer period is found (Walker 1973). Rain and wind affect the amount of insecticide sticking to the leaves and retained by the whorl. Granules can be applied by hand, by knapsack or by high clearance tractor. Use on sorghum for borer and shoot fly control is less accepted, mostly because of the high cost of granules compared to low value of crop. Trials have taken place in Africa and Asia, and carbofuran, phorate and aldicarb have been particularly effective, often as granules in the seed furrow (Jotwani and Young 1972).

On rice, gamma BHC, carbaryl, diazinon and carbofuran granules have become popular for control of stem borer, leafhoppers and other insects in Japan, Philippines, South America and elsewhere. Diazinon microgranules are often preferred to dust as they are retained by plants, and do not blow away. In the rice paddy, radioactive tracing has shown that granules release toxicant into the water and flooded soil, the insecticide then acting systemically. Microbial degradation of pesticide is not impaired, and granules are less toxic to fish and beneficial insects than sprays and dusts. Aerial application against rice pests, as well as on maize and sorghum, is described by Myram and Forrest (1969). Pesticides in clay balls and gelatine capsules are other promising particulate formulations.

On cotton, carbofuran, aldicarb and dimethoate may be used in the Americas for the seedling pest complex and as a side-dressing later, or in the irrigation water. In Africa, however, granules are less popular because of cost, supposed high human toxicity, and often absence of serious pests during the early growth of the crop.

On fruit, for example apples and citrus, aldicarb granules have given control of mites and aphids when applied to the soil and raked in, perhaps applied according to trunk diameter. On bananas, the use of pirimiphos-ethyl and other granulars against banana weevil, *Cosmopolites*, is developing, mainly in Southern America and West Indies, and trials are in progress in Ecuador, Colombia, St. Lucia and elsewhere. Granules can be applied round the plant with a measuring scoop, and it is useful to be able to check that treatments have been properly done. Granular insecticides have also been used on coffee, groundnuts, tea, tobacco, and Areca palm, for which an ingenious Indian device for applying granules at the top of the palm has been developed.

On sugarcane, endrin granules have been successfully used against borers in southern U.S.A., as well as guthion, carbaryl, endosulfan etc. Trials to replace endrin with new materials such as carbofuran and fonofos have been carried out, using aerial application. Granular insecticides are under trial in most sugar producing countries, for instance aldicarb being applied to seed furrows in Africa with Horstine applicators, and gamma BHC, phorate and carbophenothion granules for frog hopper control in Trinidad and Ecuador. It is possible that not enough granules are retained by cane whorls to give adequate insecticidal effect in leaves and stems. One would expect greater use of



granules against soil beetle grub complexes, perhaps replacing routine organochlorine spraying for resistance or other reasons.

In forestry, the single large particle of plastic or resin, releasing pesticide over a long period might become useful in difficult terrain, as tested against Mahogany shoot borer in Costa Rica.

Granular formulations of virus or other insect pathogens may become important, for ease of distribution, to incorporate a bait or synergist, or to protect the pathogen against sunlight (Ahmed *et al.* 1973). Their use is limited by the need for insects to eat the active ingredient, in many cases.

The use of pheromones is now accepted in pest management, and although pheromones are often distributed as a wet suspension of capsules, dry granules might offer some advantages. Alarm and trail pheromones, as well as attractants, have been little tested.

Bait in granular form is increasingly used for control of leaf-cutting ants cutworms, etc. It can be very selective as it is often taken into the nest. Particles as large as 10 mm have been used; pieces of citrus rind soaked in insecticide are used in Trinidad. Problems arise in storage of base in a humid climate, requiring good packaging, metering and distribution. Distribution from the air seems most economic, probably with a spinner, with measures to prevent caking and blocking in the hopper.

Regarding medical and veterinary pests, granular insecticides, particularly temephos (Abate), have been used as mosquito larvicides in water, applied from the air. They are used for midge control in U.S.A., and against disease vectors in Africa. Granules have great possibilities against pests, and in places that are difficult to reach, protected by vegetation, or where slow release of pesticide is valuable. Granular and capsular systemic insecticides are being tried for control of pests of animals.

Granular nematicides are being developed for a number of tropical crops. Acceptance is slow, but injectors to apply a measured dose of granules below the ground have been used in the West Indies. It is easier than liquid injection and more efficient in inexperienced hands. Hand application is also favoured in tomatoes, potatoes, tobacco and cotton. A microgranule of 100 - 200  $\mu$  has been developed for Basamid dazomet, distributed with a lawn-seed and fertilizer spreader. For larger areas, Horstine gravity flow applicators attached to the front of a rotavator is a practical solution. Attempts to prolong the release of nematicides from granules are described elsewhere in this meeting,

Granular herbicides are widely used overseas, sometimes because of the positive placement obtainable, sometimes because of lack of drift, or because a quick release of toxicant can be obtained. Herbicides are increasingly economic where labour is scarce or expensive, at least at critical times in the crop cycle. Motor driven applicators are available, such as the Horstine knapsack. There is the chest mounted Rohm and Haas machine for application in paddy rice. Herbicide granules applied to rice just after transplanting, together with nitrogenous fertilizer, are popular, and applied by hand, an important point in developing countries. Granular herbicide suffers from the need for moisture to release the toxicant. If the right granules can be found, the development of a

cheap knapsack or wheeled machine for row application would be valuable.

In snail and slug control, molluscicide granules, for example triphenmolph, would seem valuable. Granular baits with metaldehyde and methiocarb are used in slug control, but little has been done on methods of application. A combination of slug pellets, selective herbicide and seed is used in pasture improvement.

Granular fungicide will soon be with us, with the advantage that the dose is not limited by the amount that can be stuck on a dressed seed. Mills (1969) reported an adaptation of the Cherewick cone seeder in Canada for applying time-release fungicide pellets round barley seed in trials.

Solid particle technology should also include pelleted seed, when various chemical agents are compounded with the seed, sown individually by precision drilling methods (Spear 1970). More integrated drilling-granule applicators on the lines of the Horstine-Stanhay or German Massia pneumatic drill will probably become available. Slow release granules based on plastics, or encapsulated with polymers of lactic and glycolic acids (Sinclair 1973), or on industrial waste products such as lignins (Allen *et al.* 1973) offer many possibilities.

#### FACTORS LIMITING FUTURE DEVELOPMENTS

- a) Cost is of prime consideration. Local sources of cheap base materials must be found and local formulation techniques developed to avoid using expensive imported granules. There is scope for trials with pumice, coral, clays, sand, vegetable bases from crop by-products. This is a line of research that FAO or its member states could encourage if it was not profitable to industry, although local formulated granules are marketed in Bangladesh and East Africa.
- b) The applicator: there is always a need for a cheap, robust, hand or motor driven applicator overseas, easily modified for a range of granule sizes and types, output rates and patterns. A shoulder-mounted container, with hand-operated, high or low delivery, would be useful. It may not seem profitable to manufacture when costs are high and granules not widely accepted, but once trials can demonstrate the advantages of granules, machine application should increase. It has been said that an applicator should be designed for a specific granule only, in a package deal between machinery manufacturer, pesticide supplier, and grower, but this can only be answered with regard to the best economic pest control for a particular territory or crop. A cheap soil injection device would be useful, and a machine for trials work, perhaps attached to or built into an experimental seed drill. Sales might be few, but as with entomological equipment, there could be a demand for such field trial equipment throughout the world.
- c) Moisture: granules are limited by the need for moisture to break down the granule or liberate or leach out the toxicant, as well as to transport the toxicant through the soil and the plant (Williams 1975).
- d) Trials: these are needed overseas on the most effective granule bases, the best application position in the soil, in different types of soil (Wheatley 1972), the best size and concentration of granule, and often most important, the timing of application in relation to crop growth, insect attack, and the climate,



usually rainfall.

e) Specification: there is a need for specifications and standard tests for the properties of granules such as particle size, rate of break-down in water under still or agitated, closed or leaching conditions, and other characteristics that affect biological activity. CIPAC is considering the matter on the lines published in their handbook and supplement (CIPAC 1970,1975). Useful comments are given by Caldicott (1970) and Forrest and Hall (1970).

f) Collaboration: one feels that more feed-back between industrial granule formulators, application equipment manufacturers and the user, often an isolated farmer or scientist, would lead to more rapid development of granule technology.

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CONTROL OF SIMULIUM IN RIVERS BY PARTICULATE INSECTICIDES

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METHOD AND MATERIALS

To each man is own insecticide! To the farmer, it means his wheat, his barley or his ground nuts; to the gardener his beans or his roses; to the malariologist, his spleens and his infant mortalities; to the blind African, his children's sight. All these separate purposes are dependent upon a biological kaleidoscope. The farmer uses his insecticide or herbicide in a terrestrial environment, which is relatively stable at least for long enough for the insecticides to have the desired effect. The malariologist's mosquitoes live in stagnant water which is not washed away until the next rains. But the protection of Africans from river blindness depends upon the diminution in the numbers of the black fly, Simulium, which breeds in fast-running rivers and streams.

A river is a moving and ever-changing environment, subject to sudden spates, or diminishing sometimes to a mere trickle, very different from still waters. The creatures which inhabit a river and which are accessible to insecticides, live in very different micro-environments and have very different habits but are interrelated. There are many food chains, one of them ending in fish and man. When the separate micro-environments and habits are known with precision, it is possible to devise means of selective attack. This has been done in the case of the aquatic larvae of Simulium, which inhabits only the fast flowing parts of the river and which has feeding habits common to only few other creatures.

Simulium is usually controlled by killing its aquatic stages by pouring insecticides in a soluble form into the streams or rivers where they occur. This kills most of the other insects. The larvae of some of the stone flies and caddis which are the natural predatory suppressors of the Simulium larvae, are removed, and unrestrained recolonization by Simulium may occur. The use of soluble insecticides therefore necessitates repetition and may well produce an entirely different organization, and maintenance of which is dependent on the maintenance of the interference.

Simulium are particle feeders. They live only in the fast-flowing parts of the stream and their method is different from that of the other detritus feeders such as the Chironomids, which live in the slow-running and silted part of the stream. The size of particles ingested by British species of Simulium is about 10 - 12  $\mu$ . (1).

In 1962, my colleagues and I started a long series of experiments, 1 x 10<sup>12</sup> particles of 4 - 15  $\mu$  were put into a stream in half an hour, when the stream was flowing at a rate of 0.15 cu. ft./sec. This corresponded to a dosage of about 0.4. or 0.5 p.p.m. The next day, all Simulium larvae had disappeared from polythene tapes placed 150 yards below the point of dosage, and the tapes remained free of Simulium until a month after the dosing.

During this time no other creatures in either the water or the stream bed showed any population variation other than the minor fluctuations expected from the changing seasons and rainfall. Not even net-spinning caddis fly larvae were affected by the small particles of DDT.

Since the first dose showed a clear effect which was limited to Simulium larvae and did not affect the bottom fauna, we then gave, in June 1965, a much smaller dose. It produced an immediate, short-lived fall in the numbers of Simulium larvae and no change in the bottom fauna. The recolonization by Simulium was rapid.

Therefore, a month later, we gave a very much larger dose.

The particulate insecticide was mixed with water from the stream in large cans. A known weight of insecticide was used; the rate of flow in the stream was known and the length of time it took for the mixture to run into the stream was measured. The weight of insecticide in the three experiments was approximately 1 - 10 - 100, but the rate of flow on the three occasions was different and the length of time it took for the mixture to run into the river was different. The smallest dose gave a concentration of 0.04 p.p.m. which was maintained for 30 minutes; the middle dose was 0.2 p.p.m. maintained for 30 minutes; and the greatest dose gave 0.4 p.p.m. for 120 minutes. The effective amounts of DDT therefore, allowing for the differences in the river flow, were related in the ratio of 1 for the smallest dose, 5 for the middle dose and 40 for the highest dose.

We had contemplated using, in 1966 or 1967, a dose 10 times that of the largest dose to see how much we would dislocate the bottom fauna, but on the occasions when this experiment could have been arranged, temporary spates made it impossible to arrive at this dosage with the amount of DDT available. On one occasion, because of overnight rain, the experiment was called off when the DDT was ready at the stream.

The effects of these three doses are now considered in order of magnitude.

The smallest dose reduced the numbers of Simulium larvae but did not remove them entirely, and no change was found among bottom fauna.

With the medium dose, Simulium larvae disappeared below the point of dosage for at least 150 yards. Below the point of this observation the stream has various tributaries running into it and there are small lagoons in which the stream slows and sedimentation occurs. The bottom fauna was undisturbed by this dose.

With the largest dose, Simulium larvae were removed for 1100 yards, but there were changes in two of the creatures in the bottom. The may-fly nymph, Baetis, was removed, and the freshwater shrimp, Gammarus, whose population remained unchanged, moved temporarily a little lower down the stream. The may-fly population was restored in three weeks, in part by recruitment of newly hatched larvae from above and perhaps by hatching along the length of the stream, and also by the recruitment of larger larvae from above. There was no change in stone flies and caddis flies in the bottom of the stream. In the plankton, while the insecticide was running in, we collected may-fly nymphs, stonefly, Gammarus and caddis-fly larvae, creatures not normally found in the plankton, and rotifers. The numbers of animals in the plankton were infinitely small compared with those living in the bottom of the stream. We believe that these animals collected in the plankton after the largest dose may have been living in unusually exposed conditions similar to those in which Simulium larvae normally live.



After this largest dose, it took a month for the numbers of Simulium larvae to return to normal. Recolonization by Simulium larvae could have arisen by the natural spread or migration of larvae from the two tributaries above the dosage point and perhaps by the laying of eggs along the length of the river. It seemed to us more likely, from the way in which the larvae appeared on the tapes, progressively from above downwards, that recolonization occurred from above the dosage point.

The predators of Simulium are fish, stoneflies, and caddis flies. With all the dosages, none of the predators was affected by the insecticide and the recovery of Simulium populations therefore did not rise above the normal, as can happen when soluble insecticide is used to remove Simulium and also removes predators.

It is obvious that the other creatures in the stream, particularly the bottom fauna, had to be counted, and much time was spent in time and motion studies to devise a procedure which was of defined accuracy, and practicable, so that all the material collected could be examined during the month before the next collection was due. Nothing is easier than to collect material from the bottom of a stream and, given an indefinite length of time, to count the creatures in it accurately. But a year could be spent working exhaustively through one sample. We carried out a time and motion study for two years, and devised techniques of collection, of sampling the material collected and of examining it in different ways so that accurate assessment of the numbers of different kinds of creatures could be made. Different kinds of creatures required different techniques. We would point out here, from our experience over these eight years, that unless rigid techniques of this kind are carried out, in estimating both the populations of Simulium larvae and of the creatures living in the bottom, we do not see how any valid conclusions can be drawn as to the effect of the insecticide. Estimations based on Simulium larvae counted on sticks and stones are, through our own observations, irregular and liable to great interference by physical changes in the river, and the casual examination of bottom material by naked eye scanning is of limited value.

We have shown several other particulate compounds to be effective against Simulium larvae but we have not yet been able to follow up the effect of those particulates on the other creatures in the river.

I now wish to discuss three issues concerning the use of insecticides in rivers.

Firstly, the question of persistence. DDT in whatever form is a residual insecticide. We followed its persistence and breakdown in different layers of the sediments in different parts of the river with different rates of flow, and in different parts of the estuary. As an incidental, fungi and bacteria were found which were capable of breaking down DDT and some could use DDT as their sole carbon source. But the long-term persistence of residual insecticide is irrelevant to the control of Simulium, since the insecticide is washed over the larvae so quickly by fast running water. "Shell" Research Limited at Woodstock Agricultural Research Centre therefore provided several particulate compounds whose breakdown occurred within hours or days by physical chemical means. An insecticide with transitory effect would be equally effective against Simulium and less deleterious to other creatures in the river.

Secondly, we do not fully know the significance of any changes in the river eco-system produced by insecticides, unless they are extremely gross following an accident. The minor population disturbances such as we produced in the freshwater shrimp were restored to normal within a matter of days or weeks. This rapid restoration to normal suggests that the community of creatures in the river is resilient and in any case such a disturbance is trivial compared with the enormous range of changes produced by natural variation in the river due to drought and spates.

Thirdly, one must distinguish between screening the effect of insecticides on creatures in a small, manageable stream and its development to large scale "monitoring" when insecticides are used in control measures in the tropics over vast areas. To do this original experiments with DDT on this small stream in North Wales took a very considerable amount of time and effort by biologists to establish what the normal behaviour of the eco-system of the stream was over eight years, to know its variability and to define the range of "normal" against which interference could be interpreted. The measurement of insecticide and its breakdown products in living creatures and in the sediment of the rivers was absorbed as a very small part of the normal analytical services of a large University department of chemistry. It was the investigation of the effect of the insecticide on other creatures in the river that was expensive in labour and in time.

When an insecticide has shown sufficient promise under these experimental conditions to warrant its application in a vast tropical river system, current concern for the environment and political exigence demands that "monitoring" should be carried out. In this connection, it is worth remembering that before the numerous insecticides came into use for malarial control, control measures were dependent upon constant, intimate monitoring of the larval populations of mosquitoes; as many as 1000 men would be involved in a small province of India or Ceylon. Feed back of information was immediate. But malarial mosquitoes breed in stagnant water which is accessible and its normal biological communities are easily assessed. The large African rivers flow for the most part through desolate country of different kinds. They have their dry seasons and their floods, usually on a yearly basis, and their dry seasons and floods fall in cycles ("seven lean years, seven fat years"). No adequate assessment of a large tropical river eco-system has ever been done. The mind boggles at the manpower required for such a survey of 1500 miles of Niger in places three miles wide. One wonders, too, how far normal, spontaneous variations occur for unknown reasons. The Department of Biology at Salford University has collected information for about 10 years for very small parts of the English River Lune and we have found spontaneous variations over this period which we cannot explain. Do these occur in tropical rivers?

It can be seen, therefore, that there can be no true feed-back from the use of insecticides, whether particulate or soluble, in large tropical rivers.

Eight years ago, we suggested that since the management of temperate rivers was developing into a highly intricate technology, the time had come to consider tropical rivers in the same way, but temperate rivers are different from tropical rivers. Temperate rivers require management to take account of the water demands for industry, domestic water supplies, the disposal of sewage and industrial effluent, and of leisure pursuits such as game and coarse fisheries, canoeing, and sailing.



Water is in short supply and must be conserved. The water is often re-used several times before it reaches the sea. This re-use of water is possible because rivers tend to be self-cleaning before they reach the sea. In tropical rivers although the occasional large city has developed (nearly always on the coast), the great bodies of their waters are used for transport, irrigation and fish-hunting, as they always have been; and in recent years, for the generation of hydro-electric energy, with the production of large lakes behind dams. The rivers are important sources of fish but the fish are hunted and the stocks take care of themselves, they are not managed in small concentrations.

The "monitoring" of insecticides in the tropics must be assessed against this background.

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FUTURE REQUIREMENTS IN MICRO GRANULE MACHINERY

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METHOD AND MATERIALS

The development of machinery for micro granule application will, of necessity, go in several different directions. We have heard of the very wide range of chemicals now available in this form, and they have different functions to perform.

The earliest use of micro granules in this country came with the introduction of insecticide for the long term control of aphids in carrots and potatoes, cabbage root fly and other soil applications. The machinery developed for application was innovative and remains largely unchanged today. Since that time however, the functions have increased to include total weed killers for industrial use, wild oat and black grass herbicides, vegetable weed killers, nematocides, and products for various soil borne pests. Soon we shall be seeing broad leaved weed killers for cereals, and granules combining the functions of several of the others mentioned.

So the need for machinery changes. In the first place, the softer bases, Fullers Earth and Pumice are not always suitable, and clay and sand bases are now being used as well. Abrasion has become a major factor and it has been necessary to redesign part of the "micro band" applicator to cope with the sand based material. In future, this problem may increase and it will, I am sure, be reflected in the design of the next generation of precision placement applicators. Secondly, it seems logical that an increasing number of planters and seeders will be built with integral micro granule units. The vast majority of Sugar Beet drills, maize drills, and potato and vegetable planters have applicators which are attached after sale, and the end result is not always perfect. This is quite a natural state of affairs as, in the beginning, all the companies involved had to work hard, with loan schemes and discounts, to get the machines on to the farm, to permit the sale of their novel products. Now however, there must be very few cash cropping farmers without the need for such material, since the range had widened so much.

Having started as a formulation for cash crops, the granule took a very big step to become a wild oat herbicide and the requirements were very different. An overall application of about the same weight of granules as had been used down the row was required, but a very even spread pattern needed (and found) from the T.M.A. series of applicators. The wide acceptance of this granular formulation of a famous wild oat killer, provoked development of dual purpose machines, designed principally for granular fertilizer but capable of high outputs with micro granules. The introductions in this category continue with a fine selection of mounted and trailed machines all using the air blow principal. The virtue of a large capacity machine lies in its work rate compared with water based chemicals, applied by spraying machine.



## Calculation of work output of Micro Granule Spreader and Sprayer

<u>SPREADER</u>	1 ton (1018 kg)	<u>SPRAYER</u>	330 galls (1500 ltrs)
width	40 ft (12 metres)	width	40 ft (12 metres)
speed	6 m.p.h. (9.6 Kph)	Speed	6 m.p.h. (9.6 Kph)
filling time	5 minutes	filling time	10 minutes
work rate	29 acres/hr (12 ha/hr)	work rate	29 acres/hr (12 ha/hr)
Application rate	20 lbs/a (22½ kg/ha)	Application rate	20 gls/a (225 ltrs/ha)
Acres/fill	112a (47 ha)	Acres/fill	16.5 (6.9 ha)
Net time per fill	3 hrs 52 mins	Net time to spray load	35 mins
(assume start full finish empty)		No. of fills required to equal spreader load	7 Also 6 refills required - 10 mins/refill. Time to spray 112 acres (47 ha) = 5 hrs 5 minutes.

In addition the sprayer needs supplying with 10 tons of water in total and no account has been taken of the haulage time of sprayer when re-filling.

The micro granule spreader could accomplish an extra 33 acres in the time taken by the sprayer to cover 112 acres (47 ha).

The development of a large capacity trailer machine of pneumatic spread, enables very large areas to be covered without refilling. A machine of three tons capacity could spread over 330 acres in one fill and without the need of a support vehicle to supply water as would be the case with a sprayer. To be objective, it does appear that the trailer machines are designed principally for granular and other fertilizer, rather than micro granules, but they are suitable for fine work and may find more and more use in that area. They are the natural development of the dual purpose line of thought. One problem which will certainly exist will be estimating the quantity of granules left in the hopper, when such big quantities are involved and my own view is that some kind of weighing device may have to be incorporated, to help in that area. In any case, very precise calibrations will have to be made in a very convenient form, otherwise gross errors could creep in unnoticed.

The introduction of fungicide for late application in cereals on the continent has produced great interest in tram-line systems and this extends, although to a lesser extent, to the oilseed rape crop also. I feel sure, that in the latter case, if a chemical for pollen beetle and seed weevil could be formulated as an effective granule, it would be widely accepted. Sadly, it seems unlikely that pollen beetle and weevil can be found sufficiently different in their mode of behaviour in the flowers from bees, for it to be possible to select between them. There is a use for a high clearance spreader of micro granules in Maize in France and it is possible that the need could bring such a development in this country too.

The apparatus used is a very wide version of a precision granule applicator, mounted on a high clearance (long-legs) tractor. This machine has an under belly height of nearly 6 ft. and is ideally suited to treatment of tall crops at late stages. A number of materials are used including Chlorphrifos - (Dursban) but the most unusual must be the bacterial micro granule - which is designed to infect the corn borer with a disease, killing it some 3 weeks after the application. Bactospeine Granules or Dispel granules contain about 16,000 intestinal units/mg of *Bacillus Thuringiensis* and are spread at 30 Kg/ha. The safety factor of such a specific pesticide to other animals makes it a very attractive proposition.

More likely however, is the continued successful use of aeroplanes to spread granules on tall crops, beans being the example which springs to mind. As other materials come forward in granular form, it seems likely that farmers will use aircraft more, particularly as a number of products are designed to be applied in late Autumn, Winter and early Spring. The dry winter of 1975/76 may make us forget just how difficult November and March can be for the application of herbicides.

In the not too distant future, I feel sure that precision sowing of cereals will take its place, as a cornerstone of the build up of yields, in which attention to detail appears to be vital. Almost certainly a placed insecticide, slug killer, fungicide or all three will be needed and I feel sure that commercial precision cereal drills, will have integral micro granule hopper space. It may be that overall incorporated granular herbicides will become commonplace, and machines for that application, fed by gravity or air blown, are already being produced, for attachment to conventional drills. They are obviously designed with wild oat and black grass granules in mind, but the day when a soil sterilant, a nematocide, or an all purpose product, has to be harrowed in behind the drill may not be far off.

The other machine which I feel sure we shall see is a purpose built, light weight tool carrier, for granule spreading and high clearance spraying, self propelled, and treading lightly enough to be able to cover the not so kind land, whatever the ground conditions.

We must admit that the large farm tractor is not the most suitable carriage, for so delicate a tool as a micro granule.



GRANULAR PESTICIDES: SOME DEVELOPMENTS AND OPPORTUNITIES

FOR THE FUTURE (DEVELOPED COUNTRIES)

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Summary Uses of granular products are discussed in principle to indicate some possible developments or future requirements. They are especially suitable for application to soil and increased use of partial soil sterilants seems likely, but should be approached cautiously. Safe-handling characteristics of granular formulations will remain important for a.i.'s with high mammalian toxicities and the possibilities of developing specialised uses seems most promising for herbicides. Trends in the concentration of a.i., types of granule bases and formulations are discussed and also the factors affecting biological performance. Analysis of the doses of a.i. and granule distribution indicates that the amounts required for certain pest control purposes are related to plant density. Economical and informative evaluation methods for granular insecticide products have been devised and should facilitate future developments.

INTRODUCTION

Granular formulations of pesticides were first introduced in the U.S.A. to reduce drift, particularly of aerially applied chemicals, to provide safer formulations than dusts for distributing highly toxic chemicals safely in areas with limited water supplies and to meet certain specific problems of pesticide placement. They tend to be used mainly in the sophisticated and intensively-developed agriculture and horticulture of the developed countries but even so, the knapsack sprayer is more often used than the hand granule applicator on small-holdings, as well as in peasant agriculture. Nevertheless, the number and range of uses for granular products have been expanding steadily during the last decade, and the granular formulation has become a principal method for applying pesticides to soil, particularly those insecticides with high mammalian toxicities.

The range of granular products now approved and available for use in the U.K. is typical of many developed countries. There are, at present, nineteen different active ingredients representing one general soil sterilant, ten insecticides, of which two are also nematocidal, and eight herbicides (Anon. 1976). The safe-handling characteristics of granular formulations of potentially hazardous insecticides are evident in that eight of the ten approved insecticides/nematocides are Part II or III Scheduled Substances under the U.K., Health and Safety Agriculture (Poisonous Substances) Regulations 1975. Four of these are included in the Poisons List and so are also subject to the Poisons Rules. Only diazinon and chlorpyrifos products are excluded. In contrast, none of the herbicides is Scheduled and their development in granular formulations has been mainly for technical rather than safety reasons.



## USES OF GRANULAR FORMULATIONS

Uses of granular products and factors affecting their performance were reviewed by Walker (1971). Future developments seem likely to occur as continuations of existing trends.

### Soil sterilants

The general soil sterilant, dazomet, evolved from a dust formulation in 1963 to a prilled material by the early 1970's and to a granular formulation since 1972. This formulation is unusual in comprising about 98% of active ingredient and in being the only granular product approved specifically for use as a soil fungicide to control 'damping off' and similar organisms. It is used at such unusually large doses (220-570 kg/ha), and has to be so deeply incorporated (18-20 cm), that it is expensive to use. Its use seems destined to remain very limited outdoors, particularly if the more efficient methyl bromide injection machinery becomes more widely used for general soil sterilisation. The problems of achieving consistently good, deep incorporation of a granular product makes it unlikely that there will be great expansion in the use of dazomet, or comparable products. Such granular products should, however, continue to be used to treat relatively local, patchy disease- or pest-infected areas within fields.

Pesticides such as aldicarb, carbofuran and oxamyl have a broad-spectrum of biological activity and, when applied at appropriate doses, can substantially reduce soil fauna and micro flora, thereby effecting a partial degree of sterilisation which frequently improves crop yields in the short-term. Potatoes, onions and certain other high value crops are likely targets for expansion of use of such materials. Aldicarb, however, also offers a means of controlling populations of organophosphorus-resistant aphids on crops such as potatoes and sugar-beet, and a rapid expansion in its use for this purpose is now occurring and is likely to develop further in the near future. It would, however, be prudent to avoid over-extending its use as a prophylactic treatment to the stage where large proportions of agricultural land in some areas are treated as a routine measure. Not only are possible adverse environmental affects relatively unexplored, but the risks of undesirable vapour concentrations occurring in the atmosphere in intensively-treated areas, although apparently unlikely to be serious, are at present unknown. Any tendency for over-use to encourage unnecessarily a more rapid development of aphids or other insects resistant to the chemical could have, in the absence of effective alternatives, serious and far-reaching consequences for aphid and virus control in, for instance, potatoes and sugar beet.

There is increasing interest in the possibility of greatly expanding the growing of plants in small peat blocks, both for agricultural use and to provide mail-order supplies to the domestic market. The advantages of incorporating a broad-spectrum pesticide, or pesticides, in granular form into the peat block medium are obvious, but will create new problems concerned with persistence, phytotoxicity and safety in the transport and handling of the treated material.

### Insecticides and nematocides

Without doubt, the safe-handling characteristic of granular formulations permits much wider use of compounds with high mammalian toxicities than would be the case if only liquid products were available. This will certainly remain a valuable feature of granular formulations. They are particularly advantageous for applying pesticides to soil, the main purpose for which they are now used. Pesticides in general tend to be more persistent in soil when they are incorporated as granules than when sprayed directly on to the soil. The granule therefore represents an easy and efficient method of treating soil and achieving a satisfactory distribution of active ingredient. The considerable research and



practical experience in the use of granular products for controlling pests such as the cabbage root fly on brassicas, carrot fly on carrots, parsnips and celery and aphids on a wide range of crops accumulated during the past decade enables comparisons to be made of application rates which are roughly comparable in performance. This is discussed below.

### Herbicides

The granular formulations of herbicides have mainly been devised for specialised uses such as total weed control on paths, tracks, etc., control of weeds in waterways, and the application of relatively volatile compounds to soil. At present in the U.K., opinions do not suggest any major changes in this position, although some expansion of use may occur. Granular formulations of herbicides seem to offer fewer advantages, even for soil-incorporation, than is the case with insecticides, probably because the performance of weed-control treatments often tends to be more critically dependent than insecticidal treatments on dose, soil type, moisture status and temperature. They do, however, provide a useful means for applying relatively volatile herbicides such as chlorthiamid and dichlobenil to soil and ensuring reasonable persistence. Whether they have a future for applying mixtures of two or more a.i.'s, an increasing requirement, remains to be seen. The good progress made in developing controlled release formulations for controlling weeds in waterways, suggests that this type of specialised use seems likely to become a more important outlet for granular herbicides in the future.

### Fungicides

The development of specific granular formulations for fungicides, apart from the soil sterilant, dazomet, seems not to have attracted much attention up to the present time. There does not seem to be any obvious reason why some of the fungicides now available could not be formulated and used effectively as granules, particularly for soil treatments to control diseases such as white rot of onions (*Sclerotium cepivorum*) (Entwistle, 1976; pers. comm.). However, the commercial incentives to do this seem not to be very strong.

## GRANULE CHARACTERISTICS

Sufficient experience has now been accumulated with granular products to suggest characteristics which are either desirable or to be discouraged in future formulations.

### Concentration of active ingredient

With the exception of the dazomet granular formulation which contains 98% of the active ingredient, most granular products contain 5 or, more usually, 10% a.i., although a few herbicides contain 20%. There is now interest in reducing the concentration of active ingredient in granular products to improve the distribution and to improve the consistency of metering-out lower doses by the existing types of application machinery. Reducing the concentration from 10 to 5% a.i. will double the number of particles applied and thereby improve distribution of toxicant, but this alone does not greatly alter the performance of products against pests such as cabbage root fly (*Delia brassicae*) or carrot fly (*Psila rosae*). The reason for this is probably that the volume of soil per granule (Table 1) is still sufficiently small, even with the higher concentration products, for the a.i. to diffuse quickly through the soil matrix and counteract any tendency for maldistribution. This feature has the effect of making the efficiency of applications of granular products to soil rather less dependent on the precise geometry of application coulters and tines than might generally be supposed, although exact alignment of equipment is always essential for row-crop work.



## Granular base and formulation

With few exceptions, most existing granular formulations are prepared by applying the active ingredient to the pre-formed and pre-sized granule base, thereby coating the surface. Since this is usually more economical than incorporating the active ingredient in a carrier matrix which must then be granulated, it seems likely that the surface-coated granule will continue to be favoured for general purposes, although the more expensive impregnation method does provide a ready means of controlling both the rate of granule breakdown and the rate of release of a.i. from the granule base.

The choice of granule base in the past has depended perhaps too much on its cost so that, from time to time, granule bases have been changed with little or no warning. On occasions, new products have subsequently been less satisfactory in performance than their predecessors, much costly research and experience in their use has been discarded, and a degree of uncertainty has been engendered among growers and advisers which is not compatible with modern crop production requirements. For example, a product produced on a relatively adsorptive Fullers earth granule base was very satisfactory in insecticide evaluation trials in 1974-75. Subsequently it was marketed on a quartz substrate and not only performed differently by being phytotoxic in some circumstances (not evident in the earlier performance trials) but it also rapidly abraded application machinery.

Highly abrasive granule bases can cause serious wear in application machinery, thereby affecting the calibration and causing over-dosing. Difficulties with this have been experienced on several occasions in recent years and they have usually been overcome by modifying the design and constructional materials of the machinery. Nevertheless there is a case for avoiding excessively abrasive granule bases whenever possible.

In general, near-spherical high-density granules flow better than those that are flat, angular or of low density. Granules must not be prone to change their flowability characteristics with change in atmospheric moisture, an unfortunate characteristic observed with one product in recent years. The granule particle size should normally be within the range of 250  $\mu\text{m}$  to 2 mm and should be substantially free of fines less than 125  $\mu\text{m}$ . The number of particles/g can vary considerably without apparently greatly affecting their biological performance. The nature of the granule base should be such that it is not prone to acquire very high electrostatic charges, otherwise the product can become unpleasant and even dangerous to handle, and the flowability will be variable. The colour of the granule product is also important especially when it is to be applied to soil. Growers prefer to see where the granules are being placed and cannot do this unless the particles contrast strongly with the soil matrix in daylight. A strong, harmless odour can also be helpful in this respect.

### FACTORS AFFECTING BIOLOGICAL PERFORMANCE

#### Dose of active ingredient

Present application rates have all been arrived at empirically but, for certain uses of insecticides, there are indications of requirements for particular problems that may provide guidelines for future products.

The rates of application of granular products are consistent mainly in the amounts of a.i. applied, provided that the amount is appropriately described. The grower needs to know the amount of product to apply but for research and development purposes the amount of a.i. is usually more appropriate. Depending on the mode of use and the crop, the amount applied can be expressed per unit area (kg/ha), per unit length of row (mg/m) or per plant (mg/plant). Practical



Table 1

Summary of granule application criteria for certain pest control problems

Pest problem	Application method and rate	Particle distribution		Dose/plant	
		cm <sup>2</sup> soil/gran	cm <sup>3</sup> soil/gran	No granules	mg a.i.
Cabbage (root fly)	Broadcast (surface) 45 kg/ha	1.1	-	160	8
	Broadcast (mixed to 5 cm) 30 kg/ha	0.71	3.5	250	2.7
	Band, 10 x 1 cm deep 0.7 - 1.3 g/m row	0.09 - 0.71	0.09 - 0.71	210 - 1700	10
	Band 5 x 10 cm deep 0.7 x 1.2 g/m row	0.09 - 0.71	0.8 - 3.6	210 - 880	10
	Spot, surface, 15 cm diam. 0.17 - 1 g/plant	0.08 - 0.6	-	340 - 2100	17 - 45
Carrot fly	Broadcast, 21 - 45 kg/ha	0.55 - 1.1	2.2 - 22	14 - 67	0.6 - 1.0
	Band, 7.5 x 1 cm deep 11 - 28 kg/ha	0.12 - 0.21	0.12 - 0.21	140 - 250	1.8 - 3.8
Aphids : on carrots	Band, 7.5 x 1 cm 11 - 25 kg/ha	-	-	32 - 160	1.1 - 2.5
on sugar beet	Soil or foliage 5.6 - 11 kg/ha	-	-	38 - 880	7 - 14
on Brussels sprouts	Soil or foliage 14 - 39 kg/ha row	-	-	3100 - 12000	33 - 190



application rates then fall within reasonably well-defined ranges. For cabbage root fly control on spaced brassicas, materials applied either broadcast or as band applications usually result in from about 3-8 mg a.i. being applied as 160-250 particles/plant. Band applications along the crop rows usually apply about 10 mg a.i. as 200 - 1700 particles/plant and spot surface applications about 17 - 45 mg a.i. as 340 - 2100 particles/plant. For carrot fly control the recommended application rates for broadcast treatments provide from about 0.6 - 1 mg a.i. as 14-70 particles/carrot compared with about 2-4 mg a.i. as 140-250 particles/carrot for band applications.

At least fifteen different crops are treated with granular formulations of insecticides applied either to the foliage or to the soil to control aphids. The amounts recommended range from 5.6 to about 40 kg formulation/hectare providing from about 30 to 12000 particles/plant and from about 1 to almost 200 mg a.i./plant. If the crops are arranged in order of plant density the number of granules/plant increases steadily as plant density decreases, as might be expected, ranging from about 30 - 60 granules/carrot, to about 500/celery plant, or up to 12000/Brussels sprout plant. The amount of a.i. increases similarly from about 1-2 mg a.i./carrot to about 16 mg/celery plant and 100-200 mg/Brussel sprout plant. It is apparent that the amount of a.i. needed for aphid control increases from the smaller to the larger crop plants, as would be expected if similar lethal concentrations are needed in the sap to control these pests. It seems unlikely that the doses of chemicals used in the future will stray much outside the range of those at present in use.

#### Rate of release of active ingredient

Although at first sight there appears to be considerable scope for devising granular formulations which release the a.i. at different rates, in practice only limited use has been made of this facility. Except for special purposes which may warrant the introduction of expensive tailor-made formulations, it is difficult to imagine granular products being devised with other than rapid, medium or slow release rates. The only granular product at present available with different release rates is disulfoton; a formulation on Fullers earth releases the a.i. relatively slowly, prolonging the persistence and activity of the chemical in soil, whereas another on pumice granules makes the chemical more quickly available and is suitable for application to crop foliage. There is sufficient difference in the performance of these two formulations for aphid control to suggest that new active ingredients should initially be formulated on both slow and fast-release granule bases to indicate more reliably the extent to which the biological performance of the a.i. can be modified in this way.

Controlled release formulations seem likely to play an increasing part in the specialised application of herbicides and already much is known about the way in which they can govern the concentration of herbicide in water-ways. The overall effect of controlling the release rate can usually be likened to adjusting the initial dose and the frequency of application.

#### Granule distribution

It is of particular interest to consider the distribution of granules in soil in relation to the particular application techniques and crop pest problem. In Table 1, examples of granule distribution are shown on an area ( $\text{cm}^2$  soil/granule) and on a volume ( $\text{cm}^3$  soil/granule) basis. Following present U.K. recommendations, insecticide granules are usually applied so that each granule occupies a volume of from 0.1 - 3.5  $\text{cm}^3$  in soil. Even at the lowest granule density, the a.i. will have little difficulty in diffusing throughout the average volume of soil allotted to each granule. For controlling carrot fly damage to carrots, broadcast applications of granules provide 2-22  $\text{cm}^3$  soil/granule compared with 0.1 - 0.2  $\text{cm}^3$  soil/granule from the more effective bow-wave application. These estimates of granule



distribution in the soil explain why it is possible to use granular products in many different ways and achieve similar end results. Conversely, provided an even and not an irregular, distribution is achieved, the performance of granular insecticides in soil is not easily improved by relatively minor modifications in the granule placement equipment (Wheatley 1972a). Thus the grower often has a considerable latitude in quality of application, in many ways a fortunate safeguard, since the biological performance of the granular products is not usually very sensitive to minor variations in applicator performance.

#### Resistance of organisms

Most granular applications to soil are applied as a routine prophylactic measure before or while sowing, or during or after transplanting, the crop. There is therefore an understandable tendency to over-use the products as insurance crop protection. Unfortunately this increases selection pressure and encourages the development of resistant pests, foreshortening the useful life of the chemicals involved. During the next decade increasing attention will be given to improving our ability to forecast pest outbreaks and to identify those crops and fields most or least at risk. In this way it should be possible to rationalise the prophylactic use of granular or other forms of pesticides. Apart from the obvious saving in costs, the delay in the development of resistant strains of pests and the consequent increase in the useful life of the chemicals, will be advantageous in the long-term to all parties concerned, the grower, the agro-chemicals and crop processing industries, research workers and the public.

#### EVALUATION AND CRITERIA OF PERFORMANCE

As with other pesticide products, the cost of evaluating the biological performance of granular products mitigates against their development for many minor uses or on crops of limited acreage. The conventional field evaluation methods usually depend on the application of one, two or, at the most, three fixed doses of a product, severely limiting the information that can be deduced from such trials. Furthermore, the precision attainable is usually not sufficient to distinguish confidently differences of less than about 30% in the performance of treatments. To overcome such limitations, a log-dose procedure for granular products has been developed at Wellesbourne during the past five years, entailing a radical change in the design of the field evaluation trials, the design and construction of special application equipment and a revision of data handling and presentation. Untreated plots are arranged systematically as a 'grid' over the experimental area, rather than at random, and the treated plots are randomised within the spaces of the 'grid'. The equipment applies granules in continuous bands at logarithmically-changing application rates, each covering a 16-fold range of dose. The types of assessment needed to describe the many facets of 'performance', have been carefully selected to provide a maximum of information from a minimum of records. This has necessitated devising a computerised data-handling system and simple procedures for expressing and interpreting the results relative to standard treatments. The log-dose method was developed initially for testing the soil-applied granular insecticides against cabbage root fly and carrot fly (Wheatley, 1971; 1972b). With further development, it is now used routinely in trials against these pests (Thompson, et al., 1976) and, most recently, it has been extended successfully to evaluate products for cabbage aphid control on Brussels sprouts (Suett & Padbury, 1976).

Results obtained by the log-dose procedure have highlighted the limitations of fixed-dose tests, for instance in revealing that cabbage root fly control does not necessarily improve in a regular manner in relation to the amount of a.i. applied. The confidence with which different information on performance can be derived is perhaps the most impressive feature of the procedure. Within a single trial it is possible to determine the relative efficiencies of thirty or more treatments, obtain an indication of their selectivity with respect to natural



enemies of a pest, deduce their effectiveness, both in terms of phytotoxicity to seedlings or to plants during growth and of ultimate yield of marketable produce. Smaller differences in performance can be detected than hitherto, a feature particularly valuable for comparing the relative merits of different formulations of a chemical which may not differ greatly in some aspects of their performance. The procedure greatly reduces, and may even eliminate, the need for intermediate-scale tests and should enable product-development to advance confidently to large-scale grower trials in less time than has previously been thought necessary, perhaps saving 1-2 seasons of intermediate scale testing. To take maximum advantage of this, it is of course essential that appropriate terminal residue data be obtained simultaneously with the biological assessments of performance during the log-dose experiments. Using the log-dose procedure should thus greatly aid the development and introduction of new granular products, especially in extending their use to minor crops which do not justify prolonged and expensive evaluation trials.

Recent developments in application machinery should enable the specified application rates to be achieved and maintained more readily than in the past and should avoid problems with abrasion and drift of calibration. The early application machines were simple and cheap; in developing the second or third generation machines the advantages of economy should not be lost if at all possible otherwise sales will tend to be restricted to larger growers and the advantages of the granular products will not be made fully available to those with only limited acreages to treat. The development of improved, less specific hand applicators will be essential if the small-holders and poorer farmers in all countries are to reap the advantages of the granular formulation. However, it will also be desirable to stabilise the characteristics of formulations and, as far as possible, to avoid inessential changes in the base materials used.

#### SAFETY

Granular products permit potentially hazardous toxicants to be used with comparative safety to the operators. This has been an important feature of their development in the U.K., although not necessarily so in other countries. Indeed, some countries consider that the granular products are more hazardous than most liquid formulations because they utilise pesticides that are among the most highly toxic compounds to man, but this rather begs the question. It is unlikely that many of the present granular insecticides would be permitted to be used in the U.K. as liquid formulations.

The recent reconstructions of the U.K. Health and Safety (Agriculture) (Poisonous Substances) Regulations have increased the responsibility of all employers, employees and self-employed persons with respect to use of pesticides. Regulations made under the Health and Safety at Work Act, 1974 and introduced since 1975, imply that more and not less consideration will have to be given to the safety of all pesticide products, including granules, in the future. This is almost certain to require stringent control of formulation, particularly to avoid dust and to ensure that potential vapour hazards are minimised during use. There is need to give more thought to the form of containers used for granular pesticides so that granules can be easily and safely poured into machinery hoppers, and also to the use of polyethylene bags inside rigid outer containers. The inner bags are frequently handled without protective clothing, yet some active ingredients obviously pass through the polyethylene and contaminated the outer surface of the bags. The disposal of unwanted granular products also poses a safety problem requiring more attention.



## CONCLUSIONS

In the immediate future there is likely to be a considerable increase in the application of insecticides, nematocides and partial soil sterilants as granular formulations to soil. Herbicide products seem most likely to be developed for more specialised purposes. The wider-scale use of granular products which seems imminent should be approached with caution not only to avoid unanticipated environmental problems but also to enable the vital resistance monitoring of pest populations to be undertaken in step with the expanded use of the products.

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PROSPECTS FOR THE USE OF GRANULAR NEMATOCIDES

BY WEST INDIAN BANANA GROWERS

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Summary In field experiments conducted in St. Lucia the granular nematicides ethoprop, phenamiphos, carbofuran and oxamyl applied to bananas at planting, 2 months and subsequently every 4 months have been as good or better in improving production than has DBCP treatment applied at 2 months and subsequently every 6 months. Because granular nematicides are easy to apply banana growers might use them in preference to DBCP but not before consideration is given to the costs and benefits and also to safety precautions during handling and application.

INTRODUCTION

Banana production in the Windward Islands is often limited by nematode attack which can render fields uneconomic within a few years. Some growers replant banana fields every 2-3 years (Edmunds, 1971).

The treatment of banana fields with nematicides has been recommended for a number of years (Edmunds, 1969) but until recently DBCP (1,2, dibromochloropropane) has been the only suitable chemical available. Results obtained from experiments in the Windward Islands (Gowen, 1974, 1975) and in some West African territories (Guerout, 1974) have shown that granular (non-volatile) nematicides can give good control of nematodes and improve banana production.

METHOD AND MATERIALS

From planting, bananas require 10-12 months to produce a bunch of fruit. During this period of growth lateral shoots develop from the base of the original stem and it is the usual practice for growers to prune all but one of these 'suckers' which is selected to produce the first ratoon bunch. Bananas flower terminally and after harvest the stem dies and the selected sucker becomes dominant.

In two field experiments on a clay loam soil at WINBAN Experimental Farm, Roseau, St. Lucia, granular nematicides were applied at planting at 8 weeks and subsequently every 4 months. Granules were sprinkled by hand from specially prepared cups. At planting the chemicals were placed in the holes close to the planting material, the second and third applications were sprinkled in a 30 cm radius around the young banana stems. For subsequent applications the area of treatment was selected according to maturity. Chemicals were not applied to stems which were bearing fruit or had been harvested but in a 30 cm radius from the shoot which had been selected to produce the ratoon crop. DBCP (75% EC) diluted with water was applied with a hand injector at 8 weeks after planting and subsequently at 6 month intervals. Eight injections were made to a depth of 15 cm in a circle around the stems at a distance of 45-60 cm.



STUDIES IN SLOW RELEASE GRANULAR FORMULATIONS OF ALDICARB

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METHOD AND MATERIALS

Coal and corn grit formulations of aldicarb have already been shown to increase yields of sugarbeet in areas heavily infected with the sugar beet eelworm (*Heterodera schachtii*). Commercial formulations are rapid release, and consequently do not have a lasting effect on the parasite population level. Consequently, at the close of the season, population levels are similar to those in control plots, although yield increases are high due to initial parasite control at germination and seedling stages. A second application of conventional formulation at the singling stage has been shown to reduce the final eelworm population (Heijbroek 1973), but a second application of aldicarb could not be economically justified. A reduction in final parasited population is desirable because legislation effectively limits the grower to one crop every 3-6 years from a given field, according to the final population level. Thus, although any increase in the yield due to the effect of slow release formulations of aldicarb would be speculative, shorter rotation intervals could result, allowing more beet to be grown on a given amount of land.

Recent work by Hough & Thomason (1975) seems to show that even if relatively low levels of aldicarb could be maintained in the soil for a longer proportion of the growing season, the life cycle of *H. schachtii* would be sufficiently disrupted to significantly lower the final cyst population.

Application rates of a slow release formulation need not necessarily be much greater than those recommended at the moment, as the low persistence of aldicarb at the present rates results from relatively fast leaching and decomposition of aldicarb in the soil.

I am carrying out my own formulation program using Union Carbide Temik 10G-BC granules (coal based) and coating them with a variety of waxes and resins. It has been found that coating with several coats has proved more successful than the addition of a coat in one operation (c.f. Seaman and Warrington 1972).

Field trials will be carried out in East Anglia during the next two years in co-operation with Broom's Barn Experimental Station in order to test the effects of such slow release compounds on nematode population levels. It is hoped to assess both eelworm populations and aldicarb residue levels throughout the growing season.

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EXHIBITS

I GRANULES

H = herbicide  
I = insecticide  
S = sterilant  
M = miscellaneous  
N = nematocide

	GRANULES	COMPANY
M	Granule bases various	Atlas Chemical Co.
H	Cobex	Borax Consolidated Ltd.
M	Granamins	B.P.Nutrition (UK) Ltd.
I	Disyston P10 & FE10	Bayer UK Ltd.
S	Basamid	BASF UK Ltd.
H	Herbongran A, C and T, Herbon Gold	Cropsafe Ltd.
H	Hydon, Chlorea	Chipman Ltd.
I	Abate, Counter, Thimet, Nemafos, Stomp	Cyanamid of Gt.Britain Ltd.
I	Basudin	Ciba-Geigy (UK) Ltd.
H	Weedex, A4G, SG2	
H	Casoron G & G-SR	Duphar-Midox Ltd.
I	Dursban	Dow Chemical Ltd.
NI	Vydate	Du Pont (UK) Ltd.
H	Herbazin	Fisons Ltd.
I	Hostathion	Hoechst UK Ltd.
H	Avadex, Ramrod, Lasso	Monsanto Ltd.
H	medinoterb acetate	Murphy Chemical Ltd.
M	Slugit	
I	Dyfonate	Pan Britannica Industries Ltd.
H	Kerb	Rohm & Haas (UK) Ltd.
H	Dosanex	Sandoz Products Ltd.
NI	Dacamox	Shell Chemicals UK Ltd.
M	Sydane	Synchemicals Ltd.
H	Naptol	

I GRANULES (Cont'd)

NI	Temik	Union Carbide Ltd.
I	Dotan	Rhone-Poulenc.

II APPLICATORS

TYPE OF APPLICAOTR	COMPANY
Hand granule applicator	Ciba-Geigy Ltd.
SMC Bimigrasol granule applicator	Colchester Tillage Ltd.
Range of applicators	Duphar-Midox Ltd.
Rogor granule hand applicator	Fisons Ltd.
Kyoritsu applicating equipment	J.D.Gillett & Son Ltd.
Evrard granule applicator	Heygate Chemicals Ltd.
Various	Horstine-Farmery Ltd.
Sequip granule applicator	Eric Matthews & Co.
Herriau 'Granyl' granular applicator	Stanhay (Ashford) Ltd.
Land rover mounted granule applicator	Sandoz Ltd.
Vari-Spreader	Vicon Ltd.



