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REVIEW OF PESTICIDES AND THEIR FORMULATION [1]

by

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[1] The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. This document has been reproduced without formal editing.

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Introduction

Whereas in many sections of chemical industry products are sold subject to compliance with a straightforward specification of chemical composition or physical properties, the farmer who purchases agricultural chemicals often expects and receives far reaching guarantees concerning performance on soils and in weather of different kinds. In particular, the safety of the crop must always be guarded. Marketing of agricultrual chemicals, therefore, has to be preceded by patient experimental work in fields situated throughout the main agricultural areas of each country. Such field trials should preferably be planned in consultation with the chemical manufacturer, but they should be executed and evaluated by field biologists who are familiar with local agriculture and who have close liaison with their own Ministries of Agriculture. Development of an agricultural chemical usually occupies at least three seasons, and at an early stage in the development it is important that the manufacturer should be able to provide data to assist registration of the chemical with the local Ministry. Normally these data will include a summary of chemical and physical properties and a synopsis and interpretation of toxicological studies which themselves may be proceeding for three to five years. It is only by proceeding in this way that the chemical manufacturer can ensure the smooth commercial introduction of a new agricultural chemical.

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Reluctance of farmers to buy any agricultural chemical until its performance can be comprehensively guaranteed has sometimes caused a manufacturer to postpone by several years the introduction of a really useful product. For example, the marketing of barban for control of wild oats in cereals was for long held in abeyance because the supplier felt unable to accept alone responsibilities for its performance in the hands of farmers. There are, however, signs that this attitude is just beginning to change as more enlightened people realise that many new and useful chemicals could be made available all the more quickly if suppliers were no longer obliged to bear all risks for performance during an extended period of development.

Ministries of Agriculture, through their registration and approval schemes, ensure that the most urgent public interests are safeguarded. These schemes call for much patient research, for example, by analysis for residues remaining in crops after harvesting, and by pathological studies of toxicity and carcinogenicity of such residues. To be effective these schemes are necessarily complex, but in most countries they are administered competently and are as valuable a guide to the chemical manufacturer as they are a safeguard of the public interest.

For any agricultural chemical the investment in research, development, and technical service is measured in hundreds of thousands of dollars, sometimes in millions, and an adequate return must be built into the retail price of the product. Similar considerations explain why a chemical to be sold for selective weed control is generally more expensive than the same chemical when sold for total weed control. Price cannot be related simply to costs of production and distribution until a chemical has been marketed for many years.

Herbicides

Herbicides are classified in current literature according to several schemes. In this paper it is convenient for the time being to distinguish two classes, viz. those which are applied

(i) to growing plants,

(ii) to soil in order to prevent growth of undesirable plants.

As an example of the first class, the action of MCPA in controlling annual weeds in a grass lawn is well known. MCPA is absorbed in significant amounts by their leaves and moves through the whole plant, often with crippling effect. Such herbicides are "translocatory" and kill by "systemic" action. Another example now becoming increasingly familiar is "Weedol" which is manufactured by I.C.I. and contains quaternary ammonium compounds that kill by "contact" action. The first example introduces the idea of selectivity, for it is easy to apply a dose of MCPA which cripples many weeds without harming grasses. However, "Weedol" would damage most

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plants and the quaternary ammonium compounds of which it is essentially composed are not regarded as possessing any useful degree of selectivity. Herbicides which are effective after absorption by weeds are generally very soluble in water, but this general rule has its exceptions to some of which we shall refer later.

Herbicides of the second class include highly substituted diazines, triazines, ureas, carbamates, and others. Frequently these are applied to the seed bed soon after the seed has been planted at a depth of at least 3/4 inch; and it is sometimes easy to find by trial a rate of application which, whilst permitting the desirable seed to grow normally, will prevent the growth of indigenous weed seeds for several weeks until such time as the crop is sufficiently strong to enable it on its own to overcome any belated competition from weeds. In these circumstances a sufficient amount of the herbicide continues to reside in the upper layers of the soil for several weeks, and when herbicides are used in this way they are described as "residual" herbicides.

Most residual herbicides now in commercial use have been introduced during the last fifteen years. Still, a great deal remains to be learned about the mode of action of residual herbicides and how to apply such knowledge to practical agriculture.

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Of the various residual herbicides that would provide selective control of annual weeds, for example in root crops, rates of application vary from a few ounces to several pounds per acre. Many of the herbicides which are effective and safe when applied at rates within this range are only very slightly soluble in water. For example, diuron, whose action is highly selective after application at 5 ounces per acre to medium loam soils, is soluble in water to the extent of 42 ppm. Thus, the water in a shower of one-thirtieth inch of rain would suffice to dissolve the 5 ounces of diuron per acre if a saturated solution were attainable. During the weeks when residual weed control is commercially valuable, normal rainfall is well over one hundred times greater than would provide a saturated solution of the diuron; yet the phytotoxicity characteristic of diuron remains in the uppermost layers of a seed bed of medium loam soil. Further more, when applied by spraying in bands of width 7 inches over rows 21 inches apart, as in commercial band-spraying practice, effective weed control is restricted to the 7 inch width of the sprayed band with a precision of ± ½ inch. Persistent activity in the uppermost layers of soil, restricted almost precisely to the area of application is the chief characteristic of residual herbicides. This is in contrast to the rapidly diminishing effectiveness of other herbicides, such as dalapon, which are fugitive in a vertical profile by downward leaching and to a lesser extent in a horizontal section of soil by lateral diffusion.

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The distribution of a residual herbicide like diuron in the system soil-air-water at normal temperature is difficult to follow in commercial conditions. Laboratory studies are facilitated by ultra-violet spectroscopy (2470 Å) of the aqueous phase. For light sandy soils and medium loams of low organic content the distribution of diuron between the solution and the soil phase follows approximately logarithmic adsorption isotherms of the Freundlich kind, and as the organic content of the soil increases so also does its capacity for adsorption. Five grams of coarse washed sand separated from the other constituents of a medium loam adsorb 6% of the diuron from 20 ml of an aqueous saturated solution, 5 grams of clay adsorb 22%, but 5 grams of any soil containing 5% of organic matter adsorb up to 80% of the diuron, whilst some fen peat soils adsorb virtually the whole.

In these adsorptive processes equilibria are closely approached in 15 minutes; in desorption to a fresh aqueous phase equilibria are much more slowly attained. Although impatience in the laboratory restricts the study of desorption processes, nevertheless it is known that diuron is much more quickly desorbed from light mineral soils than from more organic loams.

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At any instant the quantity of residual herbicide which is in solution and available to plants is only a small fraction of that which has been applied to the soil. Whilst plant roots absorb herbicide from the aqueous phase of the soil, whilst the herbicide in solution is partly decomposed by bacterial activity, whilst it partly evaporates, or is slowly leached to become adsorbed again on lower depths of the soil, more of the herbicide is gradually released from the uppermost layers of the soil into the adjacent aqueous phase to provide continuity of herbicidal action, until the adsorbed reserves of herbicide are finally depleted.

This introduces the properties and mode of action of modern residual herbicides which, after application to soil, can prevent the growth of numerous annual weed species. It follows from this theory, and it is confirmed in practice, that their effectiveness against annual weeds depends both upon the adsorption and desorption characteristics of the particular kind of soil. Almost always, to attain equality of herbicidal action the dosage rate upon an organic loam soil must be greater than upon a sandy soil.

The more modern residual herbicides serve a dual purpose; not only do they prevent the germination of indigenous seeds of unwanted plants, but they also have a contact action upon the leaves of emerged weed species. For example, the recently introduced Velsicol Tunic combines the classical residual function against germinating annual weeds; besides, it can destroy perennial weeds, such as Convolvulus arvensis, if directionally sprayed upon their freshly emerged foliage as, for example, in orchards or on vineyards. This dual function may be expected to increase the economic value of residual herbicides which are currently under development.

Insecticides and Miticides

Insecticides include a diverse range of chemical compounds which may be formulated for use as toxicants against the true insect species and against other groups of arthropods such as the red spider mites. Thus, insecticides are generally understood to include miticides or acaricides; similarly, formicides and nematocides are included within the range of modern insecticides.

This whole range may be conveniently classified according to the manner in which toxicant works.

Some insecticides, eg nicotine, are substances whose vapour pressure at the ordinary temperature is small, although methyl bromide is a gaseous substance. Insecticides of this class are absorbed as the insect breathes; consequently, they are fumigants. Their volatility renders them most generally useful in confined spaces. However, many volatile insecticides of this class can be applied in the field beneath the soil surface; then they become physically adsorbed by crumbs of the soil in which they are retained long enough and from which their vapour pressure suffices to be toxic against insect pests. Chlordane, when adsorbed upon soil, exerts a minute vapour pressure which is

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nevertheless an intoxicant for many insect species.

Other insecticides of much lower vapour pressure are toxic only when digested. These may be applied to the soil if it is desired to protect the roots of plants or otherwise to foliage. In this class many of the most successful insecticides are systemic, so that even when applied to the soil they are quickly translocated to all parts of the plant upon which insects may feed.

However, economically the most important class comprises those chemical substances that are toxic to insects by mere contact with their external parts. Skill devoted to the formulation of these insecticides is then of great importance in ensuring that the toxicant can pass easily through the integument of the insect.

To be effective, insecticides must be located either in the soil or in or upon the plant tissue so that unwanted insect species cannot avoid contact with the toxicant. This is tantamount to saying that the toxicant must have a useful period of chemical stability after it has been applied to the soil or upon the foliage. Another equally important requirement is that when applied at a dosage which is insecticidally effective, the formulation of the toxicant must not itself be phytotoxic to the crop.

It is in these several essential respects that desirable variation and gradation of physical, chemical, and toxicological properties are to be found amongst the members of three important

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chemical classes, viz.,

organochlorine
organophosphorus
carbamate

compounds. There is practically no limit to the number of members that can be synthesised in each chemical class. From amongst those products that are now already commercial, it is usually easy to find an insecticide that possesses just the right degree of toxicity towards economically important insect species, together with freedom from phytotoxicity, and a limited period of chemical stability which enables edible crops to be harvested without risk of finding them contaminated by residues that would introduce hazard to the consumer or possibility of seizure in international commerce.

Use of insecticides for soil disinfection demands special properties of chemical stability. Often in agriculture it is practicable to introduce insecticides into the soil only in two ways, viz. by incorporating granular or wettable powder formulations prior to drilling the seed or alternatively by dressing the seed with insecticide. In either case the insecticide must protect first the seed, later the roots; and, the required period of protection lasts at least several weeks or even several months. In these circumstances, as for example in the protection of young sugar beet, it is important to select a toxicant which will resist early degradation in, or substantial loss by volatility from, the soil. For use in circumstances of this kind it would seem not yet possible to find insecticides superior to the well-established organochlorines, particularly aldrin, chlordane, dieldrin, heptachlor. At comparatively low cost, these insecticides provide long term

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insurance against damage by soil insects. Besides, the most sensitive analytical methods have facilitated studies of organochlorine residues in crops and in soils. These studies are far more thorough, indeed more reassuring, than have been undertaken on behalf of insecticides of any other chemical class.

As a corollary to the preceding remarks on stability it follows that the chemical class of organochlorine insecticides is by far the best suited for incorporation into compound fertilisers. The point of entry of such insecticides into the manufacturing process is important and will be mentioned in the later section on formulation.

Whereas chemical formicides are seldom necessary even in heavily infested areas, there is a great economic need for a cheap chemical nematocide especially for use in cereals, potatoes, sugar beet, vineyards, and horticulture, where virus diseases may be transmitted by nematodes. Agriculture may eventually solve this problem in its own way by introducing favourable genetic changes into host plants. Meanwhile, most of the chemicals available for use as nematocides are fundamentally soil sterilants and their use is exceedingly unpleasant and expensive. The cheapest of these chemicals, a dichloropropane/dichloropropene mixture, presently costs per hectare about ten times as much as chemical weed control with residual herbicides.

Fungicides

Modern chemical fungicides are applied for two purposes. First, by direct application to exposed surfaces of plants fungicides can act directly upon exposed mycelia. In this way, for example, tetrachloroisophthalonitrile may be applied to .../12 kill the powdery mildews. Secondly, fungicides may be applied systemically in order to prevent, or at least to protect against, the possibility of infection in new growth some time later when spores arrive. For example, certain compounds drawn from the chemical classes of benzimidazoles and pyrimidines afford systemic fungicidal protection to fruit and to cereal crops. Any fungicide of the first class, which acts only upon the plant surface where it happens to have been deposited, suffers from the disadvantage that it provides no protection to later new growth, and so the application must be repreated by a series of sprays according to the extent of new growth; whereas a systemic fungicide introduces the possibility that a single spraying may afford a life time's protection against certain specific fungi.

It is a serious disadvantage of several recently introduced systemic fungicides that they are inactive against some common diseases including, for example, those attributable to Phycomycetes; such systemic fungicides are consequently inactive against the economically important potato blight. The directions for future applied research can, therefore, be clearly foroseen.

Rodenticides

Toxicants presently used as rodenticides in agriculture include zinc phosphide and aluminium phosphide. Of these zinc phosphide is the more important; it is an acute poison (LD^{50} to rat 47 mg/kg), it is cheap, and after application in the field

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it gradually decomposes into the simple hydrates and carbonates of zinc which leave no problem and excite no question concerning residues in soil or crops.

Since the introduction of Warfarin, many other anticoagulant rodenticides have been discovered. Some of the most successful are compounds which are chemically related to the hydroxycoumarins or which are diphenyl acetyl derivatives of 1,3-indandione such as diphacinone or its chlorine substitution products. Such new compounds are being developed particularly for control of rodents in forests. Probably they will eventually be useful in protecting cereal crops against the depredations of mice and rats, but their introduction to edible crops will require patient toxicological, metabolism, and residue studies.

Formulation

Products of the chemical industry for use in agriculture are not usually available in such high purity as is necessary, for example, in pharmacy. It is a fact that some simple chemicals such as MCPA acid are often produced with purity exceeding 97 per cent; but many others, such as the slightly soluble substituted ureas, carbamates, or complicated organo-phosphorus compounds are more difficult to synthesise, and their purities as commercial products often lie within the range 80 - 90 per cent. The manufacturer must assay each batch.

Almost always it is necessary for chemical industry or for an appointed formulator to convert these products of limited purity into standardised products which are finished ready for use in agriculture. Whilst standardising the content of active ingredient, the formulator must ensure that the finished product

(a) is convenient and safe as possible for use by field workers,

(b) will be stable in storage,

(c) bears no risk of phytotoxicity to the crop upon which it is to be recommended for use,

(d) facilitates application of the active ingredient to the soil or to the plant so as to provide maximum protection against pests at the lowest cost.

To attain these ends the formulator usually converts the substance into one of the following kinds of formulations -

aqueous solution
emulsifiable concentrate
wettable powder
granule
dust
solution in organic solvent

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in which the content of active ingredient is precisely adjusted to some standard round number.

Formulation is partly an art and partly a science, and in order to be successful the formulator must bring to his task a great deal of experience which will include the following .

Aqueous solutions

It is usually a simple chemical or physical process to manufacture and standardise an aqueous solution, although experience calls for a number of precautions that are not always obvious from the start. When it is desired to formulate a phenoxyaliphatic or substituted benzoic acid as an alkali metal salt, since the process of dissolution is exothermic and will yield a highly concentrated solution, it is important to find a reliable means of checking the pH of the finished solution so that long term risk of partial precipitation of the active acid can be avoided. Thus, it is most important to check the pH of a cool aqueous dilution of the finished product.

The potassium salts are frequently more soluble than the sodium salts, whilst the alkylamine or alkylolamine salts are usually still more soluble in water. For economy in packaging and transport the solution must be highly concentrated, although the limiting concentration will be governed by the need to avoid crystallisation during long storage at low temperatures prevailing during winter. Low temperature solubilities of lithium salts are sometimes so much greater as to justify dissolution of certain

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herbicides, e.g. DNBP, in lithium hydroxide.

The biological activity of certain phenoxyaliphatic acids is dependent upon the cation used to form the salt, and in particular the dimethylamine salt of 2,4-D is a more effective herbicide than the less soluble sodium salt.

For the formulation of aqueous solutions flow sheets of plant show as the central feature a stainless steel or glass-lined steel vessel, cylindrical but with hemispherical bottom and bottom run-off valve, capacity typically 500 gallons, closed except for man-hole opening in lid, with 2 - speed stirring gear and anchor-shaped agitator. This vessel should be jacketed with circulating cooling or heating fluids, and should have metered connections to soft water and alkali metal hydroxide or amine solutions. Solids are charged through man-hole opening. The run-off valve leads to a pump in series with a small filter charged with diatomaceous earth or other filter-aid. The outlet from the filter leads via a by-pass back to the cylindrical vessel and via an alternative line to a large stainless steel or ceramic storage tank. From the storage tank lines lead to automatic drum-filling meters.

Emulsifiable concentrates

Many substances which cannot be formulated as aqueous solutions because of their insolubility are instead readily soluble in cheap aliphatic or heavy aromatic oils. If solubility in these solvents approaches or exceeds 300 grams per litre it is frequently technically possible and economic to formulate

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emulsifiable concentrates. Toxicants which are not soluble to this extent in hydrocarbons may instead be more soluble in mixtures of xylene with cyclohexanone, isophorone, or dimethylsulphoxide, although the latter are expensive in comparison with hydrocarbons. Then, by incorporating several per cent of a carefully selected and matched emulsifier pair, it is frequently possible to produce a formulation of the toxicant that will spontaneously emulsify when poured into water, even very hard water.

In order to formulate the most successful emulsifiable concentrates it is helpful to study according to the phase rule the behaviour of the system pesticide/solvent/atmosphere after tentative formulations have been applied to plant surfaces. At the same time the biologist will study the effects of these tentative formulations on plant life, insects, and fungi.

As solvent evaporates many toxicants crystallise. If the toxicant is intended as a fungicide or insecticide it may be desirable that the dimensions of the crystals be minute and that the maximum possible area of the plant should be protected by their coverage. If the toxicant is to protect the plant systemically, it might be preferable to select a solvent system that can carry it through the leaf surface. The formulator will strive to present the toxicant in such a way that the pest has no opportunity to escape contact with it. On the other hand, when the emulsifiable concentrate is to be used as a herbicide,

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the solvent/emulsifier system can sometimes be chosen so as to improve the selectivity of herbicidal activity as between crop and weed species by promoting penetration into the leaves of weed species and hindering penetration of the desirable crop foliage.

It is apparent that the activity of herbicides, insecticides, fungicides can be modified significantly by the physical properties of an emulsifiable formulation. Experience suggests that, once a formulation has been devised which has a satisfactory performance against a specific pest, it is better to permit no departure from its physical and chemical specification until the possible consequences have been examined biologically in the field.

Plant for the manufacture of emulsifiable concentrates is not fundamentally different from that described for aqueous solutions except that stores are required for a variety of organic solvents and emulsifier pairs. Flame-proof electrical equipment and various other precautions against fire and explosion are necessary, and various other regulations must be enforced to ensure health and safety of operators who work with solvents of low flash point or appreciable toxicity.

Wettable powders

A chemical substance which may not be sufficiently soluble or satisfactorily stable in available cheap solvents may often be formulated instead as a wettable powder. Then the object

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is to pulverise the substance very finely, to modify its surface properties, and to standardise the formulation so that:

(a) it can be conveniently dispersed in water in the farmer's spraying tank and will remain well suspended to facilitate spraying with almost the same mechanical ease as if it were instead a solution or an emulsion,

(b) after it has been sprayed the particles are so minute and well dispersed that if applied to the soil they dissolve quickly in the soil moisture and become uniformly adsorbed on the soil, or alternatively may provide the greatest possible coverage upon foliage to protect plants adequately against insects or fungal infections or to destroy unwanted weeds,

(c) its content of active ingredient is precisely adjusted to some convenient round number such as 50, 75, or 80 per cent.

As a general rule the first step is to mix intimately by ribbon-blender a crystalline toxicant with the carrier of wettable clay, together with surfactant, sequestrant, and deactivator or anti-catalyst where necessary. The blend is then comminuted, for example, in a pin mill. Toxicants of low melting point may sometimes have to be blended little by little into larger weights of wettable clays, and it may be necessary deliberately and continuously to cool the mill into which, by multiple passes, the whole desired proportion of toxicant is

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gradually fed. Sometimes it is preferable first to dissolve a low-melting solid, then to spray its solution gradually onto an absorptive clay in the ribbon-blender. Cheap liquid toxicants are frequently sprayed directly upon absorptive clays, and subsequently reduced and standardised to field strength by blending with fresh portions of clay. However, in order to attain the most uniform distribution of and best performance from an expensive insecticide or fungicide it is always better to incorporate a solution of the toxicant with the whole suitable quantity of clay so that no subsequent reduction of strength is necessary. The comminution of particles of toxicant with wettable clay should result in at least 98 per cent passage through 200-mesh, and for the final stage a fluid energy mill may be the most satisfactory. Final blending and standardisation are always necessary.

As integral steps within the blending and milling processes it is generally necessary to incorporate small proportions both of a surfactant and of a sequestrant for calcium and magnesium. The surfactant, of which lignin sulphonate is one of the older examples, is to assist wetting of the powder and to improve the stability of its dispersion in water. The sequestrant, which may be a polyphosphate or a salt of ethylenediaminetetra-acetic acid, is to prevent flocculation of the powder in hard water. Recommendations for use should specify not only maximum hardness but also maximum volume of the water in which 1 lb of the wettable powder is to be suspended in order to prevent inconvenience or failure through flocculation.

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The surface properties of some clays may catalyse decomposition of certain insecticides and fungicides. This propensity can be measured in advance by laboratory tests, which consequently become useful criteria in selection and evaluation of clays. Some clays, but not all, can be treated with urea or hexamethylenetetramine which serve as anticatalysts, and it may be necessary at the pre-blending stage to incorporate these substances into formulations of wettable powders.

Dusts

Dust concentrates, standardised to contain for example 25 per cent of the active ingredient, are first manufactured in the manner described for wettable powders. However, it is usually unnecessary to incorporate either surfactant or sequestrant. It is essential that the dust concentrate be very finely divided, and many specifications require at least 95 per cent to pass 200-mesh because no further milling of this ingredient is expected to be necessary.

The dust concentrate must now be converted to a field strength dust whose content of active ingredient is usually within the range 1½ - 5 per cent, and which possesses other desirable properties such as being free-flowing and conformity within reasonable limits to a standard bulk density.

To select diluents most economically, the choice will usually lie among the attapulgites which impart free-flowing properties, kaolinites which are cheap extenders capable of

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absorbing moisture, talcs and proprietary forms of calcium carbonate whose own high densities are useful in adjusting the bulk density of the finished product within close limits. Some of these materials in the natural or purchased condition would be catalytically active in promoting decomposition of certain insecticides and fungicides, and so must be deactivated by means of urea, hexamethylenetetramine, or with a proprietary deactivator. The desired proportions of the extenders and the requisite quantity of deactivator are mixed in a ribbon-blender, then passed through the mill until at least 95 per cent is minus 200-mesh.

Finally, the prepared dust concentrate is to be diluted with the prepared extender in the pre-calculated proportions. The total quantity of dust concentrate is transferred to the ribbon-blender and with the machine in motion the extender is added gradually over a period of about half an hour. The proportions are pre-calculated so that the active ingredient of the blend at this stage should be slightly greater than specification. The blend is assayed, after which a calculated final adjustment with a little more extender should bring the batch precisely to specification.

Granules

Very toxic insecticides and herbicides formulated as solutions, wettable powders, or dusts may present a hazard to agricultural workers who apply them; besides, air currents may carry dusts and sprays away from the area of application, so

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impairing effectiveness and perhaps adulterating other crops. It is sometimes practicable to minimise such hazards by formulating the same pesticides as granules, for example, within the size range 30 - 60 mesh.

Attapulgite, vermiculite, bentonite, Fullers earth and other minerals can be manufactured as sorptive granules. Capacity for sorption, and physico-chemical coefficient of adsorption, speed of disintegration in soil, catalytic properties, and cost vary according to the identity of the mineral, its heat treatment, and the size range of the granules. These are the principal factors which must be investigated to ensure the best choice of granule for each particular pesticide application.

For impregnation the granules are tumbled in a drum-blender or ribbon-blender into which a solution of the pesticide and deactivator is sprayed through well placed nozzles. As a general rule, 100 lb. of granules would be impregnated with one to two gallons. of a pesticide solution in order to assure uniform distribution throughout the structure of each granule. After the solution has been sprayed the granules are tumbled until all has been absorbed, but not for so long as to cause attrition. Afterwards the diffusion of pesticide solution into the innermost interstices continues for a few hours, and when this period of so-called "curing" is complete the granules should be apparently dry, and should flow readily. Finally, the batch is assayed.

The sorptive capacity of granules must be selected in

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relation to the desired concentration of pesticide in the finished product. For, if the sorptive capacity is too high the pesticide would have to be dissolved in an inordinate volume of solvent to assure even impregnation; to do so would be uneconomic and would introduce the risk during a long period of storage that a significant quantity of this solvent might evaporate, so leading to uncertain content of active ingredient and hence to faulty dosage rates. This kind of risk can be minimised also by choosing solvents of low vapour pressure; in this respect, whenever other considerations are favourable, mineral oils and high aromatic naphtha are admirable solvents.

When granular formulations of insecticides are intended for direct application to the soil it is advantageous to select granules that disintegrate quickly, allowing the insecticide to diffuse into the surrounding soil. But if a granular insecticide is to be broadcast from the air, for example into the whorl of maize to protect against Ostrinia nubilalis, there is an advantage in granules that disintegrate slowly and release the insecticide into the whorl during an extended period.

Certain insecticides of the organochlorine class, such as aldrin and heptachlor, can be introduced into granular compound fertilisers. At stages of manufacture prior to curing the temperature of fertiliser granules might be so high that the insecticide would decompose or volatilise; or the solvent for the insecticide might enter into a temperature exceeding its flash

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point; or the insecticide would become mixed with a crude form of granules from which fines and oversize granules still have to be separated. Of necessity the point of entry of the insecticide into the manufacturing process must be (a) after curing, (b) at a temperature below the flash point of any hydrocarbon solvent, (c) into a stream of fertiliser granules of the desired finished size range.

Having regard to these practical limiting conditions, procedures based upon two separate principles may then be selected. The principles are as follows:

(i) The insecticide solution may be sprayed upon the compound fertiliser granules in a batch process or in a continuous process. The batch process is the simpler to regulate with precision, but the continuous process is practicable and cheaper for a high output.

(ii) The insecticide may be introduced amongst the compound fertiliser granules in the form of 20% active granules of 30 - 60 mesh. Some variation in this mesh size may be desirable, because it is important to minimise the possibility of segregation or stratification of the insecticide granules within the bulk of the fertiliser granules.

Principle (i) comes nearer the ideal because by its means the

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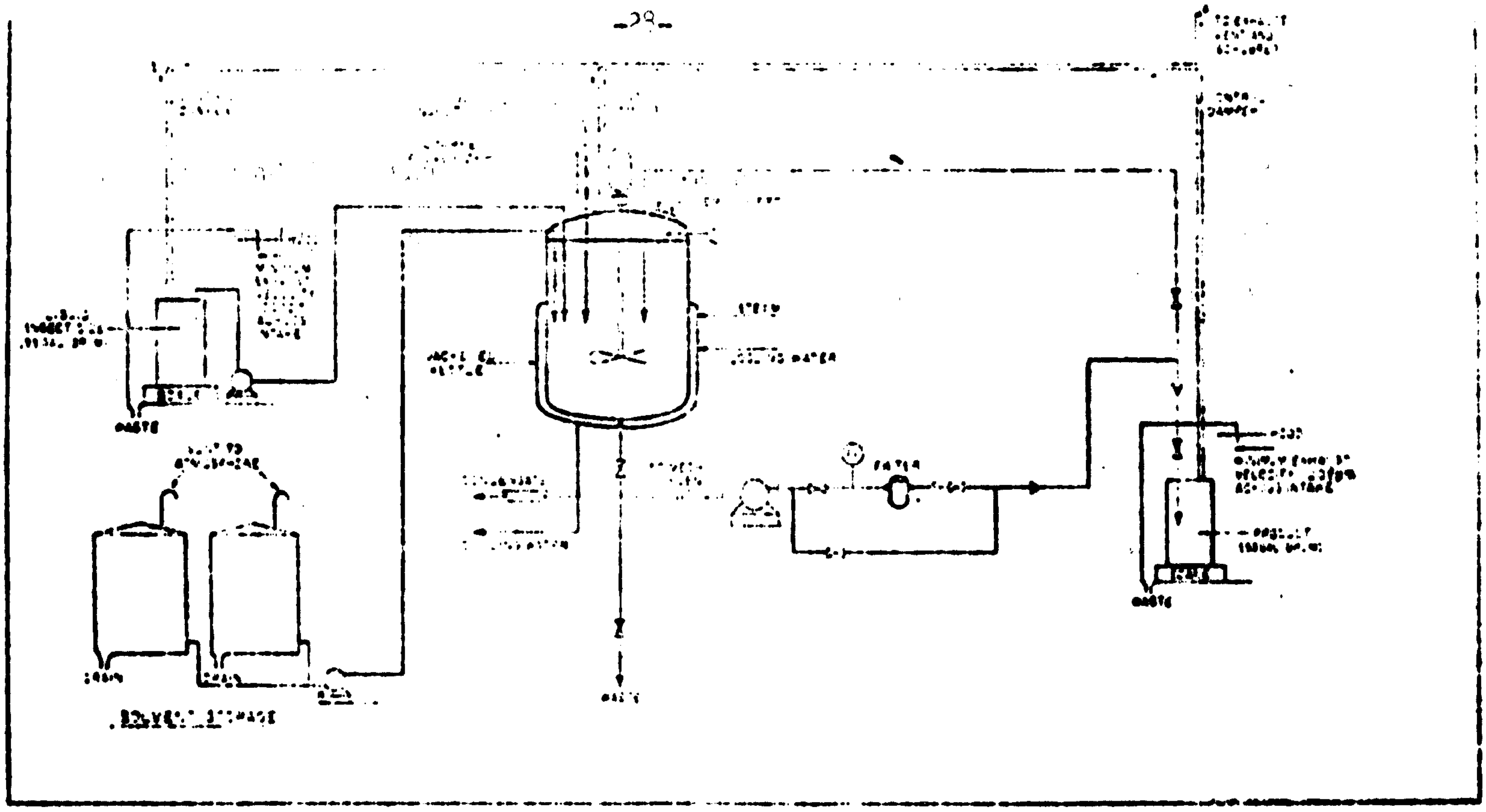
risk of segregation can be entirely avoided, and it is also the cheaper method of manufacture. Principle (ii) is the easier course for small scale or occasional production. Which of these principles is to be chosen also depends upon the manufacturing plant available, the expertise with which it can be operated, also upon the period which is expected to elapse between manufacture and use by the farmer.

Solutions in organic liquids

The technique of spraying liquids from spinning discs, without the need for dilution or emulsification by water, challenges in a new way the science and art of formulation. The ability to produce droplets within a very narrow dimensional range of volume mean diameter around 80 microns, enables liquid insecticides to be applied with unprecedented economy to plants and with least contamination of the soil and environment. This technique, sometimes known as ultra low volume spraying, is readily adaptable to the spraying of those organophosphorus insecticides which are themselves liquid at atmospheric temperature; but in order to make the technique more generally applicable, solvents of very low vapour pressure must be found for insecticides that are solids. Mineral oils, high aromatic naptha, and other distinctive liquids of improved solvent power and low vapour pressure are being studied. In certain other respects problems of formulation are simplified; for example, it is unnecessary to devise emulsification systems. Furthermore, insecticides can be packaged by the manufacturer for direct connection to a rotating disc sprayer, so that all hazards of mixing with water (that final step of formulation which is generally left to the farmer) can be eliminated.

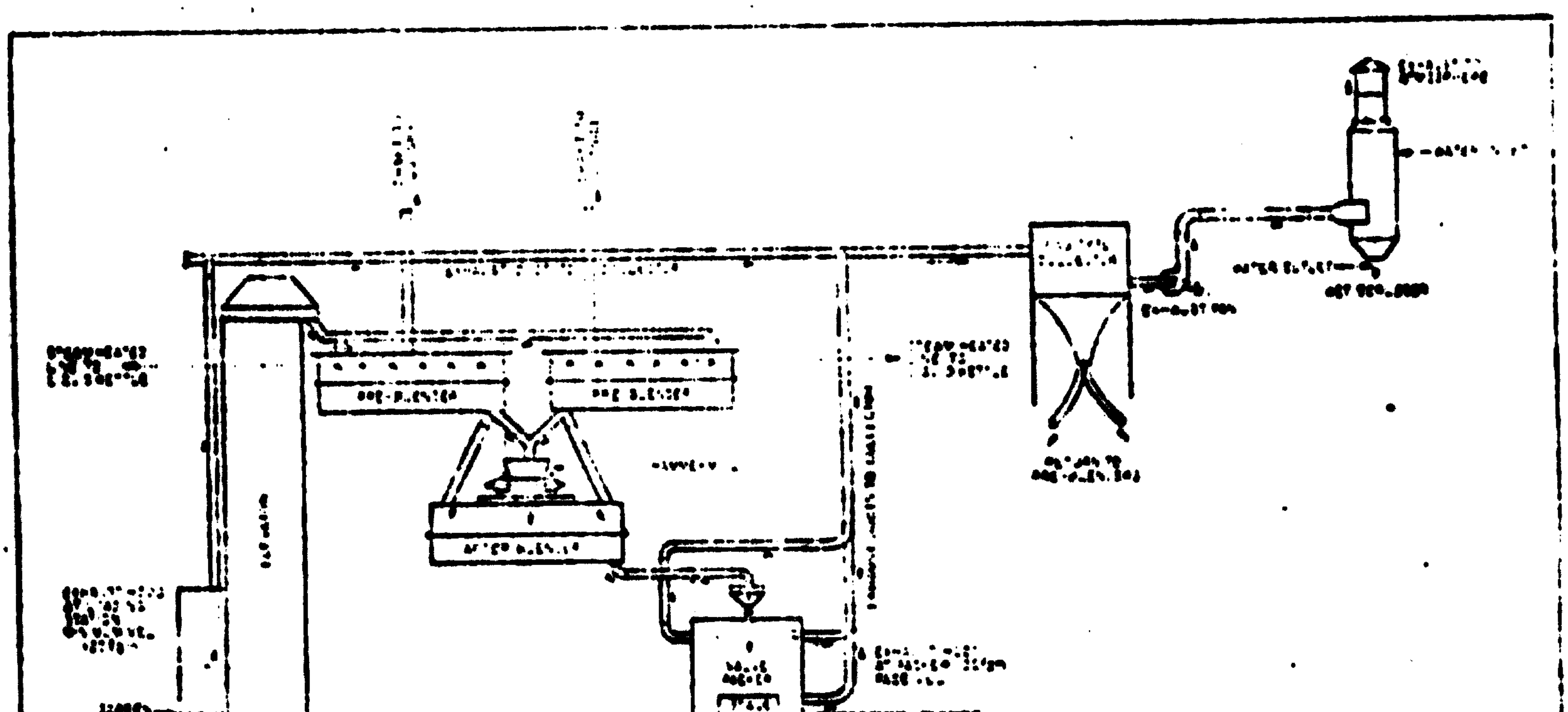
Flow sheets

Flow sheets for liquid and solid formulation plants are attached.



Liquid formulation plant

VELSICOL CHEMICAL CORPORATION • 341 EAST OHIO STREET • CHICAGO, ILLINOIS 60611



Solid formulation plant

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FORMULATION OF PESTICIDES

Investment Captial
a) Units for Solids
b) Units for Liquids
c) Combination units

The following tables list the estimated costs of the major pieces of equipment necessary to set up a formulating plant capable of producing quality liquids, granulars, dusts and wettable powders. The price estimates are US prices and must of necessity be rough approximations. We have not included in these estimates the cost of land, buildings, analytical equipment, safety and pollution control devices, etc.

The estimates of the capacities are also rough, depending upon what products are being formulated and how efficiently the personnel are able to operate.

The production of quality pesticide formulations involves considerable expertise and in the setting up of any formulating facility, experienced people will have to be brought in to assure the equipment is properly installed and to train the local personnel in how to operate the equipment.

GRANULAR, DUST & WETTABLE POWDER CENTER

	Minimal	Typical
Ribbon Blender	$ 2,500	$ 2,500
Bag Weighing Scale	300	300
Bag Loader		1,000
Mikro Pulverizer w/ Dust Collector	2,500	2,500
After Blender		2,500
Small Elevator		2,000
Miscellaneous Equipment	700	1,200
Total Cost	6,000	12,000
Daily Capacity (2 shifts)	4,000 lbs*	8,000 lbs

* applies to wettable powders, for dust formulations, figures can be increase to 16,000 lbs, granular formulations, 10,000 lbs

FORMULATION OF PESTICIDES (2)

LIQUID CENTER

	Minimal	Typical
Melt Kettle 250 gallons	$	$ 5,000
Mix Kettle 500 gallons	4,500	4,500
Hold Tank 500 gallons		4,000
Filter with pump	300	300
Pump		400
Overhead Scale	500	500
Hand Hoist	200	200
Pipe & Fittings Stainless	250	600
Wooden Platform	250	500
Total Cost	6,000	16,000
Daily Capacity (2 shifts)	12,000 lbs	34,000 lbs

MIA:

TOTAL MARKET
PESTICIDES
HISTORY & PROJECTIONS: 1965 - 1974

(M - US Funds)

<u>Market Segments</u>	Actual							%
	<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>1969</u>	Est. <u>1970</u>	Proj. <u>1974</u>	Compound Annual Change <u>1970-1974</u>
Mexico	18.7	19.4	20.0	21.5	22.6	24.0	30.0	5.7%
Argentina	12.1	13.4	13.9	14.5	15.0	15.1	17.8	4.2%
Brazil	11.4	13.8	16.8	17.0	24.0	25.0	30.0	4.7%
Colombia	15.0	15.6	16.4	17.2	18.0	18.8	22.3	4.4%
Central America	27.0	28.8	29.8	31.5	32.0	34.4	45.7	7.3%
Total Market:	84.2	91.0	96.9	101.7	111.6	117.3	145.8	5.6%

[illegible]

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