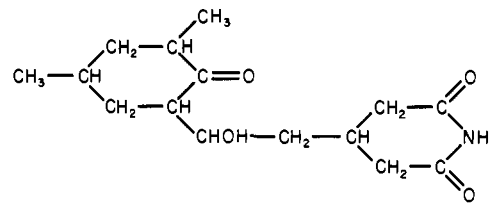

CYCLOHEXIMIDE [ACTIDIONE]

the trunks of peach trees retards the defoliation due to the bacterial spot organism throughout the season. Since in these experiments bacterial infections were reduced but not eliminated it is very probable that changes were induced in the host plant.

There is a time element involved in the absorption of antibiotic materials by plant tissues. Rain within a few hours after application adversely affects the absorption of antibiotic materials but after 24 hours rain has little effect.

Workers at the Missouri Experiment Station are carrying on a series of experiments with growth-regulation substances added to the antibiotic materials as well as experiments with cuticle solvents to increase the absorption of the antibiotic materials.

In the vast majority of instances, applications of the antibiotic materials to the soil have been disappointing. Apparently the antibiotic materials are destroyed before they can be absorbed by the roots and trans-located.

Economics

We have enumerated some of the uses of antibiotics for the control of plant diseases. However, the demonstration of the efficacy of antibiotic materials for plant disease control becomes a purely academic procedure unless the price of the materials is such that they can be used in commercial practice and still allow a normal margin of profit to the grower.

For fruit disease control we believe a cost of $50 per acre per season is close to maximum figure allowable unless it is known that damage resulting from present treatments produces excessive losses. If a given antibiotic can be purchased by the grower at 20 cents per gram activity, for example, the 30-3 p.p.m. mixture used in the California experiment mentioned earlier, would cost approximately $68 per acre per season for the treatment applied 5 times at the rate of 600 gallons per acre, per application. In some California pear orchards the loss per acre from copper injury is higher than this figure in most seasons, and in these orchards the use of antibiotic materials for the control of pear blight would be commercially feasible. The results obtained with 5 applications at 30-3 p.p.m. versus 3 at 100-10 p.p.m. are particularly interesting. The same degree of blight control was achieved with materials that would cost (still assuming a price of 20 cents per gram activity) $68 per acre per season as was obtained with a treatment that would cost $138 per acre per season. Labor charges for the two additional sprays would have to be added to the cost of the 30-3 p.p.m. treatment.

In the East where the blossom period is normally shorter than in California, it is anticipated only 3 applications will be necessary per season to control blight on apples. Recently reported experimental work in Ohio has involved the use of 50 p.p.m. treatments. At this concentration, materials for three applications at the rate of 400 gallons per acre, would cost approximately $45 per acre per season.

The theoretical price of 20 cents per gram activity has been used to illustrate how we are approaching the feasibility of general commercial use in the fruit disease control field. The problems of vegetable pathology are out of my field and I will make no attempt to discuss costs.

The control of pear blight with antibiotics in California orchards, however, poses the question of blight control on high-quality pears in the East. The feasibility of this under humid eastern conditions has not yet been demonstrated, but this year an experimental planting of 100 Bartlett pear trees was made at Beltsville. These trees will be protected solely with antibiotic materials during the blight season. Either we control blight and the orchard flourishes or we fail and know that antibiotics are not the answer to the blight problem on high-quality pears in the East. Only time will tell.

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FORMULATION

OF DRY CONCENTRATES AND DILUTE DUSTS

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Pesticide formulation is a dynamic art, relying mainly on the Edisonian method. Every formulation requires solution of its particular problems

THE PURPOSE OF FORMULATION is to provide a prescription designed to treat crop infestations under field conditions with available equipment. It is essential that the formulator have a good working knowledge of the capabilities and limitations of application machinery, the effect of weather conditions, the limitations of commercial mixing equipment, grinding equipment, packaging machinery, and other pertinent factors before attempting original work.

By the term "dry concentrate" is meant a dry, relatively free-flowing powder which contains the maximum possible amount of active ingredient. It may contain a wetting agent so that it is ready to be dispersed in water for spray application (in which case it is termed a "dry wettable"), or it may have no wetting agent and be suitable for further dilution to form a dust (in which case it is called a "dust base").

The term "dilute dust" may indicate the dry concentrate diluted with an extender such as talc or clay, in which case the finished dust tends to have the physical properties of the diluent. In the usual case, however, the so-called dilute dust will consist of several dry concentrates and/or dry chemical powders mixed in desired proportions and concentrations to provide several pesticidal treatments in one application.

Perhaps it would be better to use the term "dust" for such products.

Dry Concentrates

Most of the problems with dry concentrates, whether dust bases or dry wettables, derive from the economic pressure forcing use of the highest possible concentration of active ingredient. Thus, in the case of a DDT concentrate, wherein the technical DDT, having paraffin-like properties, must be formulated into a finely pulverized dust concentrate or suspensible dry wettable, it is relatively easy to prepare 50% concentrations of active ingredient by mixing the powdered DDT with a suitable carrier such as fuller's earth and pulverizing the mixture to meet fineness specifications.

However, there has been much pressure to produce 75% and even 90% concentrates, and, while this has been found technically feasible, the cost of the final formulation has been excessive in terms of units of active ingredient. Nevertheless, there are some special uses in which this higher cost is relatively unimportant. The same principle is an important factor in the formulation of many other pesticides such as DDD, BHC, toxaphene, chlordan, aldrin, dieldrin, the dithiocarbamates, the inorganics such as copper, the arsenicals, and even sulfur.

There appears to be a strong tendency for many technical workers as well as most ultimate users to rate these competing formulations on the basis of active ingredient content, a sound principle when buying industrial chemicals. However, formulations are not mere dilutions but are carefully designed prescriptions intended to give maximum effectiveness under field conditions.

In considering a dry concentrate of toxaphene in fuller's earth as an example, it will be evident that at relatively low concentrations the well-milled formulation will have substantially the same physical properties as fullers earth alone whereas if we have an excessively high concentration of toxaphene, the formulation would tend to take on the properties of toxaphene. The intermediate zone, in which there is a maximum percentage of toxaphene which can be incorporated into a flowable powder, is not a sharply defined critical point but may be varied up and down at the discretion of the formulator and by reason of the variability of the two ingredients. The usual commercial formulation, therefore, is arrived at by compromise between the various factors such as method of mixing, grindability, shelf-life characteristics, and, most important of all, demands of the trade.

The selection of surface active agents for dry-wettable concentrates is a matter of trial and error to get satisfactory wettability, suspensibility, and compatibility at the lowest possible cost. It is amazing that of several closely related surface active agents one may give excellent results while others are entirely unsatisfactory.

Table I illustrates some of the properties of diluents that govern their use in dry concentrates and dilute dusts.

Dilute Dusts

Talcs and kaolins, because they have good dusting properties themselves, are widely used as diluents for dusts to provide the volume-per-acre needed to facilitate the metering of the dust through the duster mechanism. If the formulation is prepared by diluting one or two dry concentrate bases with a major portion of diluent, the finished formulation will, of course, have approximately the same properties as the talc or kaolin diluent. However, the great majority of formulations are composed of many active ingredients and it, therefore, becomes necessary that the dry concentrates themselves have the right properties to make a good dustable formulation with relatively little or no diluent.

The formulator should have all available knowledge of the mode of action of the active ingredient in controlling a pest. He will then strive to incorporate ingredients that will assist the poison in reaching its objective. Thus, a contact poison must actually touch the insect

Figure 1. Fractional Sedimentation Scheme for Particle Evaluation

For particle-size determinations on sulfur, 200 g. of cane sugar and 10 g. of Santomerse are made into a solution of 1 liter with distilled water. Ten g. of the sulfur sample are stirred into 500 cc. of this solution in an 800-cc. beaker (No. 1 in the scheme shown above), allowed to settle for 4 min. and decanted into the No. 2 beaker, where it settles for 16 min. Then, it is decanted into No. 3, allowed to settle for 64 min., and decanted into the 2-liter beaker, No. 10. Residues in beakers No. 1, 2, and 3, are then made up to 800-cc. volumes and progress through another settling and decanting as shown by paths 1a, 2a, and 3a. The 4-min., 16-min., and 64-min. residues are then combined. The 4-min. residue is made up to volume again and run through the scheme once more. Each residue is then filtered through a tared Gooch crucible, washed free from sugar, dried, and weighed. A sample of each is examined under a microscope for particle-size range. The last fraction is obtained by difference and assumed to be all smaller than the lower limit of the next higher fraction. Refinements can be made on the system, limited only by apparatus available and patience of the operator

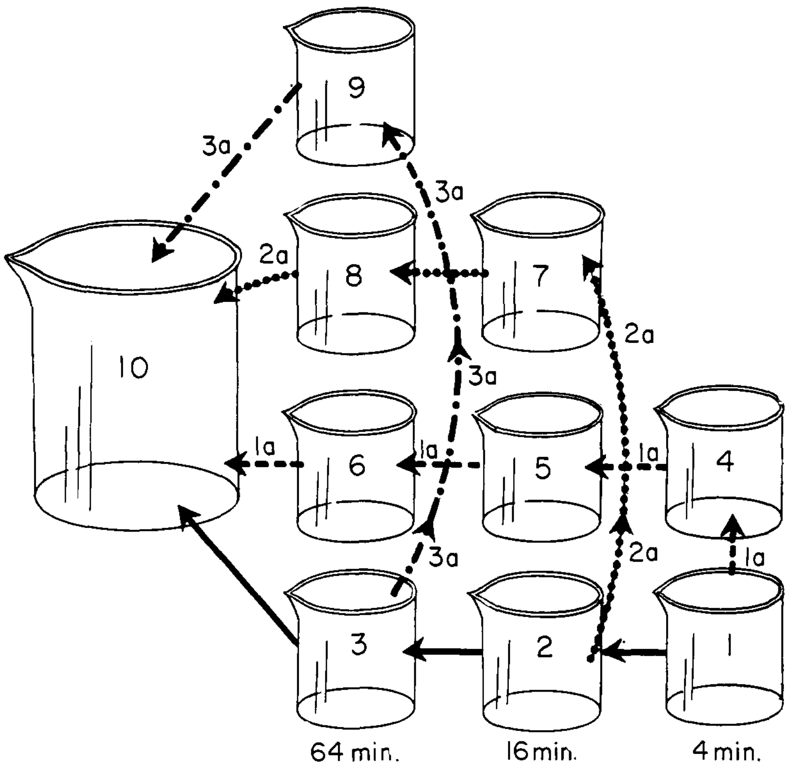

Table I. Some Properties of Common Diluents

Diluent	Oil Adsorption, %[a]	Usual Screen Analysis (Mesh)	Bulk Density Lb./Cu. Ft.	Dusting Properties	pH	Grindability	Common Uses
Fuller's earth	20–35	200–325	20–38	Flowable	7	Excellent (aids grinding)	Dry concentrates
Granular fuller's earth	15–25	15–60	50	Free flowing	7	Not ground	Granular dusts
Diatomaceous earth	20–40	325	8–15	Balling	7	Good	Dry concentrate. Bulking and conditioning agent for dusts
Expanded mica	10–20	10–60	8–15	Free flowing	7	Not ground	Granular dusts
Silica gel	40–70	325	5–15	Balling	7	Excellent	Dry concentrates conditioning agent
Organic carriers (ground fiber)	5–15	200–325	15–40	Balling	7	Poor due to tough cellulose fibers	Dust extenders, dry wettables, dust bases, conditioning agents
Calcium sulfate	5	200–325	30–50	Flowable		Good if active ingredient is solid	Dust conditioner
Talc	1–5	200–325	25–51	Sometimes flowable depending on source and particle size	8–9	Formulas usually just mixed	Dust extenders for dry-wettable formulas—conditioning agent
Kaolin	5–15	325	20–40	Balling	5–6	Good if active is a high melting point solid	Dry-wettable suspensible type, dust extender or carrier
Calcium carbonate	5	200–325	25–50	Flowable, depends on source and size	7–9	Formulas usually just mixed	Dust extenders, conditioners

[a] The percentage by weight of SAR-10 oil that can be adsorbed, without losing free-flowing, dustable properties

during or after application while a particle of fumigant, such as lindane, may be effective at a distance. Small particle size and lipoid-solubility appear to assist contact poisons whereas fumigants may be soon vaporized if the particle size is too small.

In general, the immediate toxicity is inversely proportional to particle size and, therefore, from a toxicity standpoint, it is desirable to have very small particle size. Major disadvantages of excessively fine particle size in dusts are high wind losses (smokes may travel for miles and leave no deposit), more or less rapid volatilization (depending on vapor pressure), and prohibitive cost of extremely fine grinding. These and many other factors are fairly well compromised by setting a particle-size specification for milled products in the general range of 10 to 30 microns for present-day ground dusters. Airplane dusters need larger particles and heavier dusts—say 20 to 40 microns. Precipitated products such as dithiocarbamates and insoluble coppers, commonly have ultimate particle sizes ranging between 1 and 5 microns but these products are usually agglomerated at the time of application and the agglomerates tend to be in the range of 10 to 30 microns. The dustability of the various ingredients should be reasonably uniform to prevent segregation in the dust cloud.

Since particle size is an important factor, it is essential to have a satisfactory method of measuring particle size. Many devices have been contrived, some of them very expensive and many of them depending on indirect evidence. We use a simple sedimentation technique involving only standard laboratory equipment (see Figure 1). The method gives direct incontrovertible data and may appeal especially to laboratories of limited means.

Another factor, electrostatic charge, probably has an affect on still other factors such as bulk density, flowability, dustability, and sticking properties. Unconditioned sulfur readily develops a strong electrostatic charge from friction in the grinding mill. It also sets to a hard cake in the bag after normal storage for a few weeks. A satisfactorily pulverized and conditioned sulfur has good bulk density, flowability, and dustability but might stick better if the conditioner were absent. It is probably a function of the conditioner to develop an opposite electrostatic charge during processing and this helps in all respects except attaching the particles to the foliage. Again there must be a compromise between a number of requirements to get the best possible result.

Some dilute dusts such as TEPP dusts are formulated directly to a concentration of 1 to 3% by spraying the toxicant into the diluent (in this case, anhydrous calcium sulfate) while agitated in a Day mixer or equivalent device. This is a standard technique for preparing both dry concentrates and dilute dusts with many liquid or liquifiable toxicants such as parathion, chlordan, and toxaphene.

An interesting recent development is the use of granulated powders having particle sizes in the range of 20 to 80 mesh for use in fertilizer mixtures to control subterranean insects and for airplane dusting of rice fields, marshes, and jungles in mosquito control. These are prepared by impregnating selectively screened fractions of fuller's earth and bentonite with the desired active ingredient.

After a new formulation has been prepared, it should be tested in a field applicator similar to those generally used in the area where the formulation is to be sold. It should also be tested in the commercial-size mixing and grinding equipment and packaged for long term storage tests to test stability and retention of desirable physical qualities. A portion of this commercial-size batch should be adequately field tested to determine its actual efficacy against the infestation it was designed to control. In the case of new active ingredients it is necessary to make a great many combination formulas with other active ingredients or dry concentrates which will be formulated with it. Each of these must be tested for compatibility and shelf life as in the case of all other formulations.

Obviously, therefore, pesticide formulation is a dynamic art, relying mainly on the Edisonian method. The development of every pesticide formulation poses certain particular problems which must be solved before the product can be expected to attain the final objective—customer satisfaction. Solving them requires a thoroughly coordinated effort on the part of every member of the research team.

Presented as part of a Symposium on Formulation of Pesticides before the Division of Agricultural and Food Chemistry at the 125th National Meeting of the American Chemical Society, *Kansas City, Mo., March 25, 1954.*