FORMULATIONS as Related to FIELD PERFORMANCE

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Improper formulation can make a potentially useful toxicant appear worthless in field tests

THE POSSIBILITY OF DISCOVERING a useful toxicant is dependent upon putting a new chemical into such a form that it can be readily applied to the surfaces of plants and animals. Laboratory screening and evaluation are impossible until the proposed toxicant is put into suspension or solution in a medium suitable to apply different dosages on surfaces and on or in pests. In subsequent evaluation in the field, the true economic value of a new toxicant in controlling pests is heavily dependent upon how the toxicant mixture behaves when applied to the pests and protected surfaces. In turn, how the toxicant behaves on surfaces is dependent upon the diluent and surfactant materials and their concentrations with which the toxicant is formulated. The subsequent fate of the toxicant on surfaces is determined equally by the inherent chemical and physical characteristics of the toxicant the nature of the surface and the adhesiveness of the formulation.

Wettable Powders

There are many factors that are important in devising a formulation. In wettable powder formulations the chemical reactiveness of proposed diluents must be determined if previous knowledge is not available to answer the compatibility question. The dehydrohalogenation of DDT occurring in formulations (or on surfaces) containing iron is a significant example (*3*). Another example is the destruction of parathion in the presence of a strongly alkaline carrier.

The toxicity to the pest of solid diluents is a consideration in making wettable powders. Some types of kaolinitic clays under conditions of low humidities have approached the toxicity of cryolite to the Mexican bean beetle, whereas most talcs have little toxicity under any condition. Micro abrasion of the insects' integument and subsequent rapid water loss under low humidities is related to the toxicity of kaolinitic clays (*4*). The particle size but apparently not the particle shape appears to be inversely correlated with the toxicity of abrasive diluents (*1*). The abrasiveness of solid diluents influences the choice of diluents in another manner. Highly abrasive diluents may promote more rapid reduction of particle sizes of a solid toxicant during grinding but are unfortunately the cause of excessive wear of grinding machinery and field application equipment.

The ratio of solid diluents to toxicant influences the initial and washed deposit effectiveness of the formulation (*8*). In our experience formulations with higher toxicant contents are both initially more effective and last longer in killing pests. In terms of cost, the formulations with high toxicant content are advantageous because of reduced expense of grinding and shipping. However, in some cases the diluents used may cost the same amount or more per unit weight of toxicants as the diluents in the less concentrated formulations. Added costs are often more than offset by the increased effectiveness of the formulation with higher concentration of toxicant.

The "sorption" by solid diluents of a liquid toxicant is commonly employed as a means of making a conveniently handled formulation. However, a factor of greater importance, than is generally realized, is that the degree of physical "sorption" of the toxicant may be such that only partial or no "release" of the toxicant to the pest occurs. We have found four commonly used diluents that "sorb" parathion so tightly that mixtures, especially as dusts, are completely ineffective in killing a highly susceptible insect such as the pea aphid. Chemical analyses established the presence of the total amount of parathion remaining unchanged in these diluents.

For any one toxicant an important relationship to the effectiveness of the mixture is the particle sizes to which a solid toxicant is reduced during grinding of a wettable powder. Sulphenone has been found to have greater initial and longer residual effectiveness against many species of mites when reduced to very fine particle sizes. DDT has been found to be more toxic to codling moth larvae when finely ground than when less finely ground when the insect was subjected to unweathered deposits. However, the tenacity of the deposits to water weathering may decrease with a decrease in particle size (*4*). On the other hand we have found increased subdivision results in more effective deposits after weathering in the absence of rainfall. Resuspension in water may account for these seemingly opposed results. The rate of loss by volatilization of any material of low vapor pressure such as lindane is probably increased by increased subdivision. Toxicant destruction by solar radiation may also be accelerated with the finer versus the coarser particles. It is obvious that the optimum particle size range for each toxicant and for each purpose should be established in order to obtain maximum economic effectiveness.

The problems involved in the choice of surfactants to be used with both solid and liquid toxicants in wettable powder formulations have resulted in many headaches. The chemical reactivity of the toxicant and the surfactants must be considered with several relationships in mind. There may be a direct chemical reaction of toxicant and surfactant with the reduction of activity of the toxicant or the production of a phytotoxic or animal toxic constituent. There may also be a detrimental effect increasing with time of the toxicant on the surfactant resulting in decrease of the adequacy of dispersion of the formulation. One surfactant may be superior to another in aiding more rapid penetration of the toxicant into the pest. On the other hand, increased penetration into the protected surface because of solvent action of the surfactants or increased contact of the toxicant may result in greater hazard to the animals or increased phytotoxicity to the plants that are being treated. On the other hand, in the case of herbicides deliberate searches have been and are being made for surfactants that will increase the rate of penetration of toxicants and thereby increase the effectiveness of formulations of both old and new phytotoxicants. Some surfactants may aid redispersion in water and subsequent loss of fine toxicant particles during weathering, whereas another may aid in greater adhesion.

Although the above relationships are important, the practical problem of simply finding a combination of surfactants that will wet and disperse the wettable powder will wet the protected surface and pest to the optimum degree and will tolerate the addition of other formulations of different toxicants to the same suspension is no simple task. Yet the efficiency of the formulation and, therefore, the economic evaluation in the field of the usefulness of the toxicant depends upon satisfying these relationships.

The design and limitations of spraying and dusting equipment are big factors for consideration in formulating pesticides

Emulsion Bases

Emulsifiable solutions of toxicants demand more consideration than do wettable powder formulations in some respects. The chemical compatibility of solvent and toxicant, the flammability of the solvent and solvency for the toxicant are important. In addition, the toxicity of the solvent to man, animals and plants as well as the possible increase of toxicity of the chemical because of combination with the solvents and/or surfactants are of immediate concern in the formulation of emulsifiable solutions. The choice of solvents and surfactants greatly influences the nature of the deposit as to its crystal size, shape and degree of penetration into the surface on which the formulation is applied. The choice of surfactants and their concentrations influence greatly the degree of wetting and, therefore, the magnitude of the initial deposit on application. In turn, weathering properties are related to the nature of the deposit. For example, DDT deposits from solutions of solvents with very low flash points such as xylene or other light fractions have been found to be more severely reduced in effectiveness by sunlight and ultraviolet light than those from higher flash points such as kerosene (*5*).

The advantages of more rapid kill because of the more rapid penetration of the toxicant in an emulsifiable formulation into the pest may be more offset by the increased toxicity to plants, animals and man. Furthermore, the generally increased cost of diluents, surfactants, and containers make emulsifiable formulations less attractive to the consumer.

Dusts

Dust formulations also have problems peculiar to distributing a relatively small amount of toxicant through or upon a large amount of diluent. Although it has been found that dusts impregnated with a solid or semi-solid toxicant dissolved in a solvent are more effective (*2*), the cost of solvent, solvent recovery and other attendant manufacturing problems makes this method impractical for most toxicants. At the present time many liquid as well as solid toxicants are made by blending a previously formulated concentrate with a diluent of acceptable properties. These properties are not dissimilar from those pointed out above in connection with wettable powder diluents. It may be necessary in using previously formulated concentrates to add some material in order to stick the very fine particles of solid toxicant to the dust diluent to prevent fractionation in the air and lack of deposition of finely divided toxicant upon the surfaces to be treated (*6*). The addition of highly refined spray oils frequently will improve the depositing and adherence properties of a dust. The oil is probably active in increasing the adhesion of the finely ground toxicant particles to the diluent particles.

The relationships outlined above are by no means exhaustive of those that need be taken into account in developing a new toxicant to the stage of a profitable commercial product. Since it is not possible to duplicate in the laboratory and greenhouse all of the factors that are variables in "weather," extensive field testing of a new toxicant formulation is necessary. This is particularly true with respect to phytotoxicity, and it has been generally found that greenhouse grown plants are much more sensitive to chemicals than the same variety grown out-of-doors in the same composition of soil. Advantage can be taken of this situation. Before a toxicant is tested in the field, sensitive greenhouse plants can be used to determine by trial and error with reasonable certainty, the safest formulation of the new toxicant.

Once the plant safety has been increased as much as is consistent with good judgment in making a formulation with respect to all factors, then field comparison tests can be logically carried out.

Field Testing

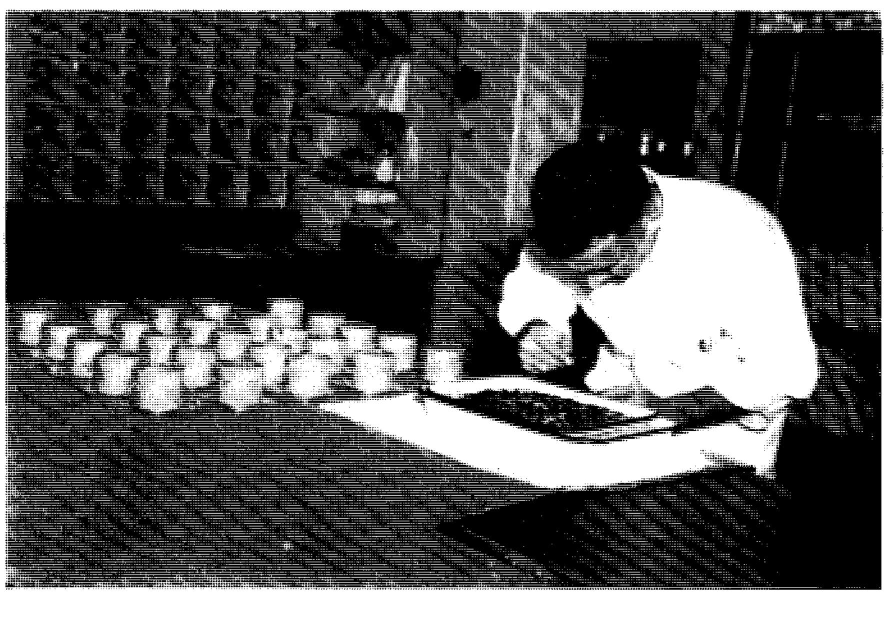
Comparisons in the field of a new toxicant with other established products to obtain an adequate evaluation of the economic usefulness of the toxicant depend upon several complex interrelationships. If the products with which the new toxicant is compared are all wettable powders, the situation would seem to be greatly simplified. As a result of our laboratory and field experiences we have found that each different toxicant demands either a different combination of surfactants even though the diluents be the same or a different proportion of the same surfactants to make an adequately dispersed suspension. The degree of wetting of a treated surface is also different with each formulation of a different toxicant with the same surfactants and diluents. Because individual physical characteristics are different for each toxicant the particle size ranges are also different although grinding was done in identical equipment for the same length of time. The end result of a wettable powder comparison is not a basic comparison of the toxicity of the chemicals but in reality a comparison of formulations of the different toxicants. If we could assume that a particular formulation of the new toxicant tested in the comparison was the most effective one possible then we would have a practical estimate of the economic usefulness of the new product. However our experience and that of others is that the first formulations of a new toxicant tested in the field are usually deficient in at least one, and usually more than one, respect. A most common problem arises in attempting to establish the dosage of a new product necessary to give pest control equivalent to that of an established product. When several dosages of wettable powders are used, decreasing the dosage per unit volume of spray mixture with most formulations decreases the degree of wetting of the pest and/or protected surface. Increasing the dosage increases the degree of wetting. This, of course, changes the character of the distribution of the toxicant and, therefore, its effectiveness especially when the comparison is made by means of hand spraying. In the case of hand spraying, the amount of wetting of a formulation spray mixture on the surface of pest and protected surface alike is extremely critical. Slightly higher than optimal wetting results in very low deposits of a formulation because of excessive run-off unless special depositing agents are used.

Because it is not possible to obtain equivalent formulations of old and new toxicants, that is, equivalent in respect to particle size range, dispersion, wetting, and therefore, depositing characteristics, means must be adopted to insure that the comparison is on a logical basis. By this, we mean that in order to correlate the efficiency of pest control by formulations, the amounts of toxicants deposited initially must be found and the degradation of the residue followed by suitable analytical methods.

Bases of Comparison

Correlation of dosages of different applied toxicants with the efficiency of pest control as measured by pest reduction or crop yield or both gives a practical answer for the particular formulation employed. However, if no initial residue deposits are obtained, the ratio of toxicants applied will not be known in terms of the relative quantities deposited on the treated surfaces. Therefore, the comparison cannot be one that will give a true picture of the relative initial activity of each toxicant. Furthermore, if the deposits are not followed by analyses it is necessary to rely solely upon a biological indicator such as an insect's continuous and equivalent reinfestation of each treated area—a circumstance that occurs infrequently. The literature is replete with examples of comparisons of different toxicants as wettable powders, emulsifiables and dusts that give only control of the pest and perhaps yield data. All too frequently the comparisons are made with formulations of different toxicants each made by a different manufacturer. While this is convenient for a manufacturer to obtain a practical answer, as to whether or not his formulation of a toxicant will give equivalent or better control of a given pest; the comparison is not an adequate one for the investigator. Residue analyses and pest control data together are essential to understand the activity of the toxicant over extended periods of time and under varied weather conditions. In turn, the understanding gained leads to an improvement of the formulation and subsequently to a more adequate economic evaluation of the new toxicant.

Laboratory tests of various formulations are made before field trials



Before field testing, sensitive greenhouse plants can be used to determine the safest formulation of a new toxicant

Direct observation of the deposits both initially and upon weathering is useful in correcting grass malfunctioning of the new formulation. On the other hand observation is no substitute for analysis. A tenacious formulation may give an appearance of great persistence after severe weathering when in reality the toxicant has been removed by water solution, or has volatilized or was chemically degraded leaving behind the obvious solid diluent clinging to surfaces treated. The toxicant may penetrate into surfaces and reissue subsequently (*3*) to give a longer effective residual even though the diluent is removed by erosion or evaporation. Solutions and emulsifiable concentrates are commonly more in this category than are wettable powders.

The kind of pest and its biology, the type of crop that is to be protected, the mode of action of the insecticide whether stomach poison, fumigant or contact and the methods of application must all be considered in formulating a new chemical. In controlling a large, active adult insect susceptible to say DDT, a highly uniform platelike deposit such as that obtained with lead arsenate used to control codling moth is not needed. Such an insect moves about picking up DDT from spots of deposits and is efficiently killed by contact. However, if the pest is a mite whose entire life history may be spent on a single leaf, then effective control can only be achieved by an excellent application of a well made formulation; that is, of optimum particle size and wetting and adhesive properties. On such a small pest, particle size range is of critical importance where a solid toxicant such as Sulphenone is employed. In this example it is apparently necessary for the mite if not directly sprayed by the wettable powder, to pick up and carry small particles for some time before enough is absorbed to cause death. Obviously the particle sizes which mites can pick up are restricted.

Since the branches of a plant usually do not wet to the same degree as do the twigs, fruit or foliage with the same surfactant combination in a spray mixture, the formulation has to be made with the biology of pest in mind. If the pest is a scale insect spending its life on the bark of the tree, the formulation must be made to achieve maximum deposit on bark which is usually absorptive of both water and oily solvents. If the pest is a fruit eating larvae, the formulation must be changed to achieve maximum deposit on such a waxy surface as that of an apple. Many toxicants are used for more than one pest on more than one kind of plant. Therefore, the formulation suitable for wetting a plant such as cotton, which is easily wet by water alone, may be either of too little or too great wetting properties for peach leaves or apple fruit. From the standpoint of achieving maximum results it is logical that a formulation be prepared that is either suitable for many crops, an exceedingly difficult accomplishment, or that several formulations be developed. The latter possibility is one which manufacturers would like to avoid because of increased cost of development and manufacturing and of maintaining complex inventories. Fortunately for the manufacturer, many toxicants are so effective that one formulation will on the average obtain acceptable, although not necessarily maximum, control of different pests on the same or different plants.

The method of application of toxicants to plants has a bearing on the general kind of formulation used. Volumes as low as one gallon per acre, as are applied in spraying cotton, necessitate extremely fine nozzle orifices. Wettable powders are in general unsuitable for this type of usage because of nozzle plugging and the necessity for constant agitation, whereas emulsifiable concentrates are well adapted. Here the droplet size of the spray is influenced by the surface tension of the mixture which is related to the concentration of surfactants and in turn, therefore, to the deposit, both qualitatively and quantitatively. In high volume application to tree fruit crops wettable powders are more commonly used because of lower costs and primarily for their reduced phytotoxicity. Where coverage because of growth habit is a difficult problem as in grapes or tomatoes, dusts flown on or applied by ground rig are more practical for pest control.

Combinations of Toxicants

Typically more than one toxicant formulation is used in the spray tank at the same time. This situation is the result of the grower's wishing to avoid the cost of repeated application. Unfortunately there are frequently objectionable results found when using more than one formulated toxicant in a spray mixture even though the toxicants are themselves chemically compatible. The increased wetting of plant surfaces by the final mixture is the usual effect. This may result in either high loss from run-off or rapid loss from the deposit by water erosion or both. It would seem that a logical answer here is to be found in making a combination of toxicants into a single formulation with the amount of wetting adjusted properly. The frustrating facts are that the growers want, or authorities recommend, different proportions of toxicants even for the same pest problems in different areas and for different times of application on the same pests. Moreover, any one toxicant may be used alone at some one time multiplying the number of different combinations of formulations beyond economic tolerance of the manufacturer. In practice the assumption is often made that one toxicant will be used with another and each, therefore, is formulated to give minimum wetting in the hope that when a combination is used the effect on wetting will not be too far from the optimum.

Since combinations of separately formulated toxicants are commonplace, the problem of compatibility of surfactants becomes important. The effects of incompatible surfactants in wettable powders are commonly met with in the field between different manufacturer's formulations and at times with different products made by the same manufacturer. The result may be a mass of flocculated toxicant in the bottom of the spray tank. In less severe cases incompatibility may not be as violent but may greatly decrease the effectiveness of the toxicant by reducing the dispersion of the fine, highly active particles. The wetting and, therefore, the distribution of the deposit may also be adversely affected by reaction between incompatible surfactants.

A toxicant such as Systox, O,O-diethyl-O-ethyl mercapto-ethyl thiophosphate, or Schradan, octamethyl pyrophosphoramide, that is absorbed by the plant and translocated from the place of application to untreated parts almost eliminates the need for making formulations and the need for thorough applications. However, the dermal toxicity hazard to mammals by Systox has been reduced in practice by formulation with an emulsifier in high concentration. It is not too much to expect that a formulation of this fantastically active, but volatile, compound may some day be achieved that will reduce the rate of loss by vaporization. This may be achieved with a choice of surfactant that will promote more rapid plant absorption.

We are convinced that more than a few potentially useful chemicals have not been developed into commercial products because of poor formulation. Adequate evaluation in the field of a new toxicant poorly formulated cannot be made. Furthermore, a poor formulation in the hands of field investigators who do not appreciate the necessity of relating the amounts of toxicants applied to the quantities deposited and to their rates of loss with the adequacy of pest control, will probably produce an evaluation that is misleading. The manufacturers' decision not to produce a new toxicant therefore, may depend upon unintentionally poor information.

References

(1) Bartlett, B. R., *J. Econ. Entomol.*, **44,** 891–6 (1951).

(2) Ginsburg, J. M., Filmer, R. S., Reed, J. P., and Paterson, A. R., *J. Econ. Entomol.*, **42,** 602–11 (1949).

(3) Gunther, F. A., *et al.*, *J. Econ. Entomol.*, **39,** 624–7 (1946).

(4) Hunt, C. R., *J. Econ. Entomol.*, **40,** 215–19 (1947).

(5) Lindquist, Arthur W., *J. Econ. Entomol.*, **39,** 55–9 (1946).

(6) Potts, S. F., *J. Econ. Entomol.*, **39,** 716–20 (1946).

(7) Steiner, C. F., Summerland, S. A., Arnold, C. H., and Fahey, F. J., *USDA, BEPQ Bull.* **E-628** (1949).

(8) Woodruff, Nancy, and Turner, N., *J. Econ. Entomol.*, **42,** 249–53 (1949).

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