

# **Advances in Pesticide Formulation Technology**



ACS SYMPOSIUM SERIES 254

# Advances in Pesticide Formulation Technology

**Herbert B. Scher, EDITOR**  
*Stauffer Chemical Company*

Based on a symposium sponsored by  
the Division of Pesticide Chemistry  
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## FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

## PREFACE

**R**ECENT ADVANCES IN PESTICIDE FORMULATION TECHNOLOGY were presented at the symposium upon which this book is based. The symposium was organized to inform industrial, university and government pesticide researchers and pesticide program administrators about these advances. I think it is safe to say that most pesticide researchers now realize that the understanding of the physical chemical principles upon which pesticide formulation science is based is just as important in the development of a new pesticide product as understanding pesticide chemical structure-biological activity relationships.

This book will be particularly useful to researchers working in the area of pesticide product development. It is hoped that the papers presented herein will serve to update these researchers on new formulation techniques as well as to act as catalysts for the development of new product development concepts.

The first chapter of the book is an overview of the most active pesticide formulation research areas, including comments on topics not covered in the symposium because of time limitations. The subsequent chapters deal in depth with the main topics (Flowables, Computer Applications, and Controlled Release Formulations) and general topics. I feel this book fulfills a very important need—the enhancement of communication among pesticide formulators and between pesticide formulators and the rest of the pesticide community.

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January 1984

# Advances in Pesticide Formulation Technology

## An Overview

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Pesticide formulation science is a very broad field because it must deal with formulation development, production and storage (1-4) as well as the interaction of the pesticide with plants, insects, mammals, soil, air and water (5). Pesticide formulations can be classified into the following types:

- Aqueous Solutions
- Emulsifiable Concentrates
- Dispersion Concentrates (Aqueous and Nonaqueous Flowables)
- Wettable Powders
- Dry Flowables (Water Dispersible Granules)
- Granules
- Controlled Release
- Others (Dusts, Aerosols, etc.)

The factors which influence the choice of formulation are pesticide physical properties (melting point, solubility, volatility), pesticide chemical properties (hydrolytic stability, thermal stability), soil application vs. foliar application, crop and cultural practice, pesticide biological properties (crop selectivity, transport), and economics.

This book is a collection of papers concentrating on pesticide formulation topics which are currently receiving the greatest attention and where the greatest advances are being made. These topics are listed below and make up the four sections of the book. The number of papers in each section is given in parenthesis.

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- Flowable Preparation and Stabilization [4]
- Use of Computers for Evaluation and Optimization of Formulations [4]
- Controlled Release Formulations [3]
- Selected General Formulation Topics [6]

Introductory remarks for each of these sections will follow. I have also added a fifth section to this overview in order to list and briefly discuss timely pesticide formulation topics which because of time limitations could not be included in the symposium program. Important references are listed for each of these five sections.

#### Flowable Preparation and Stabilization (6)

If the technical pesticide has inherent physical properties (high melting point, friable crystal, low solubility and high chemical stability in continuous phase) that allow the development of a flowable formulation, many use advantages can be gained. Flowable formulations are easy to measure and are not dusty. In addition since the flowable formulation is a predispersed system, good dispersibility upon dilution can be readily achieved. Aqueous based flowables contain no organic solvents and hence have high flash points and reduced toxicity and phytotoxicity. Water soluble or water dispersible adjuvants such as film forming agents can be added directly to aqueous based flowables. These film forming agents are used to improve adhesion on foliage and to provide controlled release. Oil based flowables where a liquid pesticide or inert oil comprises the continuous phase and an insoluble solid pesticide comprises the dispersed phase are also receiving attention these days. Flowable formulations also afford the opportunity to optimize biological activity and physical stability by varying pesticide particle size and shape.

As described in the previous paragraph, flowable formulations offer many advantages. However it is in the area of flowable preparation and stabilization where problems can arise and where extensive testing must take place to assure high formulation quality. The type of dispersing and milling equipment and type and concentration of wetting agents, dispersing agents, suspending agents, film forming agents and freezing point depressants must be chosen carefully to optimize biological and physical stability. As will be seen in the second section, computer techniques are very useful in this optimization process. Rheological measurements are used to predict physical stability, and accelerated and long term storage tests are used to confirm physical stability. There are four papers in this section which deal with these topics. The papers by Knowles et al. and Warrington et al. deal with novel

suspension systems and the prediction of stability using rheological measurements. The papers by Fraley and Dombrowski deal with dispersing and milling equipment. The paper by Glatzhofer forms a bridge between this section (Flowables) and the second section (Computer Applications). Glatzhofer describes a system where a computer is coupled to a viscometer. He uses this system to evaluate flowable formulations after accelerated and long term storage.

One topic which is not covered in this section is the preparation and stabilization of emulsion type flowables (oil in water flowables) (7). This type of flowable is just beginning to receive widespread attention and is still very much in the experimental stage. In addition to the other factors considered above, factors which influence oil droplet coalescence, such as interfacial free energy, electrostatic stabilization and steric stabilization, must be taken into consideration for this special type flowable.

#### Use of Computers for Evaluation and Optimization of Formulations

Computers are being used very effectively for evaluation and optimization of pesticide formulations. Computer assisted optimization of formulation physical and biological properties and cost (responses) vs. type and concentration of ingredients (independent variables) can be divided into three parts.

1. Experimental Design and Collection of Data (8) - Statistics are utilized to efficiently sample experimental space.
2. Correlate Experimental Data by Regression Analysis (9) - Statistics are utilized to measure the degree of correlation between responses and independent variables. Important independent variables are identified.
3. Optimize Physical and Biological Properties and Cost (10) - Construct response surfaces and choose a set of independent variables to optimize responses. Since each response may not be optimized by the same set of independent variables, compromises may have to be made which reflect the relative importance of the responses.

In addition to utilizing computers to optimize pesticide formulations, computer programs can be designed to operate equipment used to evaluate pesticide formulations and to perform complex theoretical calculations used to guide choice of ingredients. Of course, computers can also be used for formulation data storage and acquisition. There are four papers in this section which deal with these topics. Papers by Botts and Mookerjee describe the theory and programs associated with experimental design, correlation and optimization. Both authors work through actual problems.

The paper by Glatzhofer describes how a computer can be used to operate a viscometer and the paper by Meusberger describes how computer calculations based on solubility parameter theory can be used to optimize the choice of emulsifiers for pesticide emulsifiable concentrates.

#### Controlled Release Formulations (11-15)

Controlled release pesticide formulations can be used to reduce mammalian toxicity and extend activity, to control evaporation, to reduce phytotoxicity, to protect pesticides from environmental degradation, to reduce leaching and to reduce pesticide levels in the environment. Controlled release pesticide formulations can be divided into four main systems: 1) polymer membrane - pesticide reservoir systems; 2) matrix systems containing physically trapped pesticides; 3) polymer systems containing covalently bound pesticides; and 4) coated pesticide granule systems. The polymer membrane - pesticide reservoir systems are diffusion controlled and include microcapsules and macrostrips. The matrix systems can be subdivided into inert and erodible categories. The release of pesticide from an inert matrix system is diffusion controlled while the release of pesticide from an erodible matrix system is controlled by the rate of degradation of the matrix. The rate of release of a pesticide covalently bound to a polymer depends on the rate of cleavage of the specific chemical linkage which attaches the pesticide to the substrate. The rate of release of pesticide from a polymer coated pesticide granule depends on factors such as the rate of degradation of the coating and the rate of water entry through the coating. There are three papers in this section which deal with these topics. The paper by Dahl and Lowell deals with the effect of Methylparathion microcapsules on bees and describes formulation efforts underway to reduce bee toxicity. The paper by Evans describes the use of microencapsulation to combine the effects of insect pheromones (attract insects) and synthetic pyrethroids (kill insects). The paper by Peterson describes spray drying of a polymer latex on a acaricide powder formulation to reduce phytotoxicity.

#### Selected General Formulation Topics

There are six papers in this section. They deal with biological insecticide formulations (Ward), water dispersible granules (Wright and Ibrahim), analysis of formulations for quality control and identification of toxic contaminants (Plimmer), identification of surfactant metabolites (Stolzenberg et al.), electrostatic spraying (Law) and compatibility and tank-mix testing (Tarwater).

#### Timely Pesticide Formulation Topics Not Included in Symposium

Effect of Surfactants on Wetting, Penetration and Transport of Pesticides in Plants and Insects (16-17). Some of the factors which affect the wetting, penetration and transport processes are

droplet size, surface tension, contact angle, and concentration and nature of surfactant. The nature of the surfactant includes properties such as hydrophile-lipophile balance, solubility parameter, molar volume and electronic charge.

This is a topic where it is very difficult to separate effects and understand mechanism of action. Hence it is difficult to transfer information from one pesticide or biosystem to another and a great deal of trial and error work must still go on. Vegetable Oil Diluents for Pesticide Application (18-19). Vegetable oils such as soybean oil and cottonseed oil are being tested as pesticide diluents to replace water in ultralow volume (ULV) foliar applications. Most of the tests are being conducted using foliar insecticides and fungicides, however some tests using post-emergent herbicides are also in progress. For ULV applications, the pesticide is blended with vegetable oil to produce a formulation of known pesticide loading and this formulation is diluted with more vegetable oil if necessary in order to achieve an oil coverage ranging from 1/4 to 1/2 gallon per acre. Some ULV applicators using vegetable oil have claimed less pesticide hydrolysis problems, fewer adjuvants required, protection of pesticide from sunlight, less rain washoff, better spreading and penetration on insects and weeds, reduction in volatility, less drift, and the reduction of rates. However, a lot more field work (with the appropriate controls) will be required to fully substantiate these claims. In addition, formulators using vegetable oil will have to guard against the oxidation of the pesticide during manufacture, storage and application, the variability in oil composition and the impact on mammalian toxicity.

Vegetable oils with an emulsifier are also being tank mixed with pesticide formulations in water in an attempt to achieve some of the advantages listed above for ULV applications. Results are inconclusive at this time.

Pesticide Formulations for Seed Treatment (20) and Dry Fertilizer Treatment (21). Pesticide handling, application and incorporation can be simplified and made less expensive by using seeds and fertilizer granules as pesticide carriers. These techniques reduce the number of passes a farmer needs to make over a field, although cultivation is often required if herbicide coated seeds are placed too far apart.

One problem in using these techniques is getting sufficient quantity of pesticide adhered to the seed or fertilizer granule. Solutions to this problem include using a powdered clay or silica to help absorb liquid pesticides, using microencapsulated liquid pesticides, and using a polymer coating to increase adhesion of pesticide particles.

In addition to getting sufficient pesticide loading on the seeds or fertilizer granules, there are two other potential problem areas which require extensive investigation: phytotoxicity of pesticide on seeds and chemical degradation of pesticide on fertilizer granules.

Pesticide Formulations for Use with Conservation Tillage (22). Rising fuel costs and the need to prevent soil erosion and to save soil water has spurred interest in conservation tillage techniques. These techniques often require special granular formulations capable of penetrating plant residue and preventing pesticide evaporation and UV attack while the granules remain on the soil surface.

In conclusion I think it can be safely said that the advances in pesticide formulation technology which are described in this book are playing a vital role in the development of safe, efficacious and economically attractive pesticide products.

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# Stabilization of Aqueous Pesticidal Suspensions by Graft Copolymers and Their Subsequent Weak Flocculation by Addition of Free Polymer

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Graft copolymers as dispersing agents for pesticidal suspensions concentrates have been investigated using ethirimol (a fungicide) and a copolymer of polymethyl methacrylate-methacrylic acid/methoxypolyethylene-oxide methacrylate. The results showed that highly concentrated dispersions (with a volume fraction  $> 0.6$ ) can be obtained. This agent is strongly adsorbed on the particle surface and provides a steric barrier preventing flocculation.

The sterically stabilised dispersions produced can be weakly flocculated by the addition of free (non-adsorbing) polymer such as poly(ethylene oxide). Weak flocculation occurs above a critical free polymer concentration which decreases with increase of molecular weight,  $M_w$ , of the free polymer. The weak flocculation produced in concentrated (55% w/w) dispersions was investigated using rheological measurements. Steady state shear stress-shear rate curves were established and the yield value,  $\tau_y$ , was obtained by extrapolation of the linear portion of the curve. Moreover, the yield value was also directly obtained by applying a series of successive stresses of equal increments to the suspension and recording the response until flow occurred. The results showed that above the flocculation point  $\tau_y$  increases with increase of free polymer volume fraction,  $\phi_p$ . This increase took place at a critical,  $\phi_p$  value which decreased with increase of  $M_w$ . The rheological results were interpreted in terms of the energy-minimum,  $G_{min}$ , produced in the free energy-distance

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curve in the presence of free polymer. Good correlation was obtained between the increase in the depth of  $G_{\min}$  and the increase in  $\tau_{\beta}$ . Sediment height and redispersion experiments were also consistent with the weak flocculation phenomenon, showing also good correlation with the rheological data.

The formulation of aqueous concentrated suspensions of pesticides requires the use of powerful dispersing agents, which keep the particles in a deflocculated state. This is the case particularly when high volume fractions ( $> 0.4$ ) of the solid are required. Flocculation produces a rapid increase in viscosity thus causing problems during preparation. Moreover, strong flocculation is undesirable since it may cause severe thickening on storage and reduces the spontaneity of dispersion on dilution of the suspension.

Several agents may be used to obtain a deflocculated suspension, i.e., a stable suspension in the colloid sense (1). These may be classified into ionic and nonionic surface active agents, nonionic macromolecules and polyelectrolytes. Ionic surfactants produce deflocculated suspensions as a result of the double layer repulsion produced by the adsorbed chains. However, these are seldom suitable for producing concentrated suspensions since double layer overlap leads to an increase in the viscosity at moderately high volume fractions. Moreover, these systems are sensitive to electrolytes and the surfactant may not be strongly adsorbed on the particle surfaces. Non-ionic surfactants can be used as dispersing agents as a result of steric repulsion between the adsorbed layers. Provided the chains are well solvated, strong steric repulsion enables one to obtain deflocculated systems. However, these systems may suffer from desorption of the chains which are in many cases only weakly adsorbed on the particle surfaces.

In theory the best agents for producing deflocculated suspensions are those polymers of the block and graft type (2). These agents are designed to have two main groups A and B, where A has a strong affinity to the particle surface (ie. strongly and irreversibly adsorbed and being insoluble in the continuous medium) and B is a group that provides the steric stabilisation, being highly solvated by the continuous medium and of sufficient length to provide a steric barrier. A-B, B-A-B block and A-B<sub>n</sub> graft copolymers may be used for this purpose. The anchoring A group can be an insoluble hydrophobic group such as polystyrene or polymethacrylate, which has a strong affinity to the hydrophobic pesticide particle, whereas B can be a water soluble chain such as poly(ethylene oxide). This hypothesis has been tested in the present investigation by using a graft copolymer of



polymethylmethacrylate-methacrylic acid/methoxy polyethylene oxide methacrylate. The polymer is therefore, a "comb" type with polyethylene oxide chains ("teeth"). As an example of a pesticide, ethirimol (a fungicide manufactured by ICI) was used. The anchoring of the chain to the particles was assessed using adsorption/desorption isotherms, whereas its dispersing power was evaluated from measurement of viscosity as a function of volume fraction of the particles.

Although the production of highly deflocculated suspensions is a primary objective for formulation of suspension concentrates, these systems tend to settle under gravity forming dilatant sediments (clays). The latter must be prevented either by controlled flocculation or by the addition of a second disperse phase to the continuous medium (1). One method which may be applied to sterically stabilised dispersions, is to add a free (ie. non-adsorbing) polymer to the continuous medium. Recent studies in our laboratory (3) using polystyrene latex dispersions stabilised by the above "comb" dispersing agent have shown that polymers such as poly(ethylene oxide) induce weak flocculation above a certain critical concentration of free polymer which was dependent on the molecular weight of the chain.

This phenomenon has been applied to the present pesticidal suspension and the results obtained (using rheological and sediment volume experiments) are given in the present paper.

### Experimental

Materials Ethirimol, a fungicide manufactured by ICI, was a white crystalline solid (density =  $1.21 \text{ g cm}^{-3}$ ) which was used as received.

The "comb" dispersing agent was a graft copolymer of polymethylmethacrylate-methacrylic acid (methoxypolyethylene oxide methacrylate) supplied by ICI Paints Division (Slough) and used as received. The exact molecular weight of the polymer is not known, but it is expected to be in the region of 20-30,000 (as indicated by ICI Paints Division). The  $M_w$  of the polyethylene chains was 750.

Three polyethylene oxide (PEO) samples with nominal molecular weights 20,000, 35,000 and 90,000 were used. These were supplied by Fluka, Hoechst, and Union Carbide respectively, and used as received.

Adsorption Isotherms In these experiments a "comb" with a similar structure was used. The ethirimol used was a recrystallised material which had been ground (using a Coffee mill) to produce a powder with surface area  $0.29 \text{ m}^2 \text{ g}^{-1}$  (as measured by BET Kr adsorption).

About 1 gm of solid was accurately weighed into 2oz winchesters and then  $25 \text{ cm}^3$  solutions of the dispersing agent, covering a concentration of 0-1000 ppm were added. The powder was dispersed

using a soniprobe and then left stirring overnight to reach equilibrium. Ten cm<sup>3</sup> of each dispersion was then centrifuged for half an hour at 4000 g and then for another half an hour at 25,000 g. The concentration of the polymer in the supernatant liquid was determined using a colorimetric method based on complexation with I<sub>2</sub>+KI (4). The procedure has been described before (5). Desorption was investigated by redispersing the sedimented particles into distilled water, recentrifuging and analysing for any desorbed polymer.

Preparation of Suspensions A 66.8% w/w suspension was prepared by slowly adding the powder to the aqueous solution of the "comb" stabiliser (2% w/w) while stirring. Care was taken to avoid air being entrapped in the suspension. The latter was then milled using a Dyno mill (ex. Willy. A. Bachofen, Basle, Switzerland) and then left standing while being stirred. In some cases, the particle size distribution of the resulting suspension was determined using an optical disc centrifuge. Typically, the suspension gave a distribution that was >50% below 1µm indicating adequate milling.

For rheological measurements (see below) samples of the suspension concentrates were mixed with PEO solutions to give 55% w/w ethirimol, while varying the concentration of PEO. For viscosity-volume fraction curves a 60% w/v suspension was prepared by milling using 3% of the "comb" stabiliser. The resulting suspension was further concentrated by centrifugation and the sediment diluted with the supernatant liquid to give a range of volume fractions.

Sediment volume and redispersion For sediment volume experiments a 50% w/v suspension was prepared using a 2% w/w of the polymer. 5g of the resulting suspension was added to 5 ml solutions of PEO to cover a wide concentration and the resulting suspension placed in stoppered cylinders and kept in constant temperature cabinets (25 ± 1°C). The sediment height was followed with time for several weeks until equilibrium was reached. At this point the tubes were mechanically inverted end-over-end and the number of revolutions required for redispersion was noted.

Rheological measurements Two instruments were used to investigate the rheology of the suspensions. The first was a Haake Rotovisko model RV2 (MSE Scientific Instruments, Crawley, Sussex, England) fitted with an MK50 measuring head. This instrument was used to obtain steady state shear stress-shear rate curves. From these curves information can be obtained on the viscosity as a function of shear rate. The yield value may be obtained by extrapolation of the linear portion of the shear stress-shear rate curve to zero shear rate. The procedure has been described before (3).

The second instrument was a Deer rheometer (model PDR881, Integrated Petronic Systems Ltd., London) fitted with concentric cylinder platens. This instrument was used to measure of the yield value by applying a series of stress values of equal increments and recording the response until flow occurred.

## Results

Adsorption Isotherm Fig.1 shows the adsorption isotherm (obtained at room temperature  $20 \pm 2^\circ\text{C}$ ) of the "comb" stabiliser on ethirimol. The isotherm is of the high affinity type and the adsorption reached a plateau value of  $\sim 20 \text{ mg m}^{-2}$ . No desorption was detected when the centrifuged sediment was redispersed into water. The plateau adsorption value is much higher than that recently obtained on polystyrene latex particles ( $\sim 3 \text{ mg m}^{-2}$ ). However, it should be mentioned that the adsorption values were based on the BET surface area of the powder, which could be an underestimate of the true area, particularly since the powders were dispersed using ultrasonic irradiation which may result in some attrition producing fine particles which would increase the surface area significantly. Since the object of the adsorption experiment was to study irreversibility of adsorption, obtaining the absolute figure for the adsorption was not considered important and no attempt was made to measure the surface area of the particles when dispersed in solution.

Viscosity-volume fraction curves Fig.2 shows the viscosity as a function of volume fraction of particles. The results are typical of those usually obtained with concentrated dispersions (6), showing a rapid increase in viscosity above a critical volume fraction of the dispersed phase. When the volume fraction reaches the so-called packing fraction,  $\phi_{sp}$  (see Discussion Section), the viscosity reaches a very high value.  $\phi_{sp}$  may be obtained from a plot of  $1/\sqrt{\eta_r}$  versus  $\phi_s$  and extrapolation to  $1/\sqrt{\eta_r}=0$ . This gave a  $\phi_{sp}$  value of  $\sim 0.73$  for the bare particles. With an average particle size of  $1\mu\text{m}$ , the actual volume fraction (particle + adsorbed layer) will be only slightly larger than this value. Assuming an adsorbed layer thickness of  $5\text{nm}$  (which is a reasonable estimate for a layer of PEO with  $M=750$ ),  $\phi_{sp}$  for particle and layer is  $\sim 0.74$ .

Influence of addition of free polymer on the rheology of the suspensions Fig. 3 shows the effect of addition of PEO ( $M_w=20,000$ ,  $35,000$  and  $90,000$  respectively) on the extrapolated yield value obtained from the shear stress-shear rate curves using the Haake Rotovisko. On the other hand, Figure 4 shows the results obtained using the Deer rheometer in which  $\tau_B$  was directly obtained. Although the trend obtained is the same, the yield values obtained using the Deer rheometer are significantly

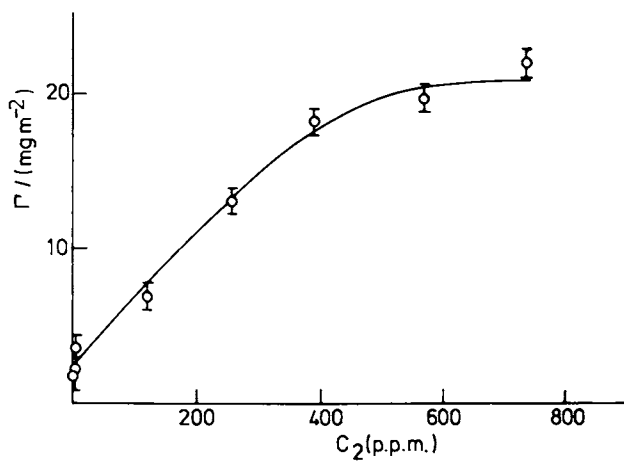


Figure 1. Adsorption isotherm of the "comb" stabiliser on ethirimol.

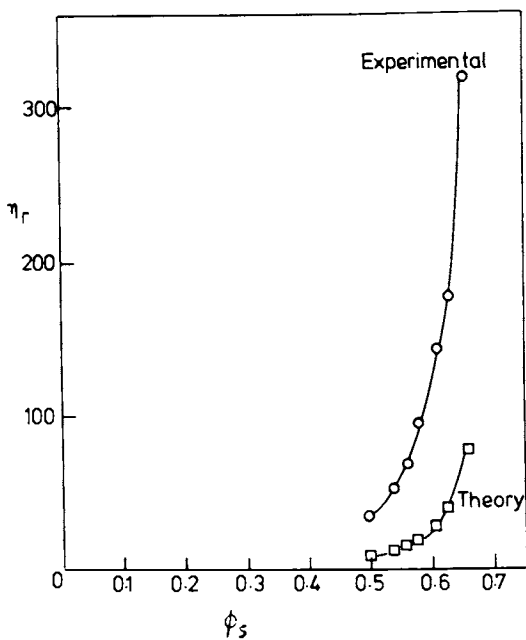


Figure 2. Viscosity - volume fraction curves

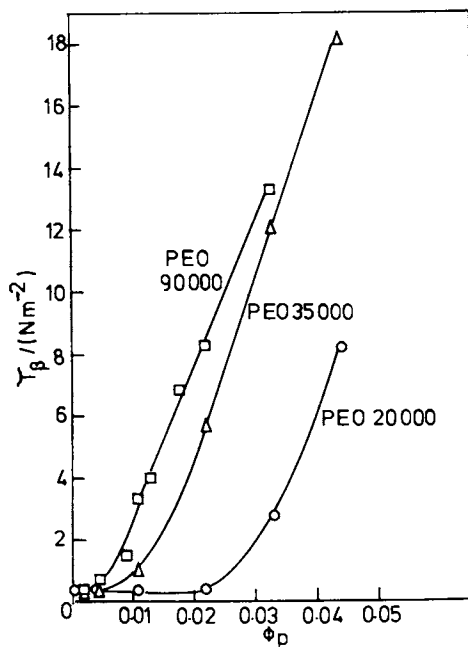


Figure 3. Effect of PEO concentration on the extrapolated yield value (using the Haake Rotovisko).

lower than those obtained using the extrapolation procedure. This is expected since the extrapolation procedure usually overestimates the yield value. The data of Figs. 3 and 4 show a rapid increase in yield value above a critical PEO concentration,  $\phi_p$ . This concentration corresponds to the critical flocculation concentration of the free polymer. However, since the rise in  $\tau_\beta$  did not occur at a sharp  $\phi_p$  value, the latter was taken as the intersection point at which the extrapolated horizontal and vertical lines meet. This gave values of  $\phi_p$  of  $0.02 \pm 0.002$ ,  $0.01 \pm 0.001$  and  $0.005 \pm 0.001$  for PEO with  $M_w$  of 20,000, 35,000 and 90,000 respectively. Moreover, the  $\phi_p$  values obtained from the two sets of rheological results were almost the same within the error of locating  $\phi_p$ .

Sediment height and redispersion As an illustration the results obtained using PEO 20,000 are shown in Fig. 5. This figure shows the variation of sediment height and number of revolutions required for redispersion as a function of PEO concentration, expressed as volume fraction of polymer in the continuous phase,  $\phi_p$ . Without added PEO, the sediment height was quite high and the whole dispersion was turbid (indicated by letter T on the diagram). On standing this dispersion settled to the bottom of the tube leaving a turbid supernatant and the sediment formed could not be redispersed after rotating the tube for more than 100 revolutions indicating formation of a hard clay at the bottom of the tube. On addition of 0.5% PEO 20,000 ( $\phi_p = 0.007$ ), the dispersion appeared turbid and the equilibrium sediment height was reduced. However, the sediment could be redispersed by application of 5 rotations to the tube. Further increase in PEO concentration resulted in a clear supernatant liquid and the sediment height reached a minimum height between 1 and 2% PEO ( $\phi_p$  between 0.015 and 0.027), above which there was a continuous increase in sediment height with clear supernatants. Above 1-2% PEO, the sediment became more viscous although no claying occurred. These viscous sediments were more difficult to redisperse and the number of revolutions required for redispersion increased sharply above 3% PEO ( $\phi_p = 0.04$ ). Thus, the sediment height experiments indicate flocculation between 1 and 2% PEO ( $\phi_p$  between 0.015 and 0.027); the exact flocculation concentration was difficult to assign. Therefore, the redispersion experiments showed claying in the absence of PEO and a highly viscous suspension above the flocculation point by the free polymer.

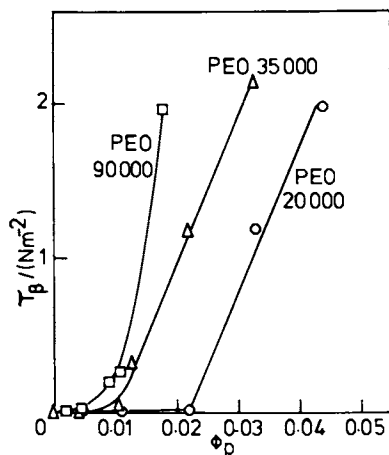


Figure 4. Effect of PEO concentration on the directly measured yield value (using the Deer rheometer)

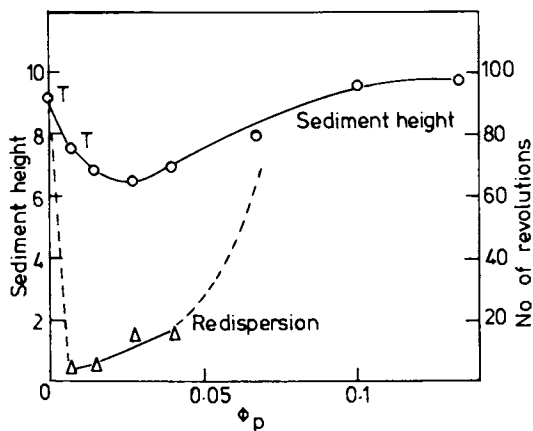


Figure 5. Sediment height and redispersion as a function of PEO 20,000 concentration.

## Discussion

Dispersing power of the "comb" stabiliser Both adsorption isotherms and viscosity-volume fraction curves show clearly the ability of the "comb" stabiliser to produce highly deflocculated suspensions. Thus, the strong anchoring produced by the backbone of the graft copolymer (no desorption was detected when the sediment was diluted with water) and the steric stabilisation due to the PEO chains which are well solvated in water, enables one to produce suspensions approaching the theoretical packing fraction (0.74 for a monodisperse hexagonally close-packed dispersion and higher values for polydisperse systems). This is shown by the  $\eta_r$ - $\phi$  curve (Fig.2) which, using the extrapolation procedure described in the Results section, gives a packing fraction,  $\phi_{ps}$ , of 0.74. The interaction in this sterically stabilised dispersion may be represented by a hard sphere model with a hard sphere radius of  $(a+\delta)$  where  $\delta$  is the adsorbed layer thickness. If this is the case, then it should be possible to fit the  $\eta$ - $\phi$  curve to the Dougherty-Krieger equation (6,7).

$$\eta_r = [1 - (\phi_s / \phi_{sp})]^{-[\eta] \phi_{sp}} \quad (1)$$

Using the extrapolated  $\phi_{sp}$  value and the theoretical value of  $[\eta]$  of 2.5,  $\eta_r$  was calculated as a function of  $\phi$  and the results are shown for comparison in Fig 2. The theoretical  $\eta_r$ - $\phi$  curve is significantly lower than the experimental curve. This may be due to the van der Waals attraction as the particles are close together in the very concentrated suspension. Therefore, the hard sphere model cannot be applied to a very concentrated dispersion without introducing a perturbation due to the van der Waals attraction.

Interpretation of rheological results The trends in the variation of  $\tau_B$  with  $\phi_p$  are similar to those obtained recently (3) using a model polystyrene latex dispersion. The  $\phi_p^+$  values obtained in the present system are also close to those obtained with the model dispersion (0.017, 0.008 and 0.005 for PEO 20,000, 35,000 and 90,000 respectively). As mentioned before the sharp increase in  $\tau_B$  above  $\phi_p^+$  indicates that at the onset of flocculation the dispersions show marked viscoelasticity. The flocculation obtained at  $\phi_p^+$  corresponds to the onset of the "semidilute" region,  $\phi_p^*$ , i.e., where the polymer coils in solution begin to arrange themselves in some



close-packed array as a result of excluded volume effects. The value of  $\phi_p^*$ , corresponding to the overlap of the free polymer in bulk solution can be calculated using the equation (8)

$$\phi_p^* = \frac{M}{b^* \langle s^2 \rangle^{1/2} N_A \rho} \quad (2)$$

where  $M$  is the molecular weight of the polymer,  $\langle s^2 \rangle^{1/2}$  is the radius of gyration of the polymer,  $b^*$  is a constant (5.63 for hexagonal close packing of the polymer),  $N_A$  is Avogadro's number and  $\rho$  is the density of the polymer. The value of  $\langle s^2 \rangle^{1/2}$  was calculated from the intrinsic viscosity of the corresponding polymer solution using the Stockmayer-Fixman relationship (9). The values for  $\phi_p^*$  derived were found to be 0.029, 0.02 and 0.01 for PEO with  $M$  of 20,000, 35,000 and 90,000 respectively. It seems that the  $\phi_p^*$  values are always higher than the  $\phi_p^+$  values.

With further increase in  $\phi_p$  above  $\phi_p^+$ , the yield value continues to increase indicating an increase in the extent of flocculation. Several mechanisms were proposed to explain the flocculation induced by the addition of free (non-adsorbing polymer). The first explanation was given by Asakura and Oosawa (10). When two particles approach each other within a distance of separation that is smaller than the diameter of the free polymer coil, exclusion of the polymer from the interstices between the particles takes place leading to the formation of a polymer free zone. This produces an attractive force associated with a lower osmotic pressure in the region between the particles. Thus, the flocculation results from depletion of the free polymer from the interstices between the particles and hence is usually referred to as depletion flocculation.

The theory of Asakura and Oosawa (10) has been either extended and/or modified by various investigators. For example, Vrij (11) has developed a theory for destabilisation based on the expulsion of the polymer from the interstitial spaces between approaching particles based on "volume restriction" as well as "osmotic" considerations. Vincent et al (8) have specifically considered the case where the particles carry an adsorbed polymer layer; they calculated the net free energy change involved when the free polymer coils are displaced from the region between the particles into bulk solution. In their theory, only mixing terms are considered; the net free energy involved in the exchange process amounts in effect to the free energy of mixing of the

adsorbed layers (at a given separation) minus the free energy gained by the demixing of the (displaced) polymer coils with the adsorbed layers. Feigin and Napper (12) have developed a theory based upon rotational isomeric state Monte Carlo procedures for calculating segment concentration profiles of macromolecules in the region between two particles. They then calculated the change in the overall free energy of mixing with distance of separation between the plates using Flory-Huggins theory of polymer solutions.

The above theories may be used for interpretation of the rheological results, in particular the increase in the Bingham yield value,  $\tau_\beta$ , with increase in  $\phi_p$ . As mentioned before (3)  $\tau_\beta$  can be analysed in terms of interparticle interactions. This may be equated to the amount of energy needed to totally separate the flocs into single units (13,14), ie.

$$\tau_\beta = N E_{\text{sep}} \quad (3)$$

where  $N$  is the total number of contacts between particles in flocs and  $E_{\text{sep}}$  is the energy required to break each contact. The total number of contacts,  $N$ , may be related to the particle volume fraction,  $\phi_s$ , and the average number of contacts per particle,  $n$ , by (13),

$$N = 1/2 \left( \frac{3 \phi_s n}{4 \pi a^3} \right) \quad (4)$$

where  $a$  is the particle radius. Combining equations (3) and (4),

$$\tau_\beta = \frac{3 \phi_s n E_{\text{sep}}}{8 \pi a^3} \quad (5)$$

Equation (5) shows that  $\tau_\beta$  is directly proportional to the energy of separation,  $E_{\text{sep}}$ , needed to separate the flocs.  $E_s$  may be equated to the free energy minimum,  $G_{\text{min}}$ , in the free energy-distance curve in the presence of free polymer.  $G_{\text{min}}$  may be estimated using the theory of Vincent *et al* (8); the details of the calculations are given in the Appendix. Fig. 6 shows the variation of  $G_{\text{min}}$  (in kT units) with  $\phi_p$  for the three PEO molecular weights used. It is clear that  $G_{\text{min}}$  increases with increase in  $\phi_p$ , thus explaining the increase in  $\tau_\beta$  with  $\phi_p$  (see Figs. 3 and 4). Moreover, at any given  $\phi_p$ ,  $G_{\text{min}}$  increases with increase of  $M_w$ , thus explaining the

increase in  $\tau_{\beta}$  with increase of  $M_w$  at a given free polymer concentration.

In principle, it is possible to calculate  $\tau_{\beta}$  from the  $G_{\min}$  values given in Fig. 6, using equation (5). If the flocs are assumed to be close-packed structures, then  $n$  must be between 8 (random-close packing) and 12 (hexagonal close-packing). However, equation (5) is based on a monodisperse suspension. With a suspension containing a distribution of particle sizes, one cannot replace  $a$  by the average particle size, since the number of contact points  $N$  in a floc is greater than that calculated using an average particle size. With a polydisperse suspension it is difficult to calculate the number of contacts without knowledge of the exact particle size distribution. Since this was not available in the present system, no attempt was made to calculate  $\tau_{\beta}$  (and hence compare it with the experimental value). However, the trend in  $\tau_{\beta}-\phi_p$  correlates very well with the  $G_{\min}-\phi_p$  curves thus confirming the validity of the model used to estimate  $G_{\min}$ .

Sediment height and redispersion The results of the sediment height and redispersion experiments (Fig. 5) are consistent with the model of weak flocculation and the rheological data described above. In the absence of any added free polymer, the dispersion is colloidally stable and any separation as a result of sedimentation leaves a turbid supernatant of colloidally stable particles. The sediment formed is hard (in technical terms a "clay") as a result of the dense packing of the particles. The latter which sediment under gravity are able to move past each other (as a result of the strong repulsive force between the particles) forming a close-packed sediment requiring a large number of revolutions for resuspension. On addition of free polymer, the sediment height initially decreases and then reaches a minimum. This is accompanied by the formation of clear supernatant liquid indicative of particle flocculation. Under these conditions, the weakly flocculated sediment is easy to redisperse. However, with further increase in free polymer concentration, the extent of flocculation increases and the yield value increases. This is accompanied by an increase in sediment height and the sediment becomes more difficult to redisperse as a result of the increase in viscosity. Thus, the sediment height and redispersion experiments are consistent with the rheological results.

### Conclusions

Highly deflocculated concentrated suspensions can be obtained using block or graft copolymers consisting of an insoluble component having a high affinity to the particle surface and soluble chains (strongly solvated by the medium) which provide the stabilising moiety. These sterically stabilised suspensions

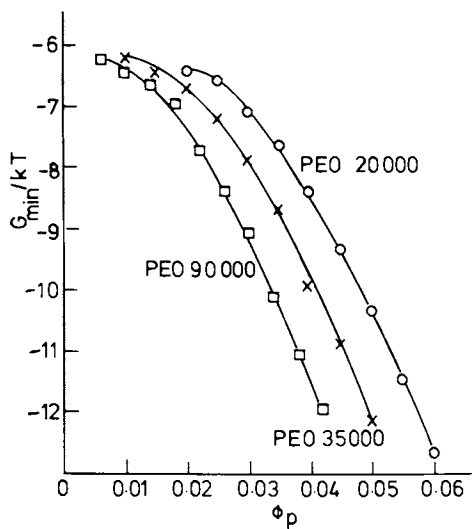


Figure 6. Variation of  $G_{\min}$  with  $\phi_p$  for three PEO molecular weights.

can be weakly flocculated by the addition of free non-adsorbing polymer, above a critical concentration which depends on the molecular weight of the free polymer. These weakly flocculated structures are easy to redisperse and, therefore, the phenomenon may be used to prevent claying.

### Acknowledgements

Most of the experiment work described in this paper has been carried out by Mr R Rajaram (Brunel University) during a six month industrial training period at Jealott's Hill. The authors are also indebted to Mr S Douglas for carrying out the adsorption isotherms. We are grateful to Mr F Waite of ICI Paints Division for valuable suggestions and stimulating discussions during the course of this study. We are also grateful to Dr B Vincent for making valuable comments.

### Appendix

#### Basic equations for calculation of free energy-distance curves

Vincent et al (8) showed that the net free energy balance involved in displacing coils into bulk solution on overlapping the sheath on their approaching particles may be approximated by,

$$G_s^p = G_{mix}^o + (n_p/2) G_{mix}^{pp} \quad (i)$$

where  $G_{mix}^o$  is the mixing interaction in the absence of free polymer;  $G_{mix}^{pp}$  is the mixing interaction between polymer coils and  $n_p$  is the number of displaced polymer coils. For hexagonal close packing (hcp),

$$n_p = 2S/3^{1/2} r^2 \quad (ii)$$

where  $r$  is the cross sectional area of the polymer coil which for hcp is

$$r = (2^{1/2} M/N_A \rho \phi_p)^{1/3} \quad (iii)$$

$S$  is the surface area of the lens shaped interaction zone,

$$S = 4\pi(a+\delta) (\delta - h) \quad (iv)$$

where  $\delta$  is the adsorbed layer thickness and  $h$  is half the surface-surface separation.

In equation (i) only mixing terms are considered (ie. any contribution from the volume restriction term was considered negligible). This is a reasonable assumption when  $\delta < 2h < 2\delta$  (15).

The total free energy is given by,

$$G_{\text{tot}} = G_S^P + G_A = G_{\text{mix}}^O - (n_p/2) G_{\text{mix}}^{PP} + G_A \quad (\text{v})$$

$G_{\text{mix}}^O$  can be calculated using equation (vi), assuming the adsorbed layer to be represented by simulated tails ie.

$$\begin{aligned} G_{\text{mix}}^O = & \frac{3\pi a kT}{15 v_1} (\bar{\phi}_p^a)^2 (1/2 - \chi) [10\delta^2 (\delta - h)^4 - 12 (\delta - h)^5 + 3(\delta - h)^6] \\ & + \frac{32\pi a kT}{105 v_1} \frac{(\bar{\phi}_p^a)^3}{\delta^3} (1/3 - \chi_2) [336 \delta^3 (\delta - h)^5 - 640 \delta^2 (\delta - h)^6 \\ & + 432 (\delta - h)^7 - 81 (\delta - h)^8] \end{aligned} \quad (\text{vi})$$

where  $\bar{\phi}_p^a$  is the average volume fraction of polymer in the adsorbed layer,  $v_1$  is the volume of a solvent molecule and  $\chi_1$  and  $\chi_2$  are Flory-Huggins interaction parameter coefficients in the virial expansion,

$$\chi = \chi_1 + \chi_2 \phi_p + \dots \quad (\text{vii})$$

For the calculation of  $G_A$  one needs to take account of the presence of the adsorbed layer. To a first approximation one may consider the interaction between the core particles (with Hamaker constant A) in a medium having a Hamaker constant equal to that of the polymer sheath,  $A_2$ , ie.

$$G_A = - \frac{\left( A_1^{1/2} \quad A_2^{1/2} \right)^2}{24h} \quad (\text{viii})$$

$A_2$  is given by (16)

$$A_2 = \left[ \frac{\bar{a}}{\phi_p} A_p^{1/2} + (1 - \frac{\bar{a}}{\phi_p}) A_s^{1/2} \right]^2 \quad (\text{ix})$$

where  $A_p$  and  $A_s$  and the Hamaker constants of the pure polymer and solvent respectively.

Finally, for the calculation of  $G_{\text{mix}}^{\text{PP}}$ , Vincent et al (8) used an extension of Flory's theory (17) for two interacting chains in solution, ie.

$$G_{\text{mix}}^{\text{PP}} = \left[ 4 \frac{\pi \langle s^2 \rangle}{3} \right]^{3/2} \frac{kT}{v_1} v_o^2 (1/2 - \chi_1) \exp \left[ - \frac{3 r^2}{4 \langle s^2 \rangle} \right] \\ + \frac{1}{9} [2 \langle s^2 \rangle]^{3/2} \frac{kT}{v_1} v_o^3 (1/3 - \chi_2) \exp \left[ - \frac{r^2}{\langle s^2 \rangle} \right] \quad (\text{x})$$

where  $r$  is the cross-sectional area of the free polymer coil and  $v_o$  is the segment density at the centre of the polymer coil,

$$v_o = \frac{M}{N_A \rho} \left[ \frac{3}{2 \langle s^2 \rangle} \right]^{3/2} \quad (\text{xi})$$

The  $G_{\text{tot}}$ -distance curves were established using the above equations. The values of the various parameters used in these

calculations are as follows:  $a = 500 \text{ nm}$ ,  $\delta = 5.0 \text{ nm}$ ,  $\bar{\phi}_p^a = 0.15$ ,  $A_1 = 19kT$ , (this value was obtained from refractive index measurements of ethirimol (18))  $A_p = 16.6kT$ ,  $A_s = 9.0kT$ ;  $\chi_1 = 0.473$ ,  $\chi_2 = 0.32$ . The values of  $R_G (= \langle s^2 \rangle^{1/2})$  are 5.52, 7.59 and 12.90 nm for PEO with  $M$  of 20,000, 35,000 and 90,000 respectively. From these energy-distance curves, the values of  $G_{\text{min}} (= E_{\text{sep}})$  were established.

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## Influence of Bentonite on the Rheology of Aqueous Pesticide Suspension Concentrates

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The influence of addition of sodium bentonite (a commonly used antisetling system) on the rheological behaviour of a pesticide suspension concentrate ( $250 \text{ g dm}^{-3}$ ) has been investigated. Steady state shear stress-shear rate curves were carried out to obtain the yield value and viscosity as a function of shear rate. The shear modulus was also measured using a pulse shearometer, and the residual viscosity was obtained in a few cases from creep measurements. The rheological parameters  $\tau_B$  (Bingham yield value),  $G_0$  (instantaneous modulus),  $\eta_0$  (residual viscosity) and  $G$  (shear modulus) all showed a rapid increase above  $30 \text{ g dm}^{-3}$  bentonite. This was attributed to the formation of a gel network structure in the continuous medium and the strength of such a gel increased with increase in bentonite concentration. The results could be qualitatively described in terms of the elastic floc model of Hunter and co-workers. Moreover, the settling characteristics of the structured suspensions were found to be consistent with the predictions from the rheological measurements. This demonstrates the value of rheological studies in predicting the long-term physical stability of suspension concentrates.

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It is now fairly well established that for the maintenance of the long-term physical stability of aqueous suspension concentrates, it is necessary to control the stability of the suspension in the colloid sense as well as the settling characteristics of the particles (1). Colloid stability is governed by the nature of the pesticide and the nature of the dispersing agent used as well as the various conditions encountered such as particle size, electrolyte concentration and temperature (1). On the other hand, the settling of coarse ( $> 1\mu\text{m}$ ) suspensions (which have a density greater than that of the medium) is usually controlled by addition of a second disperse phase that is capable of forming a "three dimensional" gel network in the continuous medium. Several systems may be used such as polymeric thickeners, fine particulate solids such as bentonite clays and oxides or combinations of the latter with polymers (1). The nature and level of the gelling agent required to prevent appreciable settling of particles and formation of hard "cakes" or clays depends on the density difference between disperse phase and medium, volume fraction of the disperse phase and interaction of the antissettling system with particles of the pesticide.

To arrive at the optimum level of gelling agent for a given pesticide suspension, it is necessary to study its effect on the rheological characteristics of the suspension. Rheological measurements provide quantitative information on the extent of structure formation in the system. As we will see later such structured suspensions exhibit viscoelasticity, i.e., their response to the strain is partly of a viscous and partly of an elastic contribution. The viscoelastic properties of a suspension concentrate may be correlated with its long-term physical stability. Information on the viscoelastic properties can be obtained using rheological measurements at small deformations (1). In this case it is possible to analyse the results in terms of the viscous and elastic components. Thus systematic investigations using rheology should, in principle, enable the formulation chemist to arrive at the optimum conditions needed for the prevention of claying of suspensions, and predict their long term physical stability. These measurements have been recently applied in our laboratory during the development of suspension concentrates and they certainly show promise both for optimisation of formulations and prediction of the long-term physical stability.

In this paper, we report some rheological results on the effect of addition of sodium bentonite, a commonly-used antissettling system, to a pesticide suspension concentrate. Steady state shear stress-shear rate measurements were carried out to obtain the yield value and viscosity as a function of shear rate. These experiments were supplemented by low deformation measurements to investigate the viscoelastic

behaviour of the structured suspension. The results obtained were correlated with the settling characteristics of the suspension concentrates.

### Experimental

**Materials** The pesticide, manufactured by ICI, was an experimental sample which was used as received. It was a white crystalline solid having a density of  $1.22 \text{ g cm}^{-3}$ .

The bentonite used was a commercial material (Bentopharm B20 supplied by Bromhead & Dennison, Welwyn, Herts and was used as received.

The dispersing agent used for preparation of the suspension was a commercial sample of lignosulphonate, namely Ufoxane 3A supplied by Borregard (Norway).

**Preparation of Suspensions** A standard  $400 \text{ g kg}^{-1}$  aqueous pesticide suspension was prepared by a wet milling process using a Dyno mill (ex. Willy. A. Bachofen, Basle, Switzerland).  $40 \text{ g kg}^{-1}$  Ufoxane 3A was used for the preparation of the mill base. The suspension produced had a wide range of particle sizes (as identified by optical microscopy) with an average size of  $\sim 1 \mu\text{m}$ , determined using a Coulter Counter (Model TAI1).  $100 \text{ g kg}^{-1}$  bentonite was prepared by dispersing the powder in water using an Ilado (Ex Ystral GmbH., Gottingen, W. Germany) stirrer. The suspension was left standing for 5 days to ensure adequate swelling of the bentonite.

The pesticide millbase and bentonite dispersion were mixed in various proportions to obtain formulations in which the final concentration of the pesticide was kept constant at  $250 \text{ g dm}^{-3}$ , and the bentonite was varied from 0 to  $57.5 \text{ g dm}^{-3}$  on the basis of the continuous phase. The pH of the resulting suspensions was adjusted to 7.0 in all cases. The same samples were used for rheological measurements and storage in 100ml stoppered graduated cylinders (see below).

### Rheological Measurements

**Steady State Measurements** These were carried out (at  $25^\circ\text{C}$ ) using two Haake 'Rotovisko' models RV100 and RV2 (MSE Scientific Instruments, Crawley, Sussex, England) fitted with an M 150 and MK50 measuring head respectively. The sensor system used was a coaxial cylinder type fitted with MV1 and NV bobs. The RV100 instrument was used to obtain steady state shear stress-shear rate curves. In this case the samples were sheared for 12 min at  $585 \text{ s}^{-1}$  and then left for 30 minutes to relax. The shear rate was then increased from 0 to  $585 \text{ s}^{-1}$  over a period of 78 s, after which the shear rate was reduced to 0 over the same period; the shear stress being automatically determined. From the shear stress-shear rate curves, the yield value was obtained by

extrapolation (see results section). Also viscosity-shear rate curves were established for each system. The RV2 instrument was used to obtain the yield value directly using the van Wazer method (2). Basically increasing increments of shear stress were applied to the dispersion, each time following the resultant angular displacement (strain) with time.

Before the yield point was reached, each angular displacement remained essentially constant with time. The stress above which there was a rapid decay with time was taken to be equal to the Bingham yield value.

Static (transient) Measurements Low deformation measurements were carried out using a Deer rheometer (model PDR81, Integrated Petronic Systems Ltd., London). This instrument was suitable for creep measurements, whereby a small stress was applied on the suspension, following the strain with time. The instrument was fitted with double concentric cylinder platens machined from Perspex, which were kept at constant temperature ( $25.0 \pm 0.1^\circ\text{C}$ ) by immersion in a thermostat bath in the instrument. The platens were approximately 60 mm in length and 50 mm in diameter with a gap of 1.5 mm. Within each gap, the shear rate varied by about 7%, which was considered unimportant for the low shear stress measurements. A constant stress was applied to the upper cylinder and its resultant displacement measured as a function of time. The instrument has a torque range of 0-33g cm corresponding to a shear stress range of 0-135 pa.

Shear Modulus Measurements The shear modulus  $G_0$  was determined using a Pulse Shearometer (Rank Bros., Bottisham, Cambridge) based on the model originally described by van Olphen (3,4) and later developed by Goodwin et al (5,6). Basically the dispersion was placed between two parallel Perspex plates each connected to a piezoelectric crystal. Using a pulse generator, a shear wave was generated at the bottom plate, which propagated through the dispersion and was detected by the upper plate crystal. The shear wave velocity through the dispersion  $U$  was measured from a plot of plate separation distance versus time of propagation of shear wave. The plot and calculations were automatically recorded using an Acorn Atom computer supplied with the instrument. The shear modulus,  $G$ , was then calculated from the expression,

$$G = U^2 \rho \quad (1)$$

where  $\rho$  was the density of the suspension concentrate.

Settling Experiments Suspensions containing various concentrations of bentonite clay (as those used for rheological measurements) were stored in 100 ml stoppered measuring cylinders at  $25^\circ\text{C}$ . The separation of a supernatant liquid and the sediment

volume formed were determined at weekly intervals (up to 21 weeks) until equilibrium was reached. The suspensions were then inverted end over end to measure the number of inversions required to redisperse any sediment formed.

## Results

Steady State Measurements Fig. 1 shows the shear rate-shear stress curves at various bentonite concentrations (calculated on the basis of the continuous phase). Hysteresis in the shear rate-shear stress curves was insignificant and the correlation between the ascending and descending curves was within experimental error. The results shown in Fig. 1 were therefore, the mean value of the ascending and descending curves. In the absence of any bentonite the suspension was Newtonian, whereas all suspensions containing bentonite at concentrations  $> 30 \text{ g dm}^{-3}$  were all pseudoplastic. This is illustrated from a plot of viscosity versus shear rate (Figure 2) which shows an exponential reduction of  $\eta_{\text{app}}$  with increase in shear rate.

Two extrapolation methods were used to obtain the yield value,  $\tau_{\beta}$ , from the shear rate-shear stress curves. In the first method, the data were fitted to a Bingham model, ie.

$$\tau = \tau_{\beta} + \eta_{\text{app}} \dot{\gamma}_{\text{app}} \quad (2)$$

where  $\eta_{\text{app}}$  is the apparent viscosity and  $\dot{\gamma}_{\text{app}}$  is the apparent shear rate. Thus, the yield value is that extrapolated from the linear portion of the shear stress-shear rate curve to  $\dot{\gamma} = 0$ . In the second method, the data were fitted to Casson's equation (7), ie.,

$$\tau^{1/2} = \tau_{\beta}^{1/2} + (\eta_{\text{app}} \dot{\gamma}_{\text{app}})^{1/2} \quad (3)$$

In this case  $\tau_{\beta}$  is obtained from a plot of  $\tau^{1/2}$  versus  $\dot{\gamma}_{\text{app}}^{1/2}$

The yield value was also measured directly using the van Wazer method (2). For comparison the yield value obtained using the above three methods was plotted versus bentonite concentration as shown in figure 3. It can be seen that the yield value obtained using Casson's extrapolation is close to the directly measured yield value using the van Wazer method. The extrapolated yield value using the Bingham model is significantly higher than that obtained by the other two methods. All results show a rapid increase in the yield value above  $30 \text{ g dm}^{-3}$  bentonite.

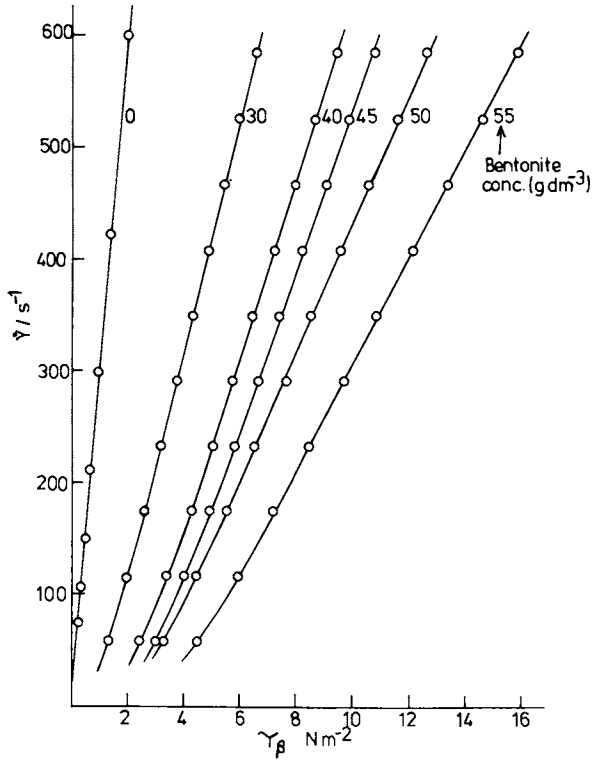


Figure 1. Shear rate - shear stress curves at various bentonite concentrations

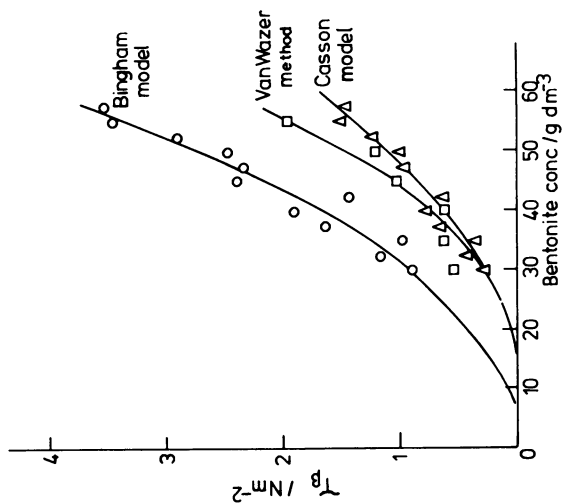


Figure 3. Yield value (obtained by three methods) vs. bentonite concentration

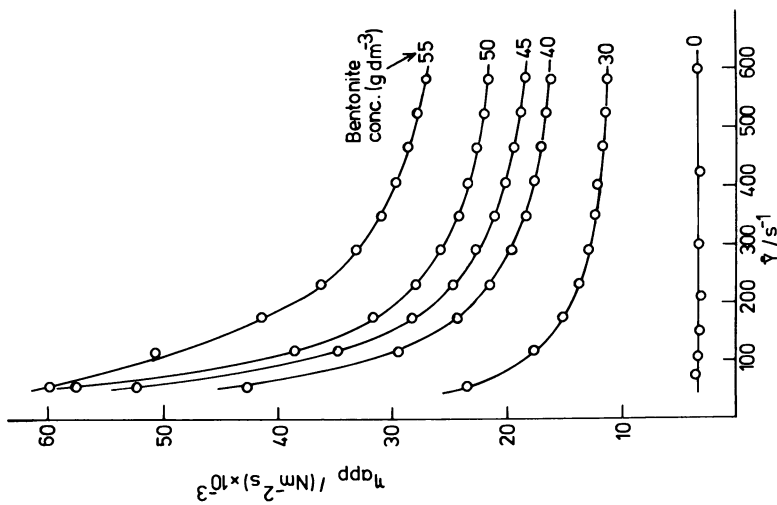


Figure 2. Viscosity vs. shear rate at various concentrations

Creep Curves Fig. 4 shows the creep curves for the formulations containing 30 and 45 g dm<sup>-3</sup> bentonite. Suspensions containing less than 30 g dm<sup>-3</sup> bentonite did not give a measurable creep curve. The creep curves shown in Fig. 4 are typical of those obtained with viscoelastic systems. They consist of three regions: (a) directly after the application of the stress one observes a rapid elastic deformation resulting in an elastic compliance  $J_0$  (instantaneous shear modulus  $G_0 = \tau/\gamma = 1/J_0$ ); (b) a slow elastic deformation, i.e. mixed viscoelastic region. In this region bonds are broken and reformed. Since all bonds do not break and reform at the same rate, a spectrum of retarded elastic compliances is obtained; (c) a region of viscous deformation, whereby the strain changes linearly with time. In this region individual aggregates flow past each other, since the time required to restore broken bonds is longer than the test period. The reciprocal slope of the linear portion of the creep curve gives the viscosity  $\eta_0$  at the applied stress  $\tau$ . Usually  $\eta_0$  increases with decreasing  $\tau$ , but reaches a limiting (Newtonian) value over a range of sufficiently small stresses. This limiting value is usually referred to as the residual viscosity  $\eta_0$ . However, since creep measurements are time consuming, the creep curves were only obtained at one shear stress. The latter was the smallest value (0.15 and 2.1 g/cm for the formulations containing 30 g dm<sup>-3</sup> and 45 g dm<sup>-3</sup> bentonite clay respectively) that could be applied to produce a measurable creep curve. Thus, strictly speaking, the viscosity calculated from these creep curves may not be identical to the residual viscosity, but it does correspond to the viscosity at some very low shear rate.

The creep curves of Fig. 4 show the three regions described above. The instantaneous compliance  $J_0$  can be used to calculate the instantaneous modulus  $G_0$  only for cases where  $J_0$  is fairly large (to give a measurable  $G_0$ ). This is the case with the sample containing 30 g dm<sup>-3</sup> bentonite which gives  $J_0 = 1.1 \times 10^{-2} \text{ m}^2 \text{ N}^{-1}$  corresponding to a  $G_0$  of  $91 \text{ N m}^{-2}$ . With the sample containing 45 g dm<sup>-3</sup> bentonite,  $J_0$  is very small and hence inaccurate, but the results indicate a much higher instantaneous modulus than for the sample containing 30 g dm<sup>-3</sup>. The viscosity calculated from the slope of the linear portion of the curve (which as mentioned above is close to the residual viscosity) was found to be  $3.3 \times 10^2 \text{ Nm}^{-2}\text{s}$  and  $9.02 \times 10^3 \text{ Nm}^{-2}\text{s}$  for the formulations containing 30 g dm<sup>-3</sup> and 45 g dm<sup>-3</sup> bentonite respectively. This again shows the large increase in  $\eta_0$  on increasing the bentonite concentration.

Shear modulus Fig. 5 shows the variation of modulus  $G$  with increase in bentonite concentration. Below 30 g dm<sup>-3</sup> bentonite, no signal was obtained using the pulse shearometer, indicating that either  $G$  is zero or too small to measure using



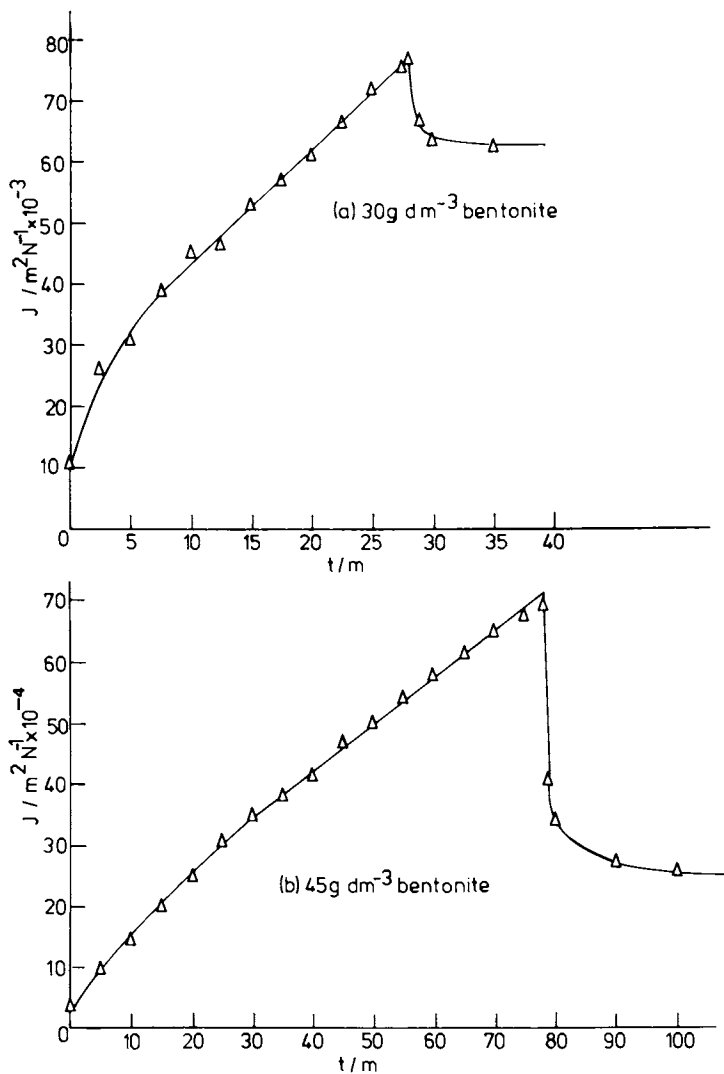


Figure 4. Creep curves at two different bentonite concentrations

this instrument. However, at bentonite concentrations  $>30 \text{ g dm}^{-3}$ ,  $G$  increased rapidly and linearly with increase in bentonite concentration. The shear modulus at  $30 \text{ g dm}^{-3}$  bentonite ( $\sim 30 \text{ Nm}^{-2}$ ) was clearly smaller than the value of  $G_0$  obtained from the creep curve, but as mentioned above, the latter value is not very accurate and in any case a direct comparison cannot be made, since  $G$  is not identical to  $G_0$ . The modulus obtained using the pulse shearometer was obtained at a frequency of  $\sim 200 \text{ Hz}$ .

Sedimentation Results After 21 weeks standing, the suspension that contained no bentonite, showed 5% separation and formed a hard sediment (clay) which required more than 30 inversions for complete redispersion. All other suspensions, which contained  $> 30 \text{ g dm}^{-3}$  bentonite clay formed a gel structure which could be broken by inversion of the measuring cylinder containing the suspension. A small separation occurred when the bentonite concentration was  $< 37.5 \text{ g dm}^{-3}$  above which no separation was observed within the period of investigation (21 weeks). The number of inversions needed to break the gel was plotted versus bentonite concentration in Fig. 6. For comparison, the extrapolated yield value is also shown as a function of bentonite concentration in the same figure. It is clear, for Fig. 6 that the number of inversions required to break the gel structure increases steeply with increase in bentonite concentration and thus the correlation with the increase in yield value is good. Both results show an increase in gel strength with increase in bentonite concentration as expected. Indeed at a bentonite concentration  $> 50 \text{ g dm}^{-3}$ , the gel was so strong that the whole suspension appeared solid.

## DISCUSSION

The rheological results obtained using both high and low deformation measurements are all consistent, showing a rapid increase in the rheological parameters,  $\tau_B$ ,  $G_0$ ,  $\eta_0$  and  $G$

above  $30 \text{ g dm}^{-2}$  bentonite (corresponding to a volume fraction of 0.008). This points to a rapid build-up in structure above this bentonite concentration. The mechanism by which a three-dimensional gel network is formed with bentonite clays has been investigated by several authors (8-15). There are generally two mechanisms for gelation. The first is based on the interaction between double layers (which occurs at large distances particularly at low electrolyte concentrations) which leads to a build-up of gel-structure since a substantial volume is occupied as the particles rotate. This mechanism was first proposed by Norrish (9,10) and later supported by Callaghan and Ottewill (16) who directly measured the internal pressure between the plate-like particles, due to the overlap of the double layers. Clearly the gel point depends on the volume fraction of

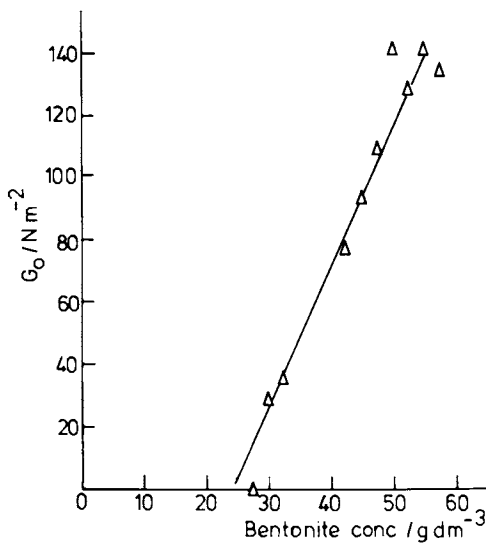


Figure 5. Variation of modulus with bentonite concentration

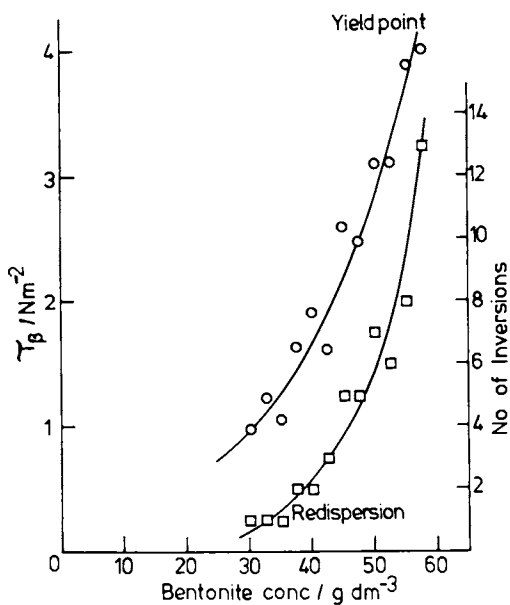


Figure 6. Correlation between gel 'strength' and yield value

the particles which determines the range of interaction between them.

The second mechanism, first proposed by van Olphen (8,11-14), assumed structure formation in bentonite gel to be due to edge-to-flat surface association of the plate-like particles as a result of electrostatic attraction between the oppositely charged double layers at the surface. This so-called "house of cards structure" is likely to occur provided the pH of the suspension is below the isoelectric point of the edges, which are then positive and become attracted to the negatively charged faces.

In the present system of pesticide suspension plus bentonite and a dispersing agent of lignosulphonate, the mechanism of "gel" formation is more complex, since there may be some interaction between the clay and pesticide particles. Moreover, the role of the dispersing agent is not very clear. However, since the trend of the increase of  $\tau_g$  and  $G$  with bentonite concentration is the same as that observed in the absence of pesticide and dispersing agent (11-14,17), it is highly likely that the mechanism of gelation of bentonite in the continuous phase of the pesticide suspension is the same as that in the absence of the pesticide. Assuming this to be the case, the gel network formed in the continuous phase is either due to the strong repulsion between the clay particles and/or due to the edge-to-face flocculation suggested by van Olphen (8). Considering the pH of the suspension (~7) and the presence of sodium lignosulphate which will neutralise any positive charge on the edges, it is highly likely that gelation in the present system is the result of double layer repulsion between the faces of the swollen bentonite gel. However, since the clay was not purified, there is also the possibility of some flocculation occurring as a result of the presence of electrolyte in the system. Whatever the mechanism, all these interactions lead to the formation of a non-Newtonian system and the build-up of viscoelastic behaviour as a result of the strong interaction between the particles. A gel point may be defined as that at which the interacting particles fill the available space. In the present system this seems to occur at  $30 \text{ g dm}^{-3}$  bentonite, corresponding to a volume fraction  $\phi_s = 0.008$ . This shows that the interaction is long-range and the extended double layers fill the available space. The measured yield value and modulus are a measure of the interaction force between the extended double layers (which as mentioned above can be repulsive if the edges are negative or attractive if a positive charge remains on the edges). This interaction force is inversely proportional to the exponential of the interparticle distance, accounting for the strong dependence of  $G$  and  $\tau_g$  on bentonite concentration.

The quantitative interpretation of rheological results with such complex systems, as those used in the present investigation, is at present not possible. However, Hunter and collaborators (18-21) introduced two models to interpret the rheological

behaviour of flocculating dispersions. The first, that is based on the extension and modification of Michaels and Bolger model (22), is the 'floc rupture' model. This implies that in the high shear region the flow unit is the single particle and the largest floc unit is the doublet, which becomes completely destroyed by the shear force involved ( $>10^3 \text{ sec}^{-1}$ ), ie. the doublet has a

life-time of the order of  $10^{-3} \text{ sec}$ . In this case, the extrapolated (Bingham) yield value  $\tau_\beta$  is given by (19,22).

$$\tau_\beta = \frac{3\phi_H^2}{a^3} E_s \quad (4)$$

where  $a$  is the particle radius,  $\phi_H$  is the hydrodynamic volume fraction of the bentonite particles and  $E_s$  is the energy needed to separate a doublet.  $E_s$  is the net energy resulting from van der Waals attraction and double layer repulsion, ie.

$$E_s = \frac{A a}{12 H_o} - V_R \quad (5)$$

where  $A$  is the Hamaker constant and  $H_o$  the distance of separation between the particles. In the case where the double layers are of opposite sign, eg, with face-edge flocculation,  $V_R$  is attractive and  $E_s$  is the sum of double layer and van der Waals attraction.

The second model introduced by Hunter and coworkers (20,21) is the 'elastic floc' model. In this case, the structural units (which persist at high shear rates) are assumed to be small flocs of particles (called floccules) which are characterised by the ability of the particle structure to trap some of the dispersion medium. In this energy dissipation is considered to arise from two processes, namely the viscous flow of the suspension medium around the flocs (which are the basic flow units) and the energy involved in stretching the flocs to break the floc doublets apart so that the amount of structure in the system is preserved inspite of the floc-floc collision. This model gives the following expression for the yield value,

$$\tau_\beta = \beta \eta_s \dot{\gamma} (a_{\text{floc}})^2 \Delta\phi_s^2 C_{\text{FP}}/a^3 \quad (6)$$

where  $\beta$  is a constant ( $= 27/5$ ),  $\lambda$  is the orthokinetic capture

efficiency which depends weakly on shear rate  $\dot{\gamma}$  ( $\lambda \propto \dot{\gamma}^{-0.18}$ ),  $\Delta$  is the distance through which bonds are stretched inside the floc with radius  $a_{\text{floc}}$  and  $C_{\text{FP}}$  is floc volume ratio, ie. the

degree to which liquid is trapped in the floc,

$$C_{FP} = \phi_F / \phi_S \quad (7)$$

where  $\phi_F$  is the volume fraction of flocs.

Both equations (4) and (6) predict a linear relationship between

$\tau_B$  and  $\phi_S^2$ . This is shown in Fig. 7 both for the extrapolated (Bingham) and Casson's yield value. In both cases the linear relationship is maintained indicating that such crude models may be applied to the rheology of the complex system of bentonite clay plus pesticide suspension. It should be mentioned, however, that the elastic floc model is a more realistic description of the system, since the assumption of a maximum of doublets in the floc rupture model is not justified with a concentrated suspension with many body interactions.

Accepting the elastic floc model as a reasonable description of the structured suspension, it is possible to calculate a few more parameters from the experimental results. For example  $C_{FP}$  may be calculated from  $\phi_F$ , which, in turn, may be obtained from the plastic viscosity,  $\eta_{PL}$  using the Mooney equation (23),

$$\eta_{PL} = \eta_S \exp\left(\frac{2.5 \phi_F}{1 - k' \phi_F}\right) \quad (8)$$

where  $\eta_S$  is the viscosity of the medium and  $k'$  is the so called "crowding factor" which may be taken as 1.4, so that  $\eta_{PL}$  becomes infinitely large and  $\phi_S$  approaches the close-packing value (24). Since the measured  $\eta_{PL}$  was that of pesticide suspensions plus bentonite then  $\phi_F$  represents the floc volume fraction of pesticide plus bentonite. Values of  $C_{FP}$  were calculated using equations (7) and (8) and plotted versus  $\phi^2$  as shown in Fig. 7. The results show that  $C_{FP}$  increased linearly with  $\phi^2$  which means an increase in the amount of trapped solvent with increase of bentonite concentration, as expected.

The low shear rheology measurements also show a rapid increase in the viscoelastic properties (modulus and zero shear viscosity) with increase of bentonite concentration above the gel point ( $> 30 \text{ g dm}^{-3}$  bentonite). Several models have been proposed to account for the elastic properties of concentrated dispersions, of which that originally proposed by van den Tempel (25) and later developed by Papenhuizen (26) seems to be the most appropriate for the present system. According to this model, if the interaction energy minimum between adjacent particles is sufficiently negative, a three-dimensional network structure may ensue, giving an elastic component. Various models can be used to represent the three dimensional structure, the simplest of which would be either an ideal network where all particles are

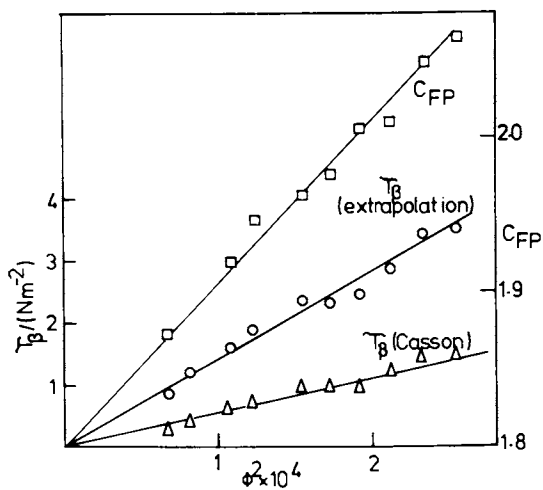


Figure 7. Variation  $\tau_\beta$  and  $C_{FP}$  with  $\phi_s^2$

arranged in a statistical network of chains, or where the particles are aggregated in clusters or agglomerates which are connected by chain particles. In the latter case, the mechanical strength of the network is mainly determined by the relatively few particles which link the agglomerates together. In the present system of pesticide suspension plus bentonite, the latter form a network in the continuous medium which now elastically supports the solid mass of the suspension. Moreover, as a result of this network a high residual viscosity is obtained as strain from the creep curves (Fig. 5).

The sedimentation results obtained with the structured suspensions, are consistent with the predictions from rheological investigations. In the absence of any bentonite clay, the pesticidal suspension exhibits Newtonian behaviour with unmeasurable yield value, modulus or residual viscosity. In this case the particles are free to settle individually under gravity forming a dilatant sediment or clay. On the other hand, at bentonite concentrations above the gel point ( $> 30 \text{ g dm}^{-3}$ ) the non-Newtonian behaviour of the suspensions and in particular their viscoelastic behaviour results from the formation of a "three-dimensional" network, which elastically supports the total mass. After 21 weeks standing in 100 ml measuring cylinders, no separation was observed when the bentonite concentration was  $> 37.5 \text{ g dm}^{-3}$  corresponding to a modulus  $> 60 \text{ Nm}^{-2}$ . Clearly the modulus value required to support the mass of the suspension depends on the density difference between particle and medium. The increase in gel strength with increase in bentonite concentration above the gel point is consistent with the increase in yield value and modulus. On the other hand, the limited creep measurements carried out on the present suspension showed a high residual viscosity  $\eta_0$  of the order of  $9000 \text{ Nm}^{-2}\text{s}$  when the bentonite concentration was  $45 \text{ g dm}^{-3}$ . As recently pointed out by Buscall *et al* (27) the settling rate in concentrated suspensions depends on  $\eta_0$ . With a model system of polystyrene latex (of radius  $1.55 \mu\text{m}$  and density  $1.05 \text{ g cm}^{-3}$ ) which was thickened with ethyl hydroxy ethyl cellulose, a zero shear viscosity of  $10 \text{ Nm}^{-2}\text{s}$  was considered to be sufficient to reduce settling of the suspension with  $\phi = 0.05$ . The present pesticide system thickened with bentonite gave  $\eta_0$  values that are fairly high and therefore no settling was observed.

### Conclusions

For full evaluation of the flow behaviour (rheology) of structured pesticide suspension concentrates and their settling characteristics, it is necessary to carry out measurements at small and large deformations. Such investigations provide valuable information on the viscoelastic properties of the suspension and if sufficiently analysed may be



used to predict the settling characteristics of the suspension concentrates.

### Acknowledgements

The application of low shear rheological measurements were the outcome of a joint research project between ICI Plant protection Division (Th. F. Tadros) and Bristol University (Prof. R. H. Ottewill, Dr G J Goodwin and Dr R Buscall). The authors are grateful to the Bristol group for establishing these techniques and their application to model suspensions.

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# The Preparation of Aqueous-Based Flowables Ranging the Sample Size from Sub-Gram to Several Gallons

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In the course of developing pesticide candidates, it is often necessary to supply commercial type formulations for advanced greenhouse testing as well as for field plot work. Often requests are submitted for these types of formulations in quantities ranging from sub-gram to several gallons. This paper will discuss the evaluation of several wet milling systems for providing precisely controlled (percent a.i., particle size, etc.) aqueous base flowables in a wide range of sample sizes. Included will be data on grind parameters (i.e., grind time vs. grind media type and charge) for the Crescent Dental Mills, as well as the .01, 1S and 01 Szegvari Attritor systems.

One of the tasks that the formulation chemist is often called upon to perform is to supply samples of formulations which are of commercial quality, yet may vary in size from a few milligrams of active ingredient to several pounds. As is often the case, especially with experimental compounds, minimal quantities of the compound are available for formulation development work. In the event that such formulations are requested for compounds having very limited solubility in solvents or solvent systems commonly used in emulsifiable concentrates, this challenge can become even greater. It is the purpose of this paper to present some techniques for supplying samples of aqueous based flowables in these size ranges.

We will be looking at several commercially available wet milling units and demonstrating their utility in meeting our stated objectives. It is not within the scope of this paper to present a treatise on grind kinetics or to correlate experimental results

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with theory. However, an attempt will be made in some cases to suggest some milling parameters (i.e., grind media type, grind media charge and sample size) which should help in delivering the desired sample.

### BACKGROUND

To set a general basis for this discussion with regards to the different mills included in this paper, it may be helpful to address the efficiency of the ball milling process as it relates to two simple equations. The effectiveness of a particular type of mill or type of grind media in breaking particles on impact is related to the momentum of the grind media which is equal to the mass of the media times its velocity. Therefore, grind time can be minimized for a specific media size by increasing its velocity and/or its mass. A second factor which affects grind time for agitated type mills (i.e., the Szegvari Attritor) has been expressed as:

$$\text{Grind time} = \frac{kd}{n} \quad (1)$$

k = a constant which factors in the effect of the material being milled, type of media and mill type.

d = diameter of media

n = RPM of the agitator

This equation shows that grind times can be minimized by reducing the media size, which essentially increases the number of media per unit volume and, therefore, number of impacts per unit time. Also, increasing mill speed has the effect of reducing grind time by increasing media momentum as well as the number of impacts per unit time. These two equations explain why a particular mill operating at a specific speed and media type has an optimum media size. This is illustrated(2) in Figure 1.

As the media size (mass) decreases, fewer and fewer effective impacts occur and the mill efficiency falls off. On the other hand, as media size increases, fewer and fewer impacts actually occur, which also reduces mill efficiency.

Another important factor when attempting to prepare flowables of specific sample sizes with small mills is media charge. The greater the media charge, the faster the sample will grind but at the same time mill capacity decreases. Reducing media charge below a specific level to increase mill capacity greatly reduces the efficiency of the mill. It's, therefore, usually necessary to compromise several factors in order to do the best job of turning out the desired sample.

More extensive theoretical approaches in wet milling are available (3).

#### EQUIPMENT

The milling equipment evaluated in this limited study was selected on the basis of their ability to supply precise and reproducible samples of a specific size range. The evaluation of other types of available mills, having similar capabilities, was beyond the scope of this study. A brief description of the mills evaluated is included below.

##### Crescent Wig-L-Bug, Model 3110-3A

This machine (Figure 2) is manufactured by the Crescent Dental Mfg. Co. and was designed to wet or dry mill very small samples. It has been used extensively in other applications (i.e., spectroscopy - infrared potassium bromide pellet technique). All of the Wig-L-Bug models are based on a very rapid reciprocating motion. The grind chamber is swung through a 6-1/2 degree arc in a figure 8 formation at 3200 RPM. This provides 200 changes in mill direction per second and results in very rapid milling of most materials to a low micron range. This machine can be equipped with a number of vial type grind chambers of various materials and sizes. The chamber used in this work consisted of a ground agate vial, 9/16 inch diameter x 1-5/16 inch long, with an agate stopper and had a total working volume of about 1.8 cc. The chamber was mounted to the oscillating arm via an available plexiglass adaptor (stock numbers 3118 and 3115).

##### Crescent Wig-L-Bug, Model 6000

This mill (Figure 3) is based on the same reciprocating motion as the Model 3110-3A, however, it is much larger in size. It is supplied with a 1/4 horsepower split phase motor and is designed to use a 7/8 inch diameter x 2 inch long stainless steel or tungsten carbide grind chamber which has a working volume of about 9 cc.

##### Attritor, Model 01

This equipment is manufactured by the Union Process Company and is used widely as a research tool in a number of industries. It is based on an agitated bed principle and has a grind chamber capacity of 750 ml. The unit comes equipped with a variable speed

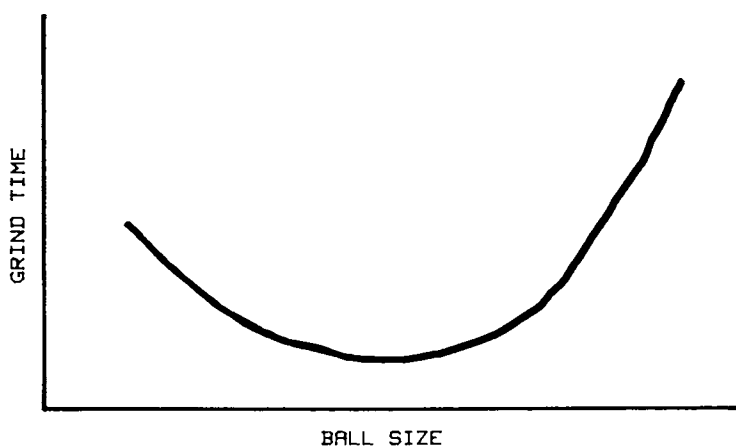


Figure 1. The Effect of Media Size on Grind Time.

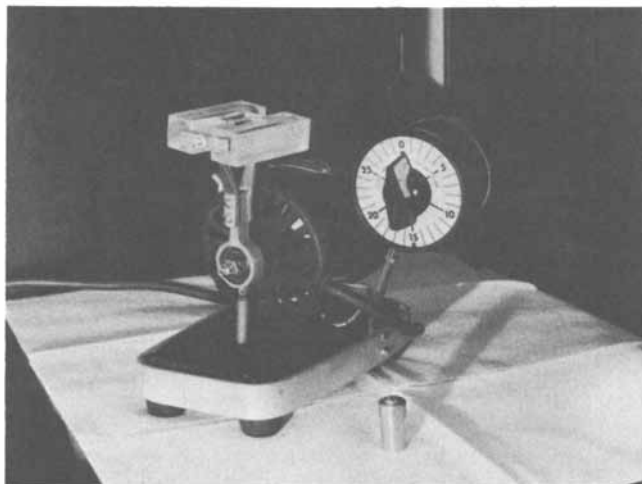


Figure 2. Crescent Mill Model 3110-3A with Grind Chamber and Grind Chamber Adaptor.

agitator and uses a jacketed stainless steel grind chamber. Typical grind media used with this unit includes spheres of various sizes and of materials such as stainless steel, ceramic, zirconium, and glass.

#### Attritor, Model 01, Mini Cup

The mini cup (Figure 4) is a simple insert adaptor which effectively reduces the grind chamber volume of the 01 Attritor to about 95 ml. The adaptor and special agitator are available from the mill manufacturer.

#### Attritor, Model 1-S

This unit is a larger batch type laboratory mill, as compared to the Model 01. The unit used had a grind tank capacity of 1-1/2 gallon and was equipped with a jacketed grind tank and variable speed agitator.

#### Attritor, Q1 System

The circulation attritor is well known in the industry, and the Q-1 system has been shown to be quite useful as a pilot plant tool in the development of commercial flowable formulations. The unit used had a 1.9 gallon, jacketed, grind tank with a variable speed agitator and which could be fitted to a 5-gallon or 20-gallon side tank via a variable speed positive displacement pump.

#### FORMULATIONS

The technique used in the routine preparation of small samples (0.5 to 200 ml) of aqueous based flowables was to work from a preformulated base which could be simply mixed with the active ingredient and milled. This approach saved a great deal of time, since the 6 to 10 different ingredients did not have to be mixed for each preparation. A typical formulation base should contain most of the essential ingredients to provide a fairly shelf-stable flowable. Its ingredients should include a good wetting and dispersing agent which has the quality of being a low foamer. A short chain glycol can be used as an antifreeze agent and a preservative should be included, since the base is often made up and held at room temperatures for long periods. It is important that a effective thixotropic agent or suspending agent be used which provides good dispersing properties when diluted for spraying and yet provides good shelf stability.

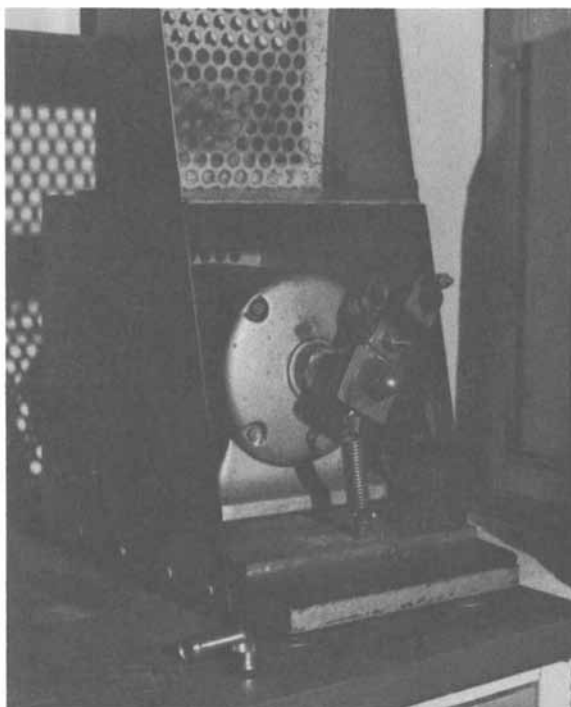


Figure 3. Crescent Mill Model 6000 with Grind Chamber.



Figure 4. Attritor Model 01 Mini Cup Adaptor.



Milling Runs

Most of the milling runs presented in this paper were made on the small Crescent mills, particularly on Model 6000. This was done in an effort to fully explore the utility of this equipment as a laboratory tool for preparing very small samples of pesticide flowables. In these runs, a preemergence herbicide, dimethyl 2,3,5,6-tetrachloroterephthalate, was selected to serve as a model compound. This material has a melting point of 156°C and can be readily milled to the less than five micron size range. In the studies with the Crescent mills, a flaked technical was used which had been mortar and pestled and screened to less than 60 mesh feed material.

The general objective of this study was to determine the sample size limits of each of the above mills. Factors which affected mill efficiency and grind times were also evaluated. In some cases, the grind times required to reduce the sample particle size to less than three microns were determined as a function of grind media type, grind media charge and sample size. All particle size analyses were carried out on a Coulter Counter (Model TA II).

Crescent Wig-L-Bug, Model 3110-3A

The grinding time data generated on this apparatus are shown in Table I.

Table I. Particle Size (u) vs. Grind Time for the Wig-L-Bug

<u>Grind Media</u>		<u>Sample Size,</u>	<u>Conc. % a.i.</u>	<u>Particle Size (u) vs. Grind Time</u>		
<u>Type</u>	<u>Charge</u>			<u>1 min.</u>	<u>2 min.</u>	<u>4 min.</u>
1 mm Glass	1.35 g (50%)	0.6	10	3.4	2.4	
1 mm Glass	1.35 g (50%)	0.9	10	5.0	3.5	2.9
1 mm Glass	1.35 g (50%)	0.9	30	5.3	3.8	3.2

Crescent Wig-L-Bug, Model 6000

A series of runs were made on this unit using 1/8 inch stainless steel grind media in which the sample size, media charge and slurry concentration were varied. Runs were also made using 1 mm glass media. The grind times versus particle size are shown in Tables II and III.

Table II. Wig-L-Bug 6000 Grind Studies (1/8-inch S.S. Media)

Media Charge, g	Sample Size, g	Conc. % a.i.	Particle Size (u) vs. Grind Time			
			1 min.	2 min.	4 min.	8 min.
35.1 (90%)	3.4	10	4.6	3.4	2.6	-
27.3 (70%)	3.4	10	4.8	4.1	2.9	-
19.5 (50%)	3.4	10	5.0	4.3	3.1	-
10.0 (25%)	3.4	10	-	-	8.0	6.0
19.5 (50%)	6.8	10	-	6.2	4.5	3.4
19.5 (50%)	5.1	10	-	6.0	4.0	3.3
19.5 (50%)	5.1	20	-	-	4.7	3.0
19.5 (50%)	5.1	30	-	-	4.5	3.5

Table III. Particle Size (u) vs. Grind Time with the Wig-L-Bug 6000 (1 mm Glass Media)

Media Charge, g	Sample Size, g	Conc. % a.i.	Particle Size (u) vs. Grind Time			
			1 min.	2 min.	4 min.	8 min.
10.5 (70%)	3.4	10	3.5	2.9	2.2	-
10.5 (70%)	5.1	10	3.6	3.0	2.4	-
7.5 (50%)	3.4	10	-	4.9	2.9	2.0
7.5 (50%)	5.1	10	-	4.9	3.1	2.2

Attritor, Model 01, Mini Cup Adaptor

The data from two grind runs are shown in Table IV. Both runs were made using 1/8-inch S.S. grind media with the agitator speed set at 75.

Table IV. Grind Studies with Attritor 01 Mini Cup (1/8-inch S.S. Media)

Media Charge (g)	Sample Size (g)	Conc. % a.i.	Particle Size (u) vs. Grind Time				
			10 min.	15 min.	20 min.	25 min.	30 min.
287 (70%)	45	10	4.6	3.8	3.2	-	-
287 (70%)	45	40	7.5	6.4	5.3	4.1	3.5

Attritor (Model 01)

Three runs were made on this model attritor to determine roughly the sample size ranges possible. A small, low concentrate was prepared, as well as a large, high concentrate. The resulting grinding times from these runs, as well as a medium size run are shown in Table V.

Table V. Grind Studies with Attritor 01 (1/8-inch S.S. Media)

Media Charge (g)	Sample Size (g)	Conc. % a.i.	Particle Size (u) vs. Grind Time				
			10 min.	20 min.	30 min.	40 min.	60 min.
970 (30%)	160	20	5.2	4.0	3.2		
2250 (70%)	400	40	6.3	4.1	3.1	-	-
1600 (50%)	550	50	6.0	4.7	4.5	3.8	3.3

Attritor (Model 1-S)

The following run (Table VI) was made using flaked technical and adding the formulation ingredients in the mill.

Table VI. Grind Study with Attritor 1-S (1/8-inch S.S. Media)

Media Charge, g	Sample Size, g	Conc. % a.i.	Particle Size (u) vs. Grind Time		
			60 min.	90 min.	120 min.
7,000 (70%)	2200	50	10	8	4

Attritor, Q-1 System

A series of runs were made on this mill, and grind times were measured to achieve a 3 micron average particle size for batch sizes ranging from 4.5 to 20 gallons. The mill used 1/8 inch stainless steel media and operated at 360 RPM, with the pump rate set at 2 gpm (see Table VII).

Table VII. Grind Time vs. Particle Size for Attritor Q-1 System

<u>Batch Size, gal.</u>	<u>Grind Time to 3 u, hours</u>
4.5	1.75
10.0	4.0
15.0	5.8
20.0	6.5

### DISCUSSION

The effective sample size ranges for the six mills, which we considered in this study, are summarized in Table VIII. As can be seen, these units in concert can cover essentially the entire range of sample sizes from a few milligrams of a.i. up to 50 kg. This capability should cover sample needs for most research and field development programs. The stated sample size ranges shown in Table VIII are based on the smallest practical sample size for each unit of a 5% flowable, and the largest sample possible of a 30 or 50% flowable.

Table VIII. Sample Size Capability of Mills

<u>Mill Type</u>	<u>Effective Sample Size Range, g a.i.</u>	<u>Grind Times, Min.</u>
Crescent Wig-L-Bug (3110-3A)	0.025 to 0.3	1 to 4
Crescent Wig-L-Bug (6000)	0.15 to 2.0	2 to 10
Attritor 01 (Mini Cup)	1.5 to 20	10 to 30
Attritor 01	15 to 250	30 to 90
Attritor (1-S)	200 to 1400	90 to 180
Attritor (Q-1 System)	900 to 50,000	120 to 480

The Crescent mills were found to be extremely versatile in providing the ultra-small samples. Grind curves for the 3110-3A model are shown in Figure 5 and indicate a very fast grind with the 1 mm glass media at the 50% charge level. In dealing with the two Crescent models, it was often found to be convenient to transfer the media with the sample and separate out the media after dilution for spraying. In the case of the smallest Crescent mill, the adaptor plus sample was a little too heavy for the unit and should be modified to provide smoother operation.

The grind curves for the Crescent 6000 mill are shown in Figures 6, 7 and 8. Figure 6 suggests an optimum media charge of about 40 percent. This would supply appreciable sample room and still retain a reasonable grind time. Comparative grind times for two different media types are shown in Figure 7 and demonstrate that the smaller glass media is perfectly acceptable, if not better than the stainless steel media. As is expected, as sample size is increased, grind time is increased (Figure 8). Total void space for this mill at 50% media charge is about 6.8 ml. It is interesting to note that a sample which occupied slightly more than 90% of the void space was still milled to the 3 u level in about 10 minutes.

Based on our experience in conducting this study, the Crescent mills have good versatility and should find utility in a number of research areas. Some that come to mind include:

- 1) Greenhouse evaluation of pesticides
- 2) Small scale particle size vs. efficacy studies
- 3) Radiolabelled studies
- 4) Sample preparation for toxicology studies

The 01 Attritor mini cup adaptor, sold by Union Process, does a good job at filling the sample size gap between the larger Wig-L-Bug and the 01 Attritor. As shown in Figure 9, reasonable grind times are possible for flowables of various concentrations. Making quantitative transfers in any milling procedure can be very difficult, as was true with this unit. It is, therefore, suggested that samples be ground at a high concentration (i.e., 50 to 55%) and that they then be let down to a lower concentration (i.e., 10 or 12%) with the mill washings. It is suggested that a formulation base be used in the washing step to maintain the desired physical properties of the formulation.

Grind curves for the attritor 01 and 1-S are shown in Figures 10 and 11. The units are similar in many respects and are capable of covering a wide sample size range. Generally, smaller samples can be handled in either unit by reducing the media charge to fit the sample size. It is suggested that at least 1/4 to 1/2 inch of liquid be maintained above the grind media. In the case with the 1-S, it is better to build the batch in the mill. In order to facilitate sample transfer, viscosity modifiers should be added to the formulation after the transfer.

The attritor Q-1 system was quite effective at handling samples from 2 gallons up to 20 gallons. The grind time to achieve a 3 micron grind versus sample size for a 40% flowable is shown in Figure 12. An optimal size range for this unit is in the 5 to 15 gallon range and would typically require 2 to 6 hours to achieve a

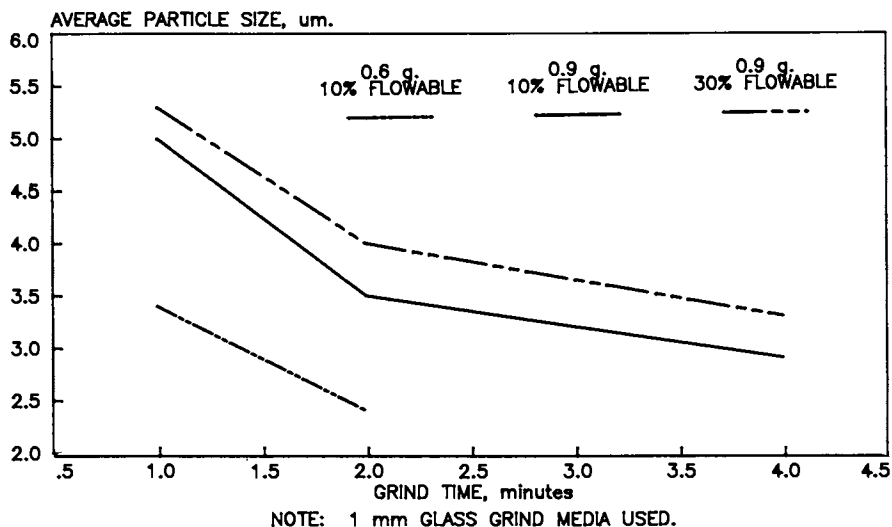


Figure 5. Particle Size vs. Grind Time (Crescent 3110-3A).

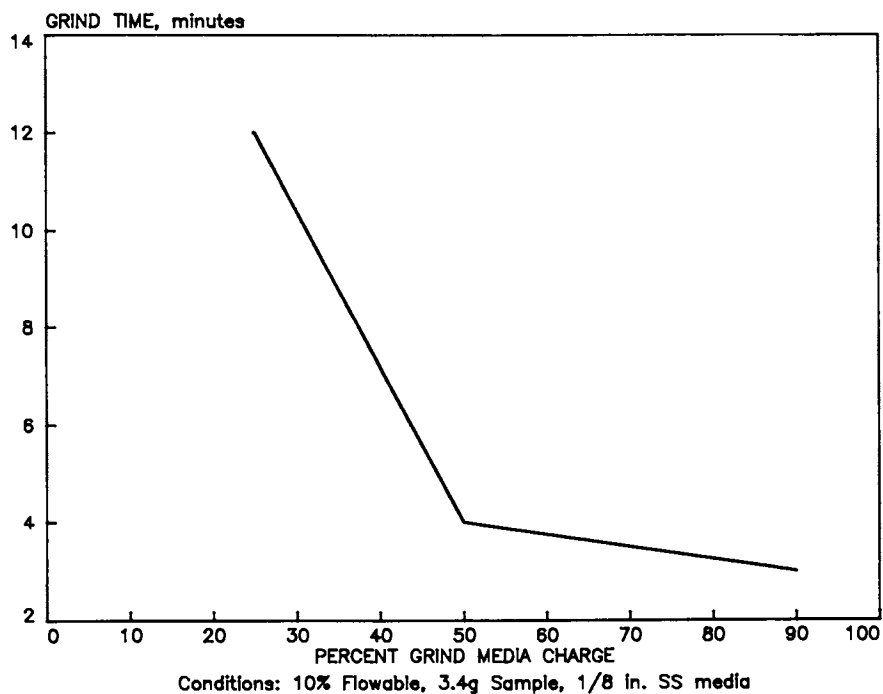


Figure 6. Milling Time (to 3  $\mu\text{m}$ ) vs. Grind Media Charge (Crescent 6000).

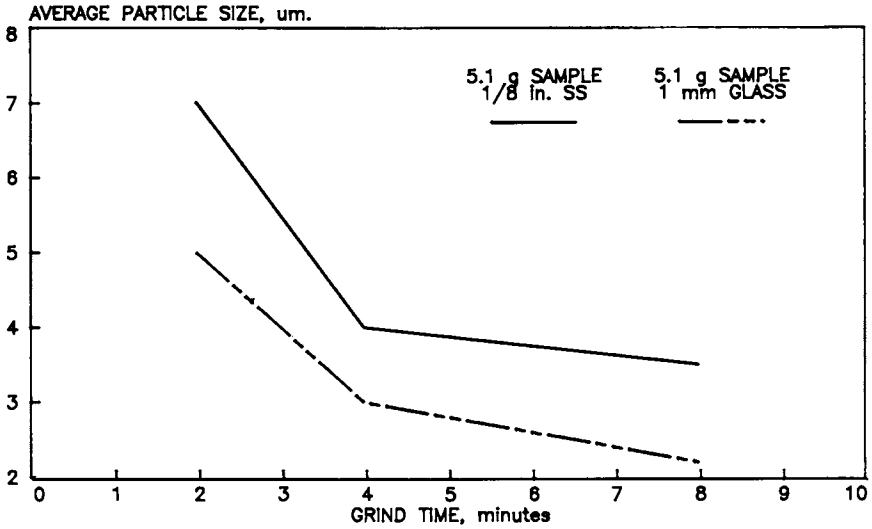


Figure 7. Particle Size vs. Grind Time - 10% Flowable (Crescent 6000).

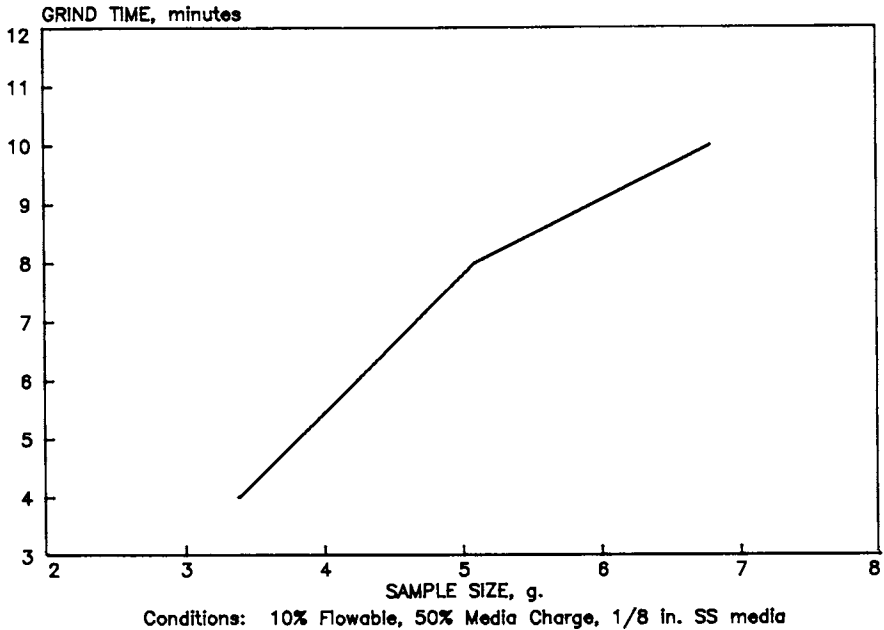


Figure 8. Grind Time (to 3  $\mu\text{m}$ ) vs. Sample Size (Crescent 6000).

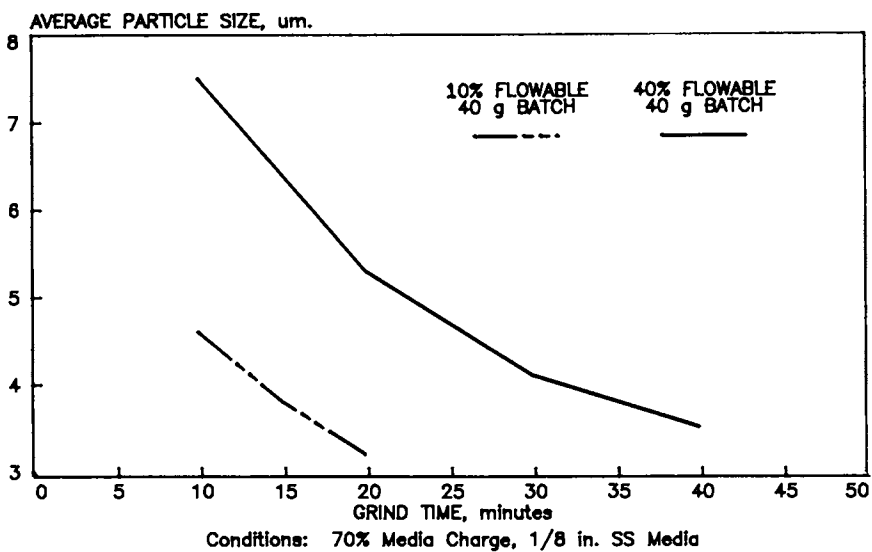


Figure 9. Particle Size vs. Grind Time (Attritor 01 - Mini Cup).

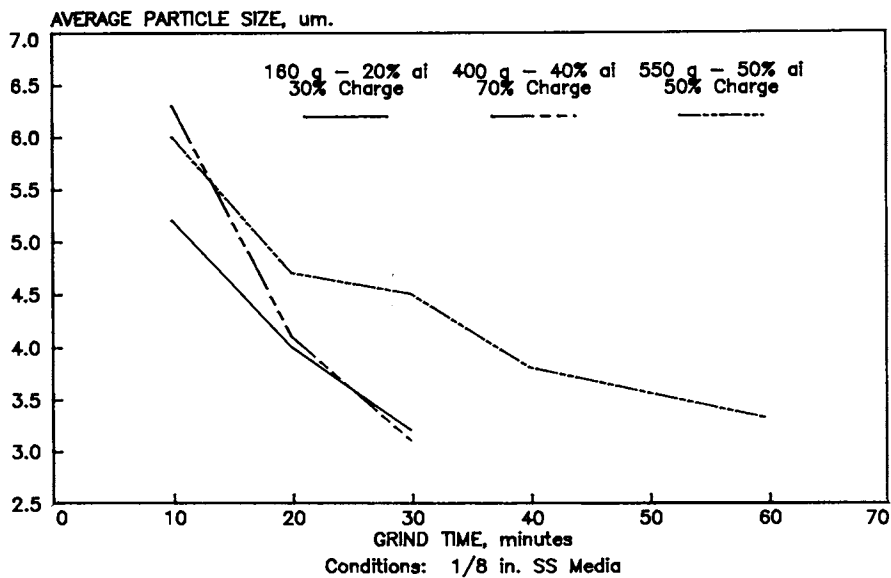
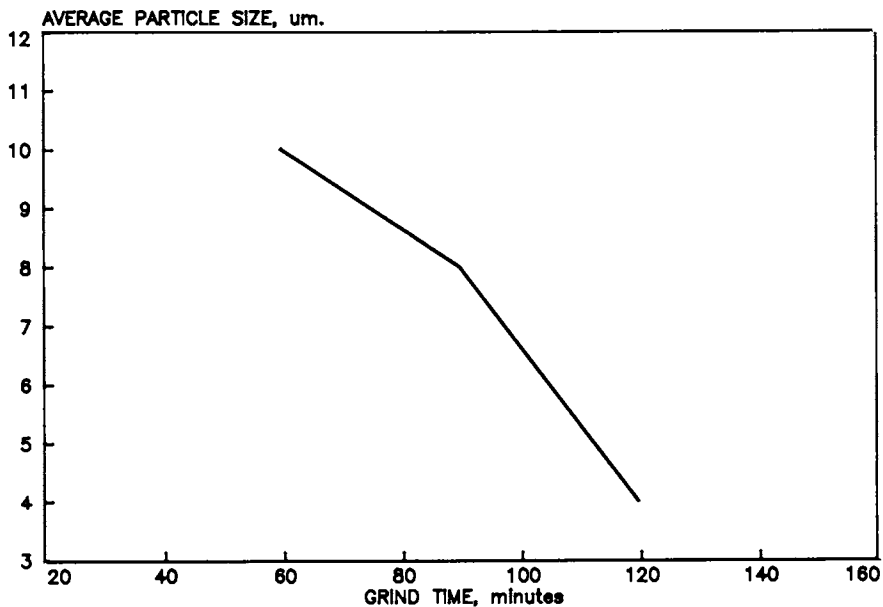


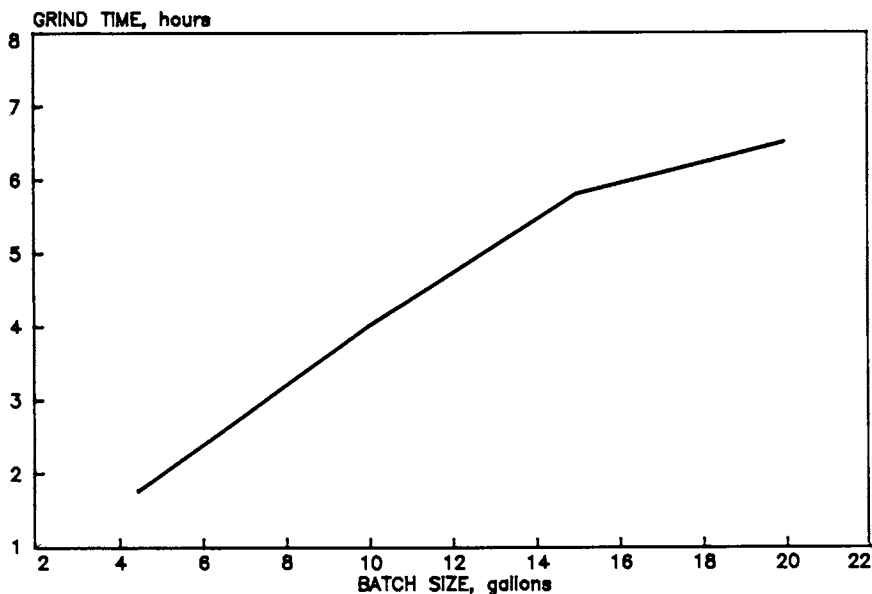
Figure 10. Particle Size vs. Grind Time (Attritor 01).





Conditions: 1/8 in. SS Media, 50% af, 2200 g. Batch, 70% Media

Figure 11. Particle Size vs. Grind Time (Attritor 1-S).



Conditions: 40% af Flowable, 1/8 in. SS Media

Figure 12. Grind Time (to 3  $\mu\text{m}$ ) vs. Batch Size (Attritor Q-1 System).

3 micron average particle size. With repeated runs, the Q-1 systems could easily supply samples as large as 100 gallons or more for an extensive field testing program.

The performance and utility shown with some, if not all, of these units could probably be duplicated by other equipment available on the market. It was not the purpose of this paper to recommend a specific type of equipment, but rather to provide examples of how appropriately sized equipment can effectively be used in a research and development effort.

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## Dispersion and Grinding of Pesticides

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The incorporation of insoluble, powdered solids into liquid media is generic to the chemical coatings, printing ink and pigment dispersions and likewise to the preparation of dispersion concentrates of pesticides.

Lessons learned from paints and inks in achieving complete wetting of powders and separation of particles to micron levels with dispersion stability to forestall settling and caking are quite applicable to aqueous and nonaqueous flowables.

Available simple mixing and dispersing systems will be discussed relative to producing stable wet concentrates of pesticides.

Agricultural chemicals known as pesticides include herbicides, insecticides, and fungicides. These have been marketed as granules or powders and today there is a large market for water based suspensions. The suspensions contain in addition to the active ingredients, additives like surfactants, emulsifiers, and sometimes antifreeze. Suspensions ease filling and handling problems in the field, as well as storage problems in humid areas.

Conditions for a good quality suspension require that at least 90% by weight of the active ingredient have a particle size below 10 microns and preferably be less than 5 microns in diameter. (1)

Pesticidal suspensions are most efficient if they can be produced with the active ingredient in a finely divided state with no agglomerates and with sufficient dispersion stability to prevent undo settling and compaction while in storage.

The dry ingredients could be dry ground, but a wet grinding system would avoid the heat elimination problem and dusting that attends dry grinding to below 20 microns(2). Micron sized particles have strong cohesive forces which promote reagglomeration in 30 to 50 micron clumps in the

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dry state(3). In practice, wet grinding has an extra benefit because during the comminution, the active ingredient can blend with the dispersants necessary for stability and homogeneity.

High shear wet grinding equipment can reduce the particle size of the active ingredient to the needed size range and also activate the clays used in many formulations to stabilize the suspension. High shear equipment has not always been used for production of dispersions.

The ball mill is one of the earliest machines that made dispersions by the impact action of cascading steel balls or round pebbles in a cylindrical drum that slowly turned on its long axis. (figure 1) The drum's axis of rotation was horizontal and the slurried mixture sloshed inside under the action of the balls. The balls create impact and shear action as they slide and cascade over one another as the drum rotates. Ball diameter is from 12 to 50 mm. Spheres of this size have a tremendous mass, compared to a single crystal or grain of clay that might be 1 mm. or 1000 microns in size. The ball mill is capable crushing strong crystals or aggregates. It is a simple effective mill, but not a high speed process. It is also a batch mill and large volume batches will need a very strong secure machine.

It was noted that smaller media was more effective after some premixing, in getting particle sizes down in the micron range, but that the rotation of the drum had to be slowed to prevent media from freezing to cylinder sides and losing the cascading action. (4) A method of agitating the media with a stirring shaft was developed and much smaller media could then be employed.

The Attritor, the invention of the late Dr. Andrew Szegvari, is such a device (5), Closely related to the ball mill, but with a vertical cylinder, it has a central rotating steel shaft and projecting steel rods which stir the media in the stationary drum. (Figure 2) Originally a batch process like the ball mill, recirculating systems have been added to the grinding chambers to pump slurry into the bottom and then draw off the suspension from the top of the column. The milling action is still predominantly impact, but there is an element of shear from the rods pushing through the media bed which contributes to the dispersion process. These mills are used to produce pesticides and have the ability to cope with lumpy slurries and still produce fine dispersions. Several hours or many passes through the recirculating systems are required to process a batch.

The Attritor raised the viscosity limits of formulation practice beyond that of the ball mill, even with the smaller media because of the action of the steel rods.

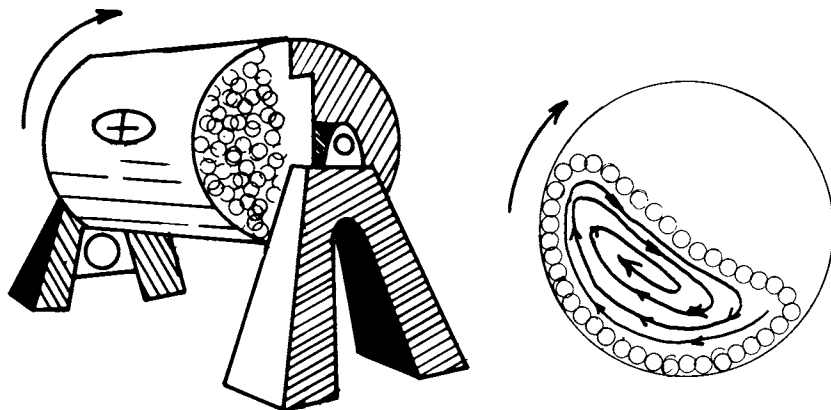


Figure 1. Typical ball mill with schematic flow diagram showing internal circulation.

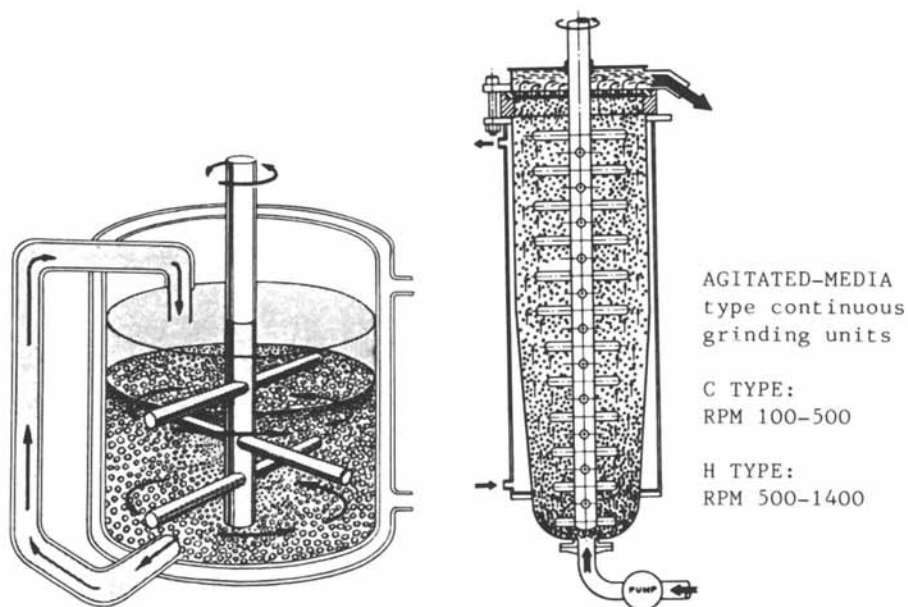


Figure 2. Attritor schematic diagram Reproduced with permission of Union Process Co. house publication

There is incentive to reducing media size because this produces more contact points per unit volume and increases the surface area for shearing action. The viscosity limit is approached as the slurry loses mobility at the central shaft and media action is lost.

Hochberg and Bosse of E. I. DuPont de Nemours, with the "Sand Grinder" patent (6) took the idea of using small spherical media in the form of Ottawa silica sand with an average diameter of .7 mm to a practical machine. Later glass, ceramic and steel media materials would become available and sand grinders would evolve into bead mills, shot mills, and small media mills. (Figure 3)

Like the earlier mills, the sand mill is gravity dominated and the media must be able to resist floating in a moving slurry with ever increasing viscosity as milling proceeds. Larger media will have more mass and therefore be able to work with higher slurry viscosity. Since the dry ingredients in pesticides are mixed with low viscosity water, viscosity is built up by the suspended solids.

The original sand grinder used a central shaft with a series of annual rings which spin between 1220 and 2400 rpm to achieve a peripheral disc velocity of about 2000 ft./min. or 10 meters/sec. (Figure 4) Unlike the ball mill or Attritor, this media is accelerated 200 - 300 G's by this centrifugal force as compared to 1 G in the ball mill.

The continuous milling action of the production mills depends on a regulated pumping system to push slurry into the bottom of the milling chamber with a controlled residence time before it is discharged at the top of the mill through the media separator. The original mills have cylindrical screens at the top to retain media and an external collection trough to receive the slurry. There are rings or discs in the upper screen zone to create a centrifugal pumping action to assist the passage of the slurry through the screen. The presence of the screen in the upper location lengthened the shaft assembly and this in turn placed a limit on rotational speed to avoid destructive vibration. Sand mills or bead mills with a vertical stirring shaft are called vertical mills and are older than the horizontal small media mills which reverted back to a horizontal cyclinder like the oldest ball mills.

Vertical mills have open screens which can be visually checked during operation. There are also closed or pressurized vertical mills in which instruments like pressure gages and thermometers must be used to check operation. This is very significant to good operations because the mill must achieve an internal equilibrium so that a significant amount of grinding media will be in the milling chamber and interacting with the suspension and not pushed up into the screen or separator system. The mass

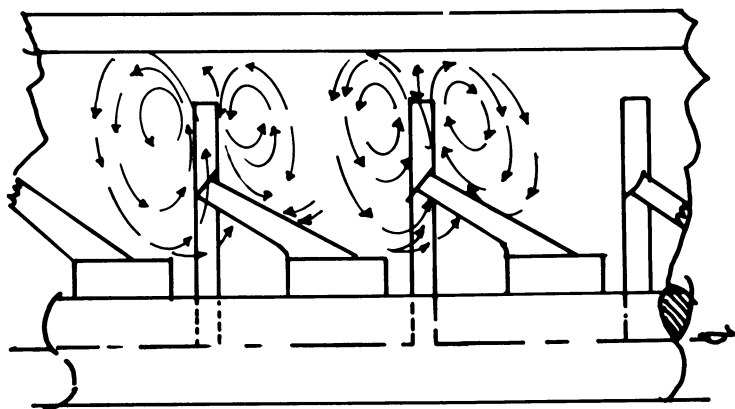


Figure 4.  
Schematic diagram of vertical mill  
describing acceleration and circulation  
path of media. Reproduced with permission  
of Chicago Boiler Co. from literature  
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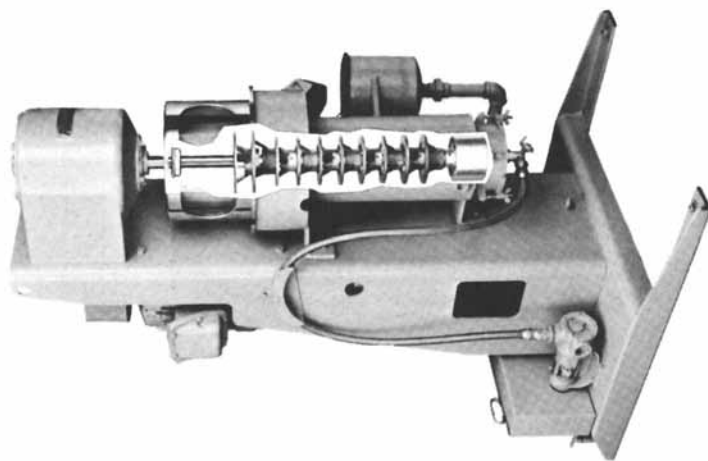


Figure 3.  
Red Head small media mill Model 8P  
Photograph courtesy of Chicago Boiler Co.

of the sand or the spherical media must be such that at the flow rate of the suspension into the mill, it will be fluidized or separated, and yet not be floated up and out by the combination of viscosity and flow rate. In practice this is easily adjusted on an open vertical mill by observing the height of the screen effluent. Too much viscosity or too high a flow rate will bring the mixture of media and suspension to the overflow point on an open screen vertical mill. In a closed mill system, this is determined by slowly bringing up the flow rate and observing internal pressure and temperature in the mill.

Any closed mill will have a restricted opening which is the media separation system. A higher flow rate for an opening of fixed area will result in a higher pressure to push it through. Excessive viscosity or flow or both in the suspension will carry the media into the discharge end of the mill and result in high pressure and also high temperature because the packed media will be skidding against the discs and circulation will be lost.

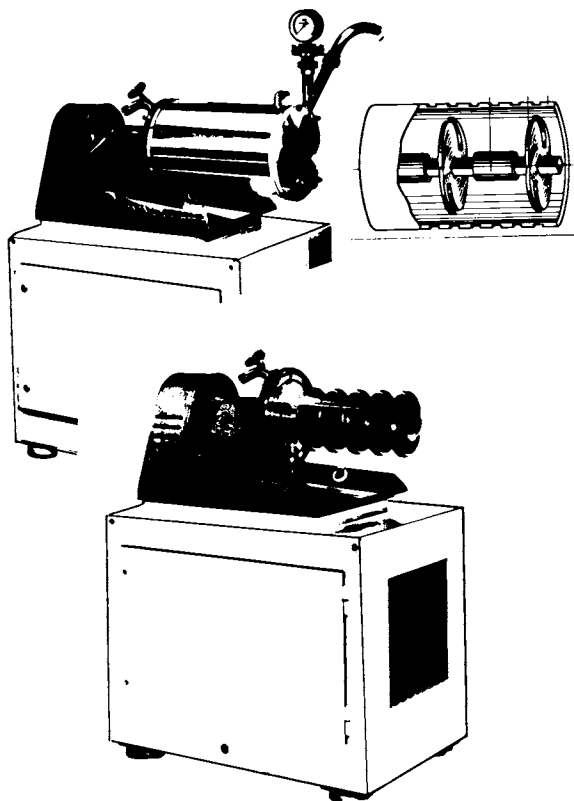
The vertical open screen mill is the least expensive mill to purchase and maintain or operate with nominal training. A disadvantage of vertical open screen mills in pesticide production is that the high shear circulation in the cylindrical screen permits large amounts of air to be incorporated in thixotropic suspensions. These same suspensions can be difficult to handle in the gravity collection systems which require that they flow away of their own weight into the tray. Thickening in the absence of shear is avoided in the pumping path of closed mills because feed pump pressure is used to convey the suspension through a closed pipe system.

The most serious difficulty with a vertical small media mill is that gravity compacts the media tightly around the shaft. The annular ring discs which produce shear also create frictional resistance with the media when the mill stops. The tightly compacted media against the shaft can make starting difficult. High starting torque motors are recommended and often the shaft must be jogged with short impulses of power to free it up and start. This makes remote control operation much more complicated and, in some localities with limited electrical capacity, using reduced voltage starting systems for the main drive motors becomes impossible.

The solution which came from Europe is the closed horizontal mill. (figure 5) A horizontal shaft in the horizontal grinding chamber is easy to turn with the grinding media distributed along its length.

The vertical sand grinder literature (7) established that media and slurry were to maintain equal volumes in the milling chamber for optimum interaction.





**Figure 5.** Dyno-Mill horizontal small media mill Type KD 15 (15 Liter chamber). Reproduced with permission of W. A. Bachofen AG, copyright 1974

Establishing equilibrium conditions in the mill also meant that in practice a certain amount of media was always in the screen zone at the top of the mill. The horizontal mills do not have external screens or separators and so the media concentration in the milling chamber can be maintained at optimal level.

The shorter shaft and disc assembly in the horizontal mill is capable of higher speed without destructive vibration (3400 ft./min or 17 meters/sec.). The high shear rates enhance media action for particle size reduction (impact action) and agglomerate separation (shear action).

All small media mills or sand mills have water cooling jackets to carry away process heat. In practice, a 50 degree F. temperature difference is desirable between coolant temperature and product temperature at 10 m/sec.

Minimum flow rate is determined by suspension heat susceptibility. Available mechanical energy is high and 5 to 7 H. P. per gallon is available from the power train. High flow rates or minimum residence time make power consumption reasonable.

The outstanding operational problem with small media mills is that they are quite dependent on a previous stage in the process to provide them with lump free slurry. The distribution of the wet and dry ingredients must be sufficient to permit trouble free pumping without settling problems in the lines. This step can be accomplished with a batch process system using a high speed disc impeller in either single shaft or multishaft design. (Figure 6).

When equipped with a variable speed shaft drive system the high speed disperser is capable of incorporating dry ingredients into the liquid at low speed to minimize dusting. When immersion and wetting are complete, the disc speed can be brought up to 4000 - 5000 ft./min. This high shear rate is capable of doing a considerable amount of deagglomerating though particle size reduction should not be expected.

Power levels are usually figured on the basis of 1 HP on the shaft for each 10 gallons of suspension or slurry in the premix tank at 10,000 cps viscosity.

In practice the powders are incorporated with some degree of turbulence in the liquid phase. The liquid volume should be restricted to get the highest viscosity consistent with getting circulation to all parts of the mixing vessel. High particle concentration will help get good interparticle action among the slurried agglomerates. Careful attention to temperature rise will ensure that no heat damage is done.

The desired effect at this point is to get laminar flow and good vortexing. Only 10 to 20 minutes after the last dry ingredients are added, results should be evident. Longer times without results are indicative of improper

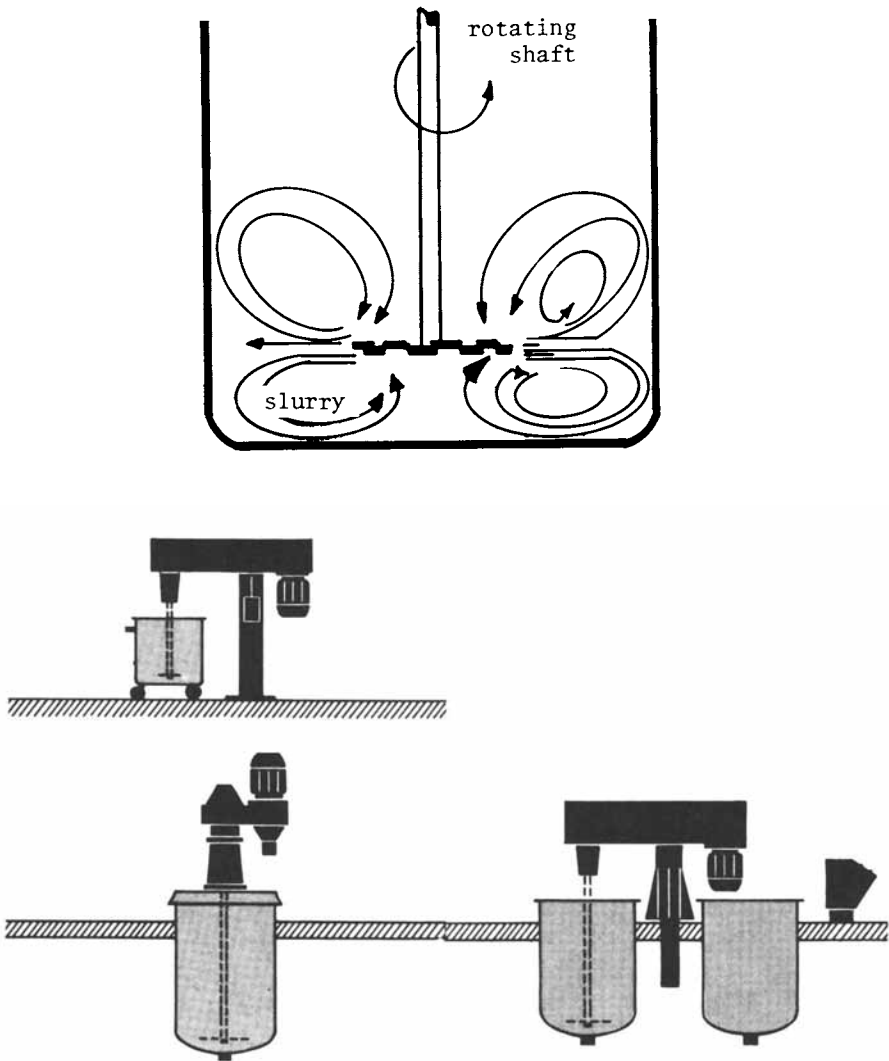


Figure 6. High Speed Disc dispersion systems. Idealized flow in mixing vessel and typical installations. Reproduced by permission of Diaf AG from house literature. Copyright 1979

ingredient balance and can even lead to heat problems. Practical formulation data in an early definitive work was published by Frederick Daniel (8) which is especially useful for oil based systems.

A process concept which may help to fix the technique in mind is to consider the high speed disc to be deagglomerating at a high viscosity, followed by a letdown step or reduction in viscosity for the small media mill. The initial high viscosity produced good interparticle action in the slurry. This is continued in the small media mill but at reduced viscosity in the presence of permanent agglomerates called grinding media!

Because no more than 1 percent of the particles are probably in contact with the discs in the mill, good circulation and repeated contacts are essential to the statistics of deagglomerating the billions of particles in the the suspension. Excessive viscosity impedes the action and increases heat in the mill. The mills will work over a wide range of viscosities but production efficiency will suffer if the mix is wrong. Appropriate laboratory tests made with similar equipment should be made and certainly when making ingredient substitutions.

Excessive viscosity will result in incomplete dispersion, high powerdraw and damaging temperatures. Very low viscosity causes high mill wear, high media wear, and sometimes unwanted particle size reductions.

Some products will not grind easily and may have strong crystals up to 1 mm in size or at least significant numbers beyond 150 microns. Slurry particles as large as this will cause very low production rates in the small media mill or necessitate repeated passages through the mill. The 1 to 1.5 mm media diameters frequently used for milling must have a 10 to 1 size advantage over the crystals for effective milling. Large particle might require a 2 stage system with large 2 or 2.5 mm media in the first mill followed by a second mill with smaller media.

This duplication can be expensive and in Europe, cheaper rotor stator mills are used often to achieve the gross reduction. (9) These include tooth colloid mills, Trigonal tooth ring mills, and abrasive disc mills (stone mills). High shear loading is achieved by controlling the gap (0.03 mm to 2 mm) between the rotating parts. The slurry is pumped through the center or outward between the rotor and stator surfaces. These mills are not as common in the USA owing to the availability of micronized dry ingredients.

Actually excessive particle size reduction of the active ingredient will increase surface area and therefore surfactant demand. This is not easy to measure with instruments but soon apparant in practice.

The latest combination of high speed disc dispersers and small media mills offer the pesticide manufacturer versatile high capacity tools which require minimum plant floor space and installation problems.

The combination of shear and impact action is sufficient to break the typically small crystals of active ingredients to desired size and the high shear will activate suspension agents adequately for desired stability. As compared to the older ball mill or Attritors, their action has more impact and pulverization effects than a small media mill.

With proper selection of raw materials which do not require pulverization, it is possible to formulate suspensions for high production with minimum process time. Premixed ingredients with particle sizes in the 30 to 60 micron range can be efficiently processed with small media mills at profitable flow rates. This is an achievable condition for a wide range of products.

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## A Computer-Based Technique for the Evaluation of Sedimentation Rates/Shelf Life of Pesticide Flowables

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In the development and maintenance of a quality pesticide flowable formulation, the rate at which the suspension forms a non-redispersible sediment under various storage conditions is a highly important product characteristic which must be thoroughly evaluated. This paper will describe equipment and methodology which are useful for the fast and accurate determination of the relative stability performance and shelf life of flowable formulations. The methodology described utilizes a MINC computer/data acquisition system interfaced to a Brookfield Digital Viscometer. Viscosity versus sample depth measurements for evaluation samples are obtained by using a Brookfield Heliopath lowering stand and modified "T-bar" viscometer spindles. Data acquired via this system permits accurate and reproducible evaluations of relative formulation stability performance after 0.5-3 months of accelerated 50°C sample storage or after 3-6 months of ambient temperature storage.

The formation of non-redispersible sediment in a pesticide flowable formulation is often the primary cause of product failure during inventory/shelf storage. In order to develop and maintain a quality pesticide flowable formulation, a formulator needs evaluation techniques which will enable him to quickly determine the relative stability performance of a sample in a non-subjective manner. Accurate sample characterization and early prediction of shelf life is also highly desirable. Many methods for flowable sample evaluation, such as sediment 'probing', are subjective and destructive to the integrity of the sample. Often, samples have to be 'aged' at elevated temperatures to obtain measurable differences in stability performance within reasonable time constraints. The purpose of this paper is to describe equipment and methodology which can be utilized to measure the relative

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viscosity versus sample depth for aqueous flowable suspensions stored in various sized containers. The utility of the integration of a computer into the data acquisition system will be discussed and the potential usefulness of the methodology to quickly evaluate a flowable sample's quality, sedimentation rate, and its expected shelf life will also be demonstrated.

### The Viscometry System

The relative viscosity versus sample depth of a pesticide flowable sample can be determined by lowering a rotating spindle (with 1 thin bar extension) into the sample at a fixed rate of descent until the bottom is reached. The apparent viscosity at any depth is relatively proportional to the measured torque on the spindle shaft at a given spindle rotation speed. The terms "relative viscosity" and "apparent viscosity" are being used to describe the resistance encountered by the rotating spindle in the concentrated suspension. Viscosity, by strict definition, is not the property being measured. Evaluation of a sample in this manner can easily be performed by using the following commercially available equipment:

1. A Brookfield Digital Viscometer (Models LVT, 0.25X RVT, and 0.5 RVT) with analog recorder output.
2. A Brookfield Heliopath Lowering Stand with a 17 inch (or greater) stand support rod.
3. Specially 'modified' T-Bar spindles without the vertical extension tip below the thin, horizontal extension arms. (Available through Brookfield Engineering Laboratories by custom order.)
4. A computer data acquisition system or an X-Y recorder capable of processing a 0-10 millivolt analog signal.

The Digital Viscometer outputs data as values within a range of 0.0-100.0 units. The magnitude of the readings for a given sample is dependent on the spindle type, spindle RPM, sample temperature, and model of viscometer used. The models differ from one another because of changes in the spring constant of the spindle torque measurement system. The LVT, 0.25X RVT, and the 0.5X RVT models are sensitive enough for useful measurement of sediment in typical aqueous based flowables. T-bar spindles are available with various horizontal bar lengths for increasing or decreasing viscosity sensitivity. They are designated T-A thru T-F, with T-A (47.5 mm long) being the most sensitive and T-F (11 mm) being the least sensitive. The mouth width of the sample container will determine the maximum spindle size which can be used in many

cases. Figure 1 shows the various system components mounted for actual use. Note the presence of a 'collar' on the Heliopath Stand support column which 'stops' the descent of the spindle at a set depth (set to be equal to the bottom of the sample container).

The following viscometer components and operating conditions are currently being used in the determination of relative viscosity versus sample depth in flowable samples:

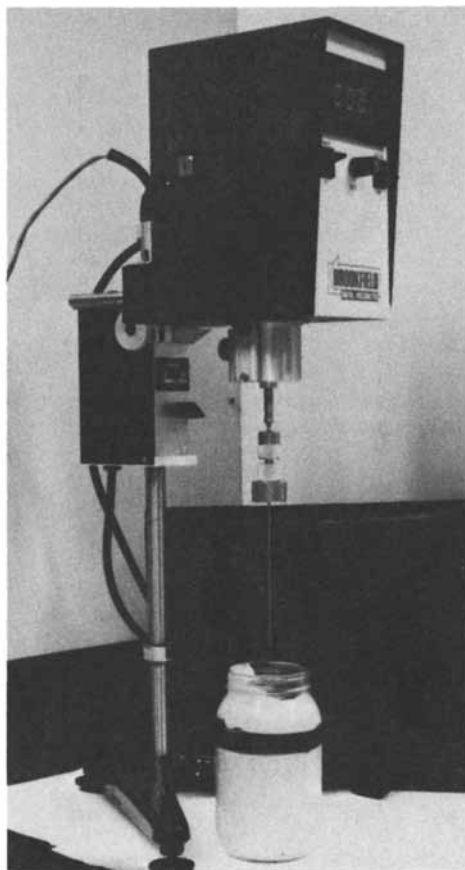
- T-Bar spindles (T-A, T-B, T-C, T-D models were modified to eliminate the vertical extension below the horizontal spindle arm; vertical lengths used are 120 mm and 400 mm).
- Spindle Rotational Speed = 5 RPM. This speed was chosen because it minimizes sample disturbance and eccentric spindle motion, while still providing acceptable sensitivity.
- Rate of Spindle Descent = 1.00 mm per 2.570 seconds  
(Not adjustable) = 1 inch per 65.35 seconds
- The spindle is placed as close to the top of the liquid (without being wetted) prior to the start of descent, and the horizontal extension arm is 'centered' in the middle of the container opening.

The graphic portrayal of a 'typical' viscosity versus sample depth evaluation performed on a 16 oz. sample jar is depicted in Figure 2. Important evaluation parameters for the resultant curve are also depicted. The total time necessary for the evaluation of this sample (approx. 90 mm deep) was four minutes. Similar data has been generated for flowable suspensions in sample containers as tall as 15 inches (i.e., 5 gallon pail). This is accomplished by using 400 mm long spindles in conjunction with an extension for the Heliopath Stand supporting rod to provide the amount of stand travel necessary to permit the spindle to 'probe' the entire sample depth.

#### Computer Data Acquisition and Handling System

Figure 3 is the schematic of the data acquisition system which is currently being used to generate the viscosity versus sample depth 'profiles'. The 0-10 millivolt analog output signal from the viscometer is preamplified to improve resolution before it is converted to a digital value via the A/D convertor. The effects of transient "noise" are minimized using signal averaging techniques. The A/D convertor is controlled by a clock which specifies the collection of a digital viscosity value averaged





**Figure 1. Brookfield Digital Viscometer with "Modified" T-Bar Spindle Mounted on a Heliopath Stand.**

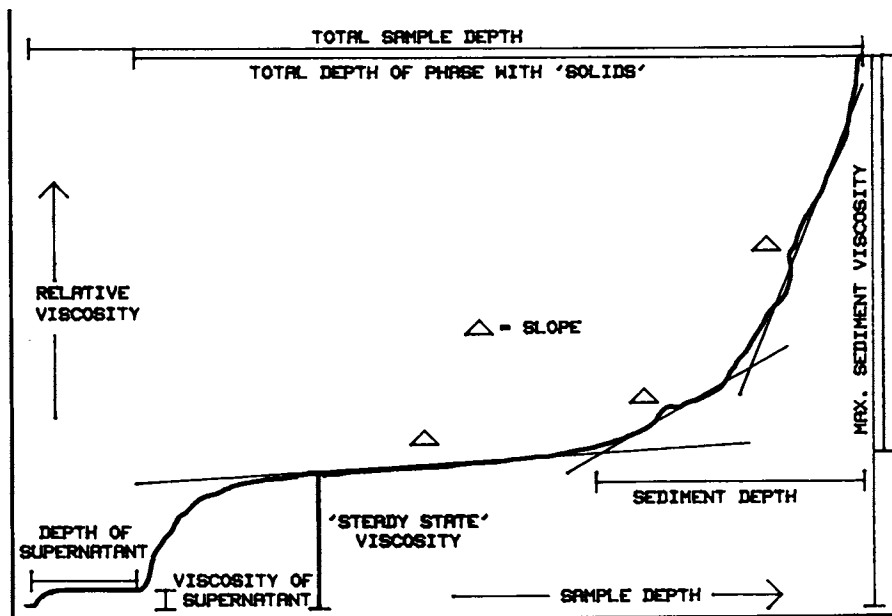


Figure 2. "Typical" Graph of Relative Viscosity vs. Sample Depth with Important Evaluation Parameters.

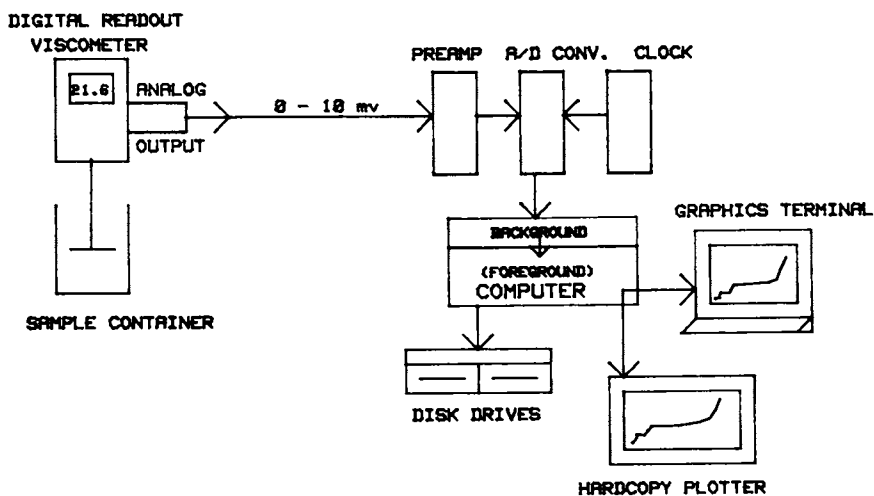


Figure 3. Schematic Diagram of the Data Acquisition System.

every 0.514 seconds, which is equivalent to 0.20 mm of spindle descent through the sample. The digitally converted data is handled by the computer in a 'background' processing mode which enables the points to be graphically displayed immediately as they are collected and also simultaneously stored on floppy disks for further use. A multi-colored plotter is used for hard copy generation of the 'profile' curves. A variable speed X-Y strip chart recorder could be substituted for the whole data acquisition end of the system. But, this type of system is not advisable, except for method evaluation purposes, because of the difficulty involved in handling strip chart data.

The computer system used for this purpose is a Digital Equipment Corp. (DEC) 'MINC' laboratory data acquisition system consisting of the following components:

- PDP 11/23 Processors with 'MINC' Basic Language (V3.0).
- VT 125 Graphics Terminal.
- MINC Preamp (4 channel) and A/D Converter (16 channel) Modules.
- DEC RX02 Dual 8-inch Disk Drives.
- Hewlett Packard 9872 Plotter (4 color).

Any computer system which is capable of being configured in a similar manner to the schematic diagram could be used for this type of data acquisition.

### Data Interpretation and Portrayal

Data interpretation of viscosity versus sample depth 'profile' curves usually entails using an X-Y plotter of the data to determine various important parameters which yield information about the sample. Figure 2 portrays the most important curve characteristics and slopes which need to be calculated. The determination of these values is greatly facilitated by the use of the computer. Current programming enables the use of curve smoothing routines and first derivative analysis to aid in the calculation of slopes and to "pick" points of interest. Values of these important parameters can then be cross-compared with other samples or controls and correlated with previously acquired data for rankings of relative performance and estimation of shelf life. Comparison of samples is highly facilitated by the ability to 'overlay' profile curves graphically and to 'blow up' specific regions of these overlays (i.e., supernatant region) for more accurate visual portrayal. Figure 4 portrays the 'profiles' of three different flowables stored in 16 oz. jars for 10 months at 50°C. The stability performance of the samples can be 'ranked' by comparing the depth of the supernate and the sample depth at which the curve goes 'off-scale'. Note the characteristics of the most 'stable' formulation compared to the least 'stable' formulation.

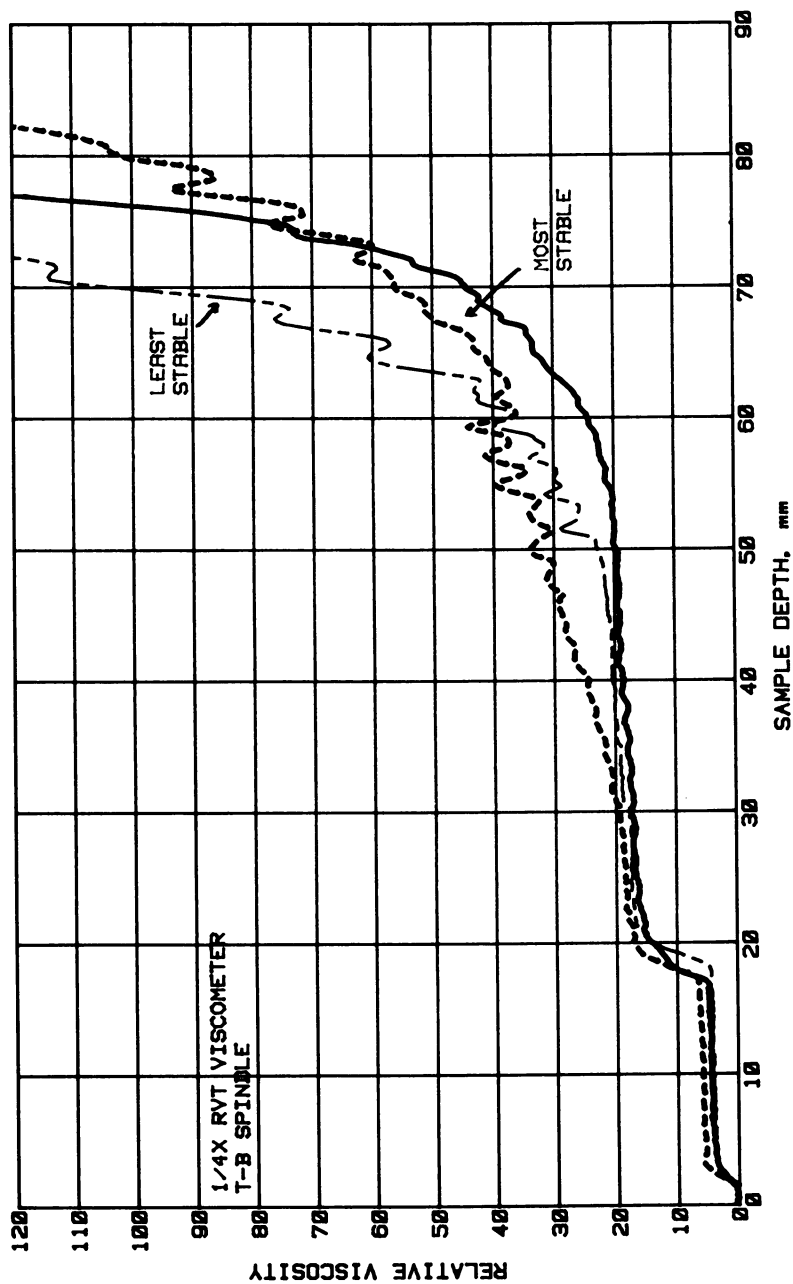


Figure 4. Comparison of Three Different Flowable Samples After 10 Months at 50°C.

Figure 5 illustrates the formation of the supernatant layer and sediment for a single sample versus storage time under ambient conditions. The computer provides the capability to mathematically 'normalize' the curve data to permit direct comparison of samples evaluated with different spindle sizes or viscometer models. 'Normalization' routines could also conceivably be developed for a more accurate comparison of samples with different sample depths, different initial viscosities, and different storage times and temperatures. It is often possible to make valid sample comparisons and shelf life predictions after sample storage durations of 0.5-3 months at 50°C and 3-6 months at room temperature using this technique, depending on the quality and type of flowable system.

This viscosity versus sample depth methodology also provides a means to discover 'abnormal' flowable sample characteristics, which would be difficult to detect via more conventional evaluation methods. Evaluation of 'abnormal' characteristics would be 'curds or lumps' in sample, thick layers midway in the sample (see Figure 6), and other signs of 'premature' sample failure. Freeze/thaw performance can also be readily determined using this methodology. Figure 7 shows the relative performance of three flowable samples after exposure to 5 freeze/thaw cycles. Only small amounts of sediment are present in these samples, but the overall sample thickening illustrated by two of these samples is highly indicative of poor freeze/thaw performance.

#### Applications for Utilization of This Methodology

This methodology has application and usefulness in the following areas pertinent to pesticide flowables.

##### 1. Formulation Development

- Comparison of different flowable ingredients and ingredient concentrations.
- Comparison of different manufacturing processes.
- Freeze/thaw studies.

##### 2. Relative Sample Quality Comparison

- Shelf life determination at various storage temperatures.
- Inventory control of production material.
- Field complaint analysis.

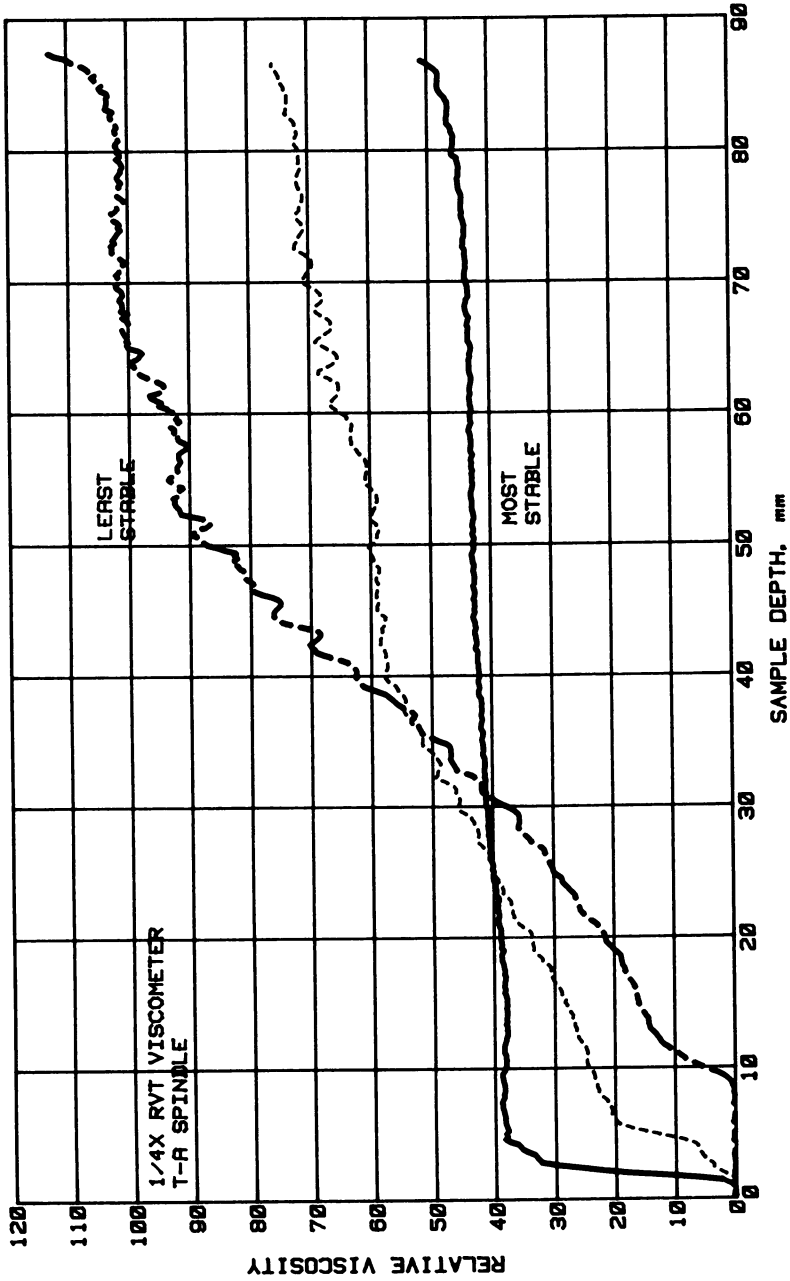


Figure 5. Comparison of "profile" Curves for the Same Flowable Sample After Various Ambient Temperature Storage Intervals.

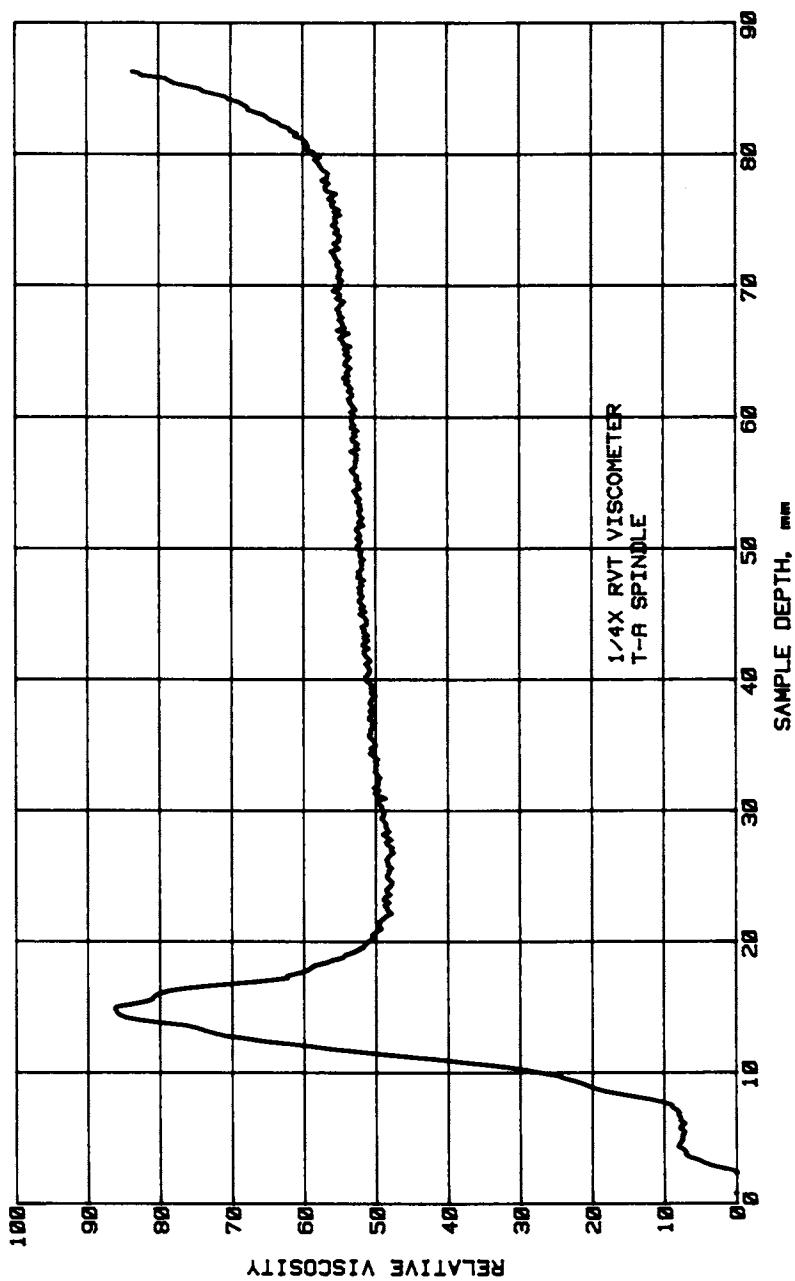


Figure 6. "Abnormal" Thickening Occurring in a Sample Below the Supernatant Layer.

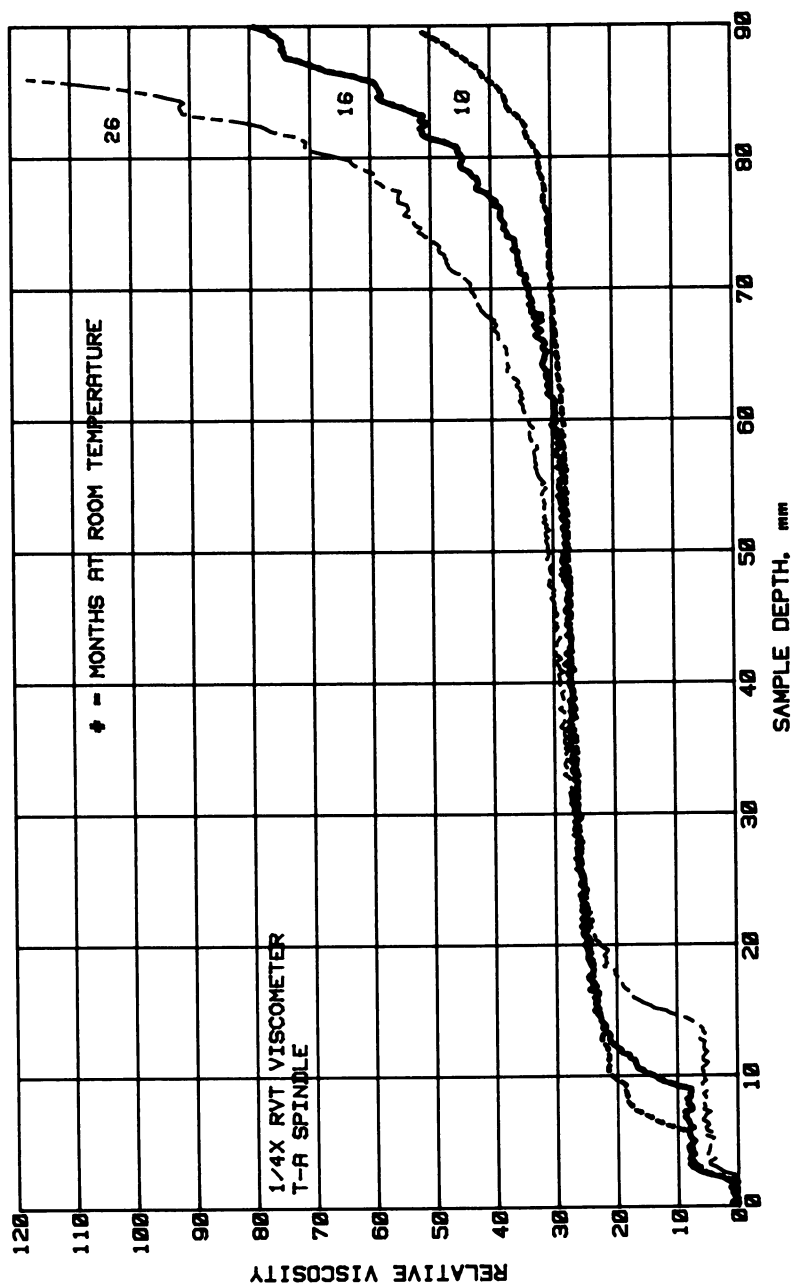


Figure 7. Comparison of "profile" Curves for Three Different Flowable Samples After Five Freeze/Thaw Cycles.



### 3. Flowable System Research

- Shelf life prediction from 'accelerated', high temperature storage data.
- Comparison with other commercial products.
- Sediment redispersion/mixing studies.
- Flowable rheology studies, i.e., structure breakdown and reconstitution.
- Packaging/inventory/transportation studies.

Evaluations have currently been made only on aqueous based flowables; however, the methodology should be applicable to other suspension systems such as paints, coal/oil slurries, etc.

### Conclusion

This technique/methodology is highly useful for characterizing a pesticide flowable formulation's stability performance. The components of the viscometry system are commercially available, and the system is easy to configure and use. Use of a computer system to acquire, process, and portray the resulting data is highly recommended, although a strip chart recorder could also be used. Computer systems capable of providing the proper data acquisition and graphics facilities are also readily available and need not be solely dedicated to this application.

Storage stability studies and the samples generated by these studies consume extensive amounts of time, space, and effort during evaluation. This methodology provides an objective, more complete analysis of these valuable samples and permits decision-making determinations of the results of these studies to be reliably made much earlier in the study than is possible with more conventional methods.

### Acknowledgement

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## Using Computers in the Development of Pesticide Formulations

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The cost of discovering and developing a new pesticide normally runs into the millions of dollars. With costs of this magnitude it is important that all tools available be evaluated for reducing development costs. One tool which is becoming more affordable and useful is the computer. With the appropriate software necessary for operating this tool, some possibilities are opening up for its use in the development of pesticide formulations. The study reported on here deals with the use of some commercially available computer programs and our use of them for developing pesticide formulations. Three commercially available software programs marketed by COMPUSERV INC. and used in this study are COED, RSM and PERSM.

Computer technology is rapidly growing today. As a consequence of this growing technology, computers are becoming more affordable and useful (1). With the appropriate software necessary for operating them, many uses are now being found for them.

A computer is a device which can receive, store, and act on a set of instructions in a given sequence. The instructions can readily be changed and the data upon which the instructions act can be changed, too. The difference between it and a programmable calculator is that the computer can handle text as well as numbers. This versatility gives the device an almost human-like data processing capability.

There are some tasks the computer is very good at doing. There are other tasks which it does not do well. For example, it can quickly do some of those tedious things that we find hard to justify if they involve a lot of calculation or searching through data. It can calculate and carry out instructions very quickly

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and accurately and become a definite timesaver. On the other hand, it is not a very creative device because it does only what it is told to do. Someone has to give a computer exact and minute instructions in order to achieve a specific result. They, indeed, are best suited for repetitious and time-consuming tasks. Both conditions are usually needed for their most profitable use.

### Pesticide Development Costs are High

The cost of discovering and developing a new pesticide runs into millions of dollars (2-3). Part of this cost can be attributed to research necessary for producing satisfactory formulations. As formulations become more sophisticated the development costs become increasingly higher. In order to help reduce formulation development costs, we need to continually evaluate promising new tools for their cost-saving potentials.

### Statistical Calculations

Already, the microcomputer has proven useful to us in making statistical calculations for production control purposes.

Figure 1 shows a graphical representation of some 297 Technical purity data points. This example was produced by a microcomputer (Hewlett-Packard 9845B/System 45 Database) in our Quality Control Section. This statistical information is helpful to the Formulation Chemist for designing formulations and assigning formula specifications. It was produced quickly and accurately with minimum effort.

### Literature Searches

Another tedious and time-consuming task can be literature searches. We find these searches can be handled quite easily by computer. A person skilled in searching the many databases available can do so in a very short time.

Before this study was started, several computer databases were searched to determine what information had been published concerning the topic -- "Using Computers in the Development of Pesticide Formulations". Databases used for these searches included:

- Chemical Abstracts
- Conference Papers Index
- Engineering Conference/Meetings
- Engineering Index
- International Pharmaceutical Abstracts
- International Software Database
- Microcomputer Index
- National Technical Information Service

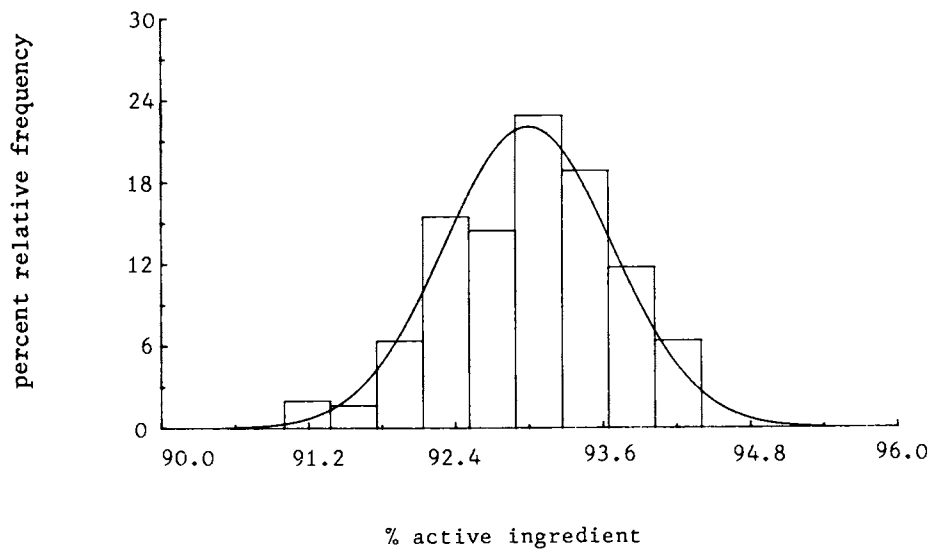


Figure 1. Pesticide Technical:1982.

The strategy varied according to the scope, coverage, point of view and special features of each database. Basically, the computer was asked to pull any citations containing one or more synonymous terms from these concepts:

Pesticides  
Formulations  
Computerization

No information was located which dealt specifically with the design and evaluation of pesticide formulations. Some information was found on the use of computers for analyzing pesticide formulations and using mathematical models for simulating release rates of formulations (4-5), but nothing on the actual development of a formulation per se. When the search strategy was changed to include pharmaceutical formulations, some pertinent examples were found. Schwartz and co-workers (6-8), for example, reported on computer optimization techniques for pharmaceutical formulations. Other workers reported on using computers in storage stability programs (9), developing cosmetic formulations (10), color matching of nail lacquers (11), and optimizing tableting processes and tablet formulations (12-13).

This literature search and our subsequent evaluation of some commercially available computer programs re-enforced the fact that computers are tools and they need skilled people to use them. Computers have to be fed the right data, and their output is subject to interpretation. This will be further illustrated when we consider the interpretation of a contour map produced by one of the programs to be mentioned.

#### Evaluation of Computer Programs

The study reported on here deals with the evaluation of some commercially available computer programs and our use of them for designing and evaluating several pesticide formulations.

To describe our use of these programs, a simple procedure will be shown for the optimization of an experimental synthetic pyrethroid formulation FCR 1272 2EC. It was originated by the parent company of Farbenfabriken Bayer GmbH, Leverkusen, West Germany. In world wide laboratory, greenhouse and field testing it has been proven to be an excellent non-systemic, foliar insecticide for the control of chewing insects.

Three computer programs used in this study were COED, RSM, and PERSM. These programs are presently being marketed through CompuServe, Inc., of Columbus, Ohio.

COED, Computer Optimized Experimental Design, is a proprietary product of the B. F. Goodrich Company. This program was developed by the B. F. Goodrich Chemical Divisions' Statistical and Computer Group and has been used internally at B. F. Goodrich since January of 1975 (14).

RSM, Response Surface Methodology, and; PERSM, Perspective Views of RSM Surfaces, are programs marketed exclusively through CompuServe, Inc. Detailed instructions for operating these programs will not be discussed here. These instructions are readily available from the vendor for those interested (14-16).

A portable data terminal with acoustic coupler for transmission of signals by telephone was used to access both the computer and the programs. This route was attractive because no capital investment in expensive programs or a computer was necessary.

### Experimental Design

In manufacturing pesticide formulations, slight overages in active ingredient are normally allowed for in the formula to insure that label guarantees are still met after reasonable storage periods. If too much overage is allowed, active ingredient is given away unnecessarily and the cost to manufacture the product is higher. If there are wide differences in purity for a pesticide technical, the formulation chemist needs this information to better design a practical formulation. He must design the formulation in such a way as to accommodate these purity variations.

The COED program was first used in this study to design experiments for describing the effect ingredient concentration has on emulsion performance. The COED program operates in this manner. First, a set of independent variables are specified. These are each entered into the program at given levels in such a manner as to cover a specific range for the variable. Next, possible effects from independent variable interactions and curvilinear effects on the variables are described. Last, one or more dependent variables to be acted upon are entered,

The FCR 1272 2EC formula used here had already been partially developed by traditional methods (Figure 2). It contains four ingredients.

Figure 2

Basic Formula for FCR 1272 2EC	
Active Ingredient (AI) @ 88%	29.7%
Emulsifier A	4.0%
Emulsifier B	3.0%
Solvent	63.3%
	<u>100.0%</u>

The concentration of three ingredients is sufficient to describe the formula given since the sum of all four must add up to 100%. These three concentrations were our independent variables. Ranges for these independent variables were set using the levels given in Table I.

Table I. Experimental Design Variables

Variable No.	Ingredient	Levels, % (w/w)		
		1	AI @ 88%	28.7
2	Emulsifier A	3.0	4.0	5.0
3	Emulsifier B	2.0	3.0	4.0

Prior calculations showed that about 26% of a pure Technical would produce a 2 lb/gal emulsifiable concentrate. This Technical normally averaged about 88% purity and would require 29.7% in the formula on an "as is" basis. Levels 1% above and below this value were chosen to give a reasonable range to fit within manufacturing specifications. Emulsifiers and emulsifier levels were chosen as a result of previous experience with similar systems.

All three variables were specified in the program as being curvilinear and interactions amongst them were considered. This allows the program to consider nonlinear equations in its curve-fitting routine. After the appropriate data had been entered into the program, it then generated 12 experiments to be performed. The chances of detecting differences in the dependent variables sought were calculated by the program as follows:

Small	59%
Medium	91%
Large	99%

The experiments generated by the program were printed out. They are listed in Table II.

Table II. Computer Generated Experiments

Experiment No.	Variable Number		
	1	2	3
1	28.7	5.0	3.0
2	29.7	3.0	3.0
3	28.7	3.0	4.0
4	30.7	5.0	2.0
5	28.7	3.0	2.0
6	29.7	4.0	4.0
7	30.7	4.0	3.0
8	30.7	3.0	2.0
9	29.7	5.0	2.0
10	30.7	5.0	4.0
11	28.7	5.0	4.0
12	30.7	3.0	4.0

The dependent variable chosen to be measured was "Performance". The "Performance" variable was determined according to the numerical scheme given in Table III.

Table III. Rating Scales

Factor	Value Range
Foam	0.5-2.5
Spontaneity	0.5-2.5
Emulsification	1.0-5.0
Emulsion Stability	1.0-5.0

The rating scheme was biased towards Emulsification and Emulsion Stability. The use pattern for the product under study was the guide for this bias. These two properties were considered more important in the performance of the product than foam or spontaneity.

The computer generated formulas were prepared and evaluated as a group. Numerical values were assigned for each property and totaled to give a "Performance" value. The rating scheme is set up so that the higher number reflects the better performance.

The "Performance" ratings experimentally obtained from the 12 experiments designed by the COED program are given in Table IV.

Table IV. Data Points for Calculating "Performance"

Experiment No.	Spontaneity	Emulsification	Emulsion Stability	Foam	Total Rating- "Performance"
1	2.0	5.0	5.0	1.3	13.3
2	1.0	2.0	2.0	1.5	6.5
3	1.0	1.5	1.0	1.5	5.0
4	2.5	5.0	3.0	1.5	12.0
5	2.5	5.0	3.0	1.5	12.0
6	1.5	5.0	4.0	1.5	12.0
7	2.0	5.0	5.0	1.3	13.3
8	2.0	4.0	3.0	1.5	10.5
9	2.5	5.0	3.0	1.5	12.0
10	2.0	5.0	5.0	1.3	13.3
11	2.0	4.0	5.0	1.3	12.3
12	1.0	2.5	1.0	1.5	6.0

At this stage, we get a rough idea of what is happening. We can see that formulas 2, 3, and 12 give poor "Performance".

To get more information from these data points, they were next entered into the Data Analysis portion of the RSM program.



### Using RSM for Data Analysis

The Data Analysis portion of RSM performs a statistical analysis to validate the experimental results obtained in the COED designed program. A set of contour maps is then produced to illustrate how the dependent variable "Performance" varies as a function of Emulsifier A and Emulsifier B concentration. The variable AI is held constant. The program calculated that 99.6% variability could be explained.

Figures 3, 4, and 5 show the contour maps generated. The most important factor affecting the dependent variable is printed out on the x-axis. This is identified as Emulsifier B. The second most important factor is identified on the y-axis and is Emulsifier A. The factor contributing least to the "Performance" is held constant and is identified as the active ingredient (AI).

Numeric and alphanumeric characters are used to represent the value of the dependent variable "Performance". Note in Figure 3 that "Performance" values of 15, 16 and 17 are plotted out on the contour map. These are projected values which go beyond the limit of the rating scale that was set up. These kinds of occurrences again point to the fact that computers are tools and their output should be subject to interpretation. As one becomes more adept at using these programs, these aberrations can sometimes be eliminated by using the proper restrictions allowed for in the program.

These contour maps (also called response surfaces) give some useful insights into the nature of the FCR 1272 2EC formulation being studied. They indicate that within the limits studied:

1. The purity of the active ingredient has little effect on physical performance.
2. Emulsifier B has the most effect on "Performance", but its concentration can fluctuate slightly without harm.
3. Emulsifier A can fluctuate widely.

These are useful insights, but they should be kept in perspective. This particular study did not take into account other important variables such as temperature and water hardness. The effects produced by these other independent variables can be handled separately in other studies, and their respective contour maps generated. These could also be used as factors in calculating the "Performance" variable.

### Using PERSM

The equations generated by the Data Analysis portion of the RSM program are compatible with the PERSM program for drawing 3-dimensional perspectives.

To use these equations, the RSM file containing them is transferred to the PERSM program. PERSM will list the independent

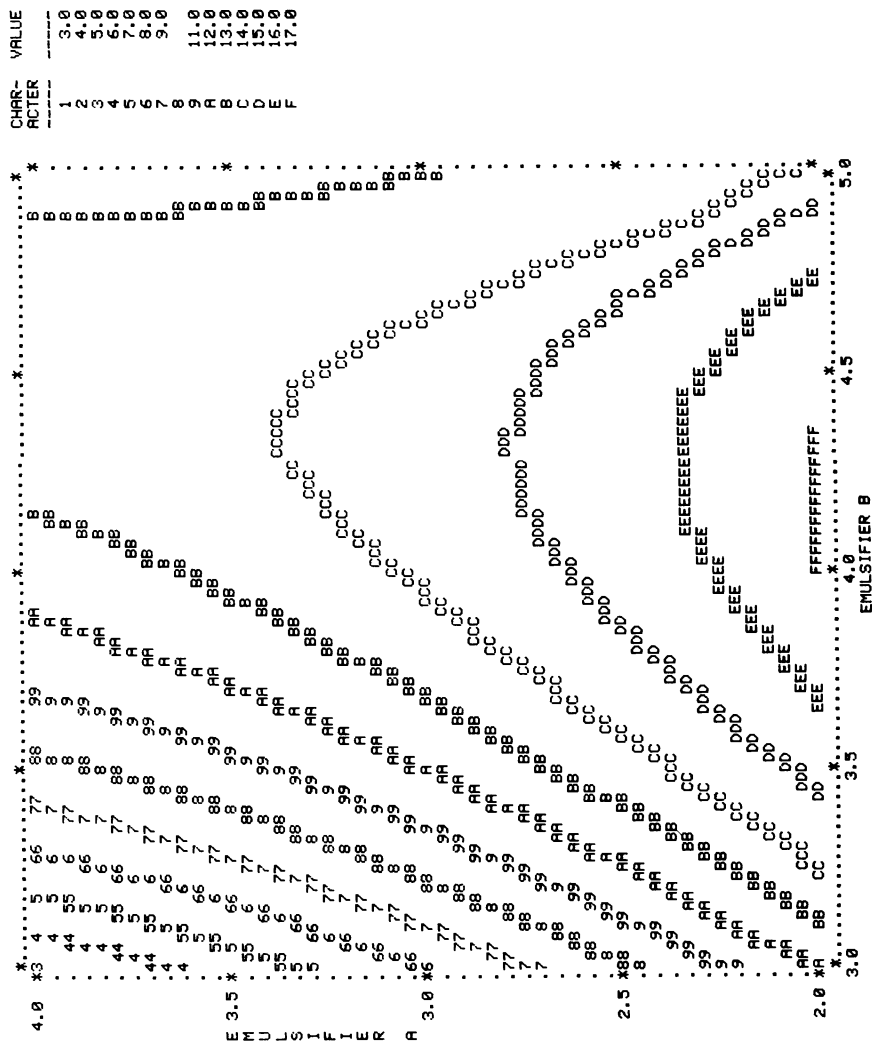


Figure 3. Response Surface for Performance, FCR 1272 2EC, AI = 28.7%.

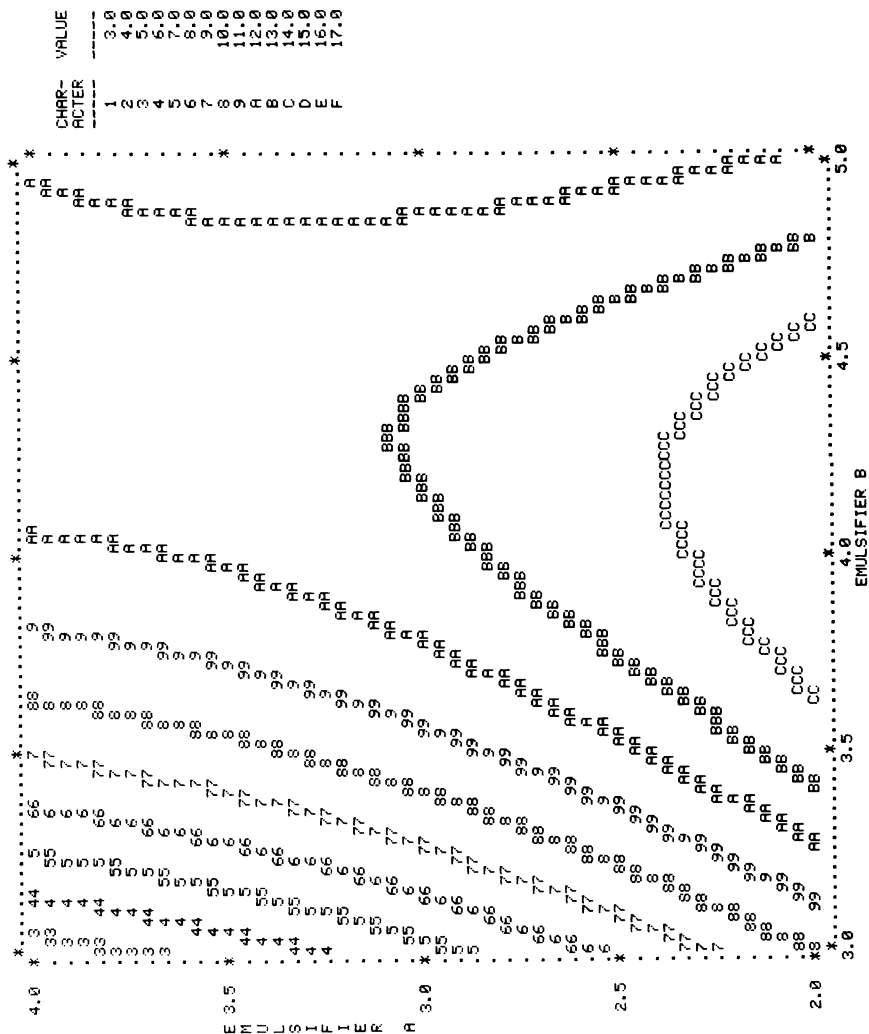


Figure 4. Response Surface for Performance, FCR 1272 2EC, AI = 29.7%.

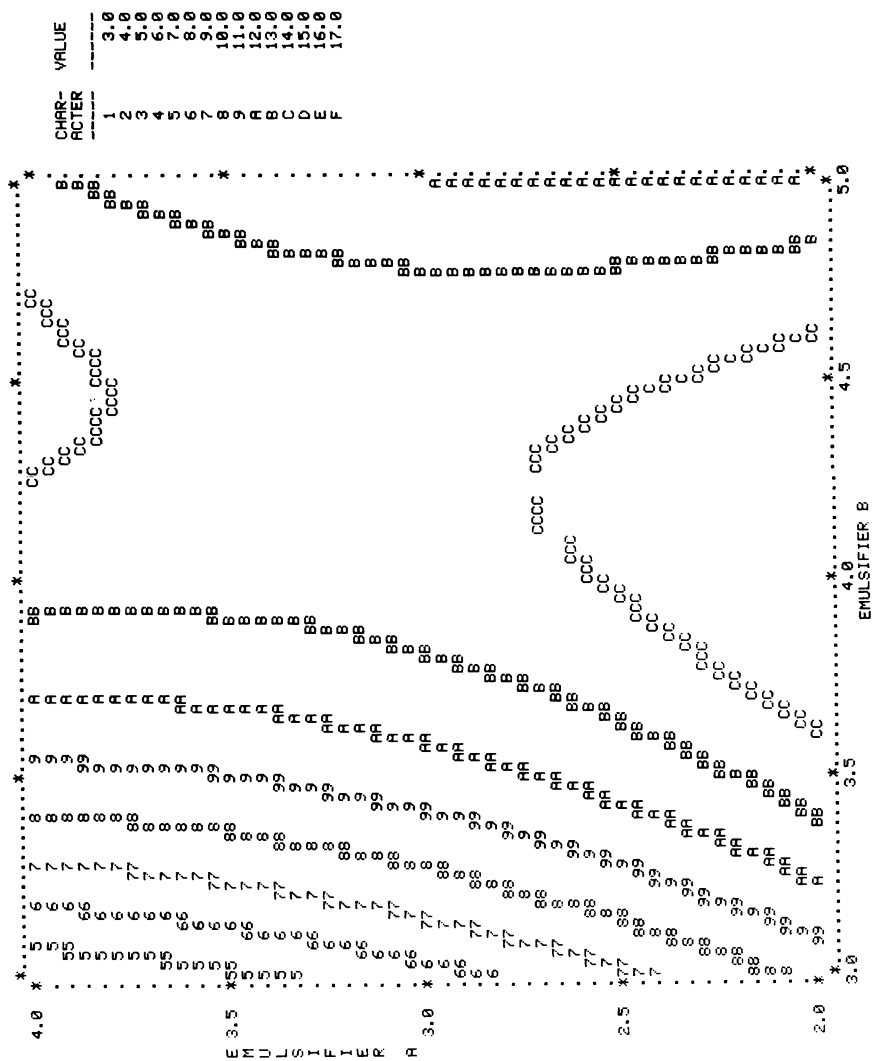


Figure 5. Response Surface for Performance, FCR 1272 2EC, AI = 30.7%.

variables from the file (2 to 10), two of which can be chosen for the x and y axes. That is followed by the dependent variables, (1 to 8), one of which can be selected as the response to be displayed in the z-direction. Figures 6 and 7 show results obtained from our study with the FCR 1272 2EC insecticide. Figure 6 shows AI held at the low end of the range studied and Figure 7 shows it at the high end. It is possible to hold AI constant at one intermediate value in the range studied and to rotate the 3-dimensional perspective through different angles for better viewing.

It can be seen from these two figures that the response surface is saddle-shaped and has slightly more tilt at the low AI concentration. Overall they're very similar and show that active ingredient of the purity range studied should perform satisfactorily in this formulation.

These are visual perspectives and it is very difficult to locate actual values from the drawing.

Other experiments tried with these three programs are illustrated in the following figures:

Figure 8 shows another experimental formula with a different solvent system. The active ingredient concentration is at a lower (200 gram/liter) level, also. The emulsifier levels tried here are higher and the resulting response surface has a broader shape.

Figure 9 shows a response surface for a commercial Dylox 1.5 Oil flowable formulation. The dependent variable of interest here is viscosity. It is typically linear with respect to thickener concentration.

Figure 10 shows a response for a commercial Matacil 180 Oil flowable formulation. Unexpectedly, we found the response surface to be non-linear with respect to thickener concentration.

### Conclusions

In our evaluation of computers for developing pesticide formulations, we find them to have a definite place. They can carry out many tedious routines and free people for more creative tasks. They can quickly and accurately retrieve, store and do statistical calculations on sets of data. They can graphically display the results of statistical calculations for visual interpretation. They can do literature searches and they can help in the optimization of formulas. Their potential as powerful tools for developing pesticide formulations is great.

We must remember that they are still just tools, though. Computers and computer programs need skilled people to operate them. Their value is dependent upon their skillful and imaginative use.

It is hoped that this brief description concerning our use of computers for developing pesticide formulations, at the Agricultural Division of Mobay Chemical Corporation in Kansas City, Missouri, will help stimulate discussion on this subject.

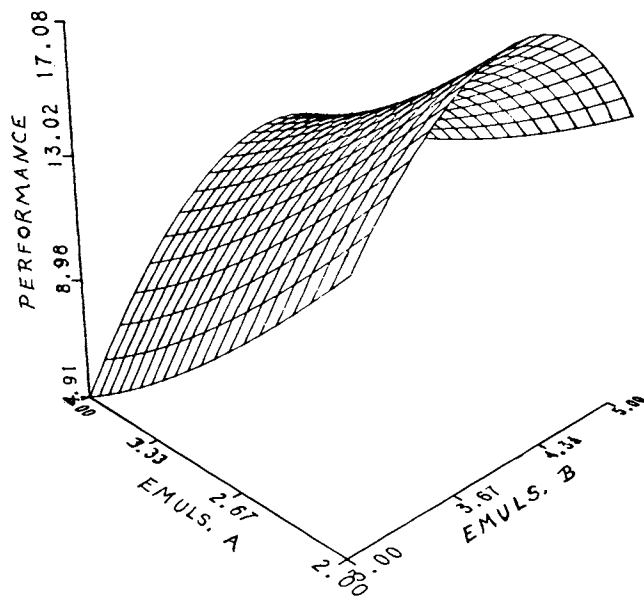


Figure 6. 3-Dimensional Perspective, FCR 1272 2EC, AI = 28.7%.

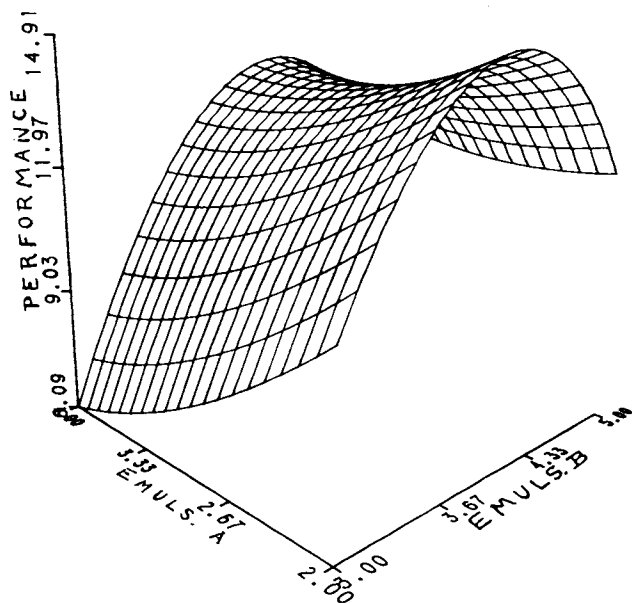


Figure 7. 3-Dimensional Perspective, FCR 1272 2EC, AI = 30.7%.

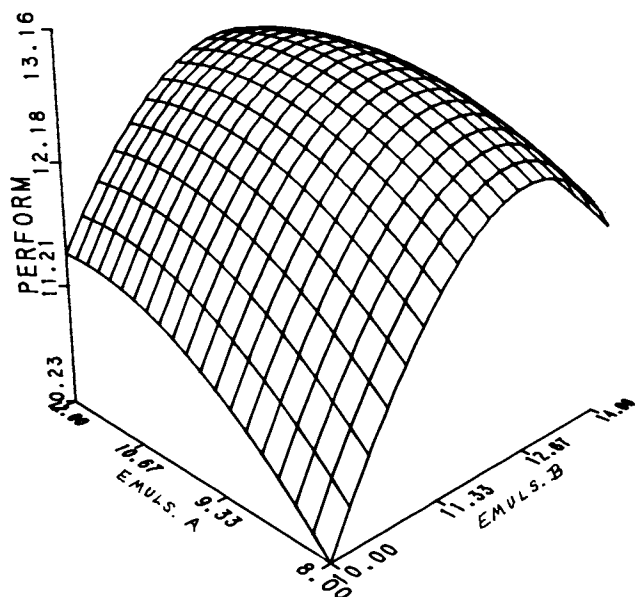


Figure 8. 3-Dimensional Perspective, FCR 1272 200 EC, AI = 19.3%.

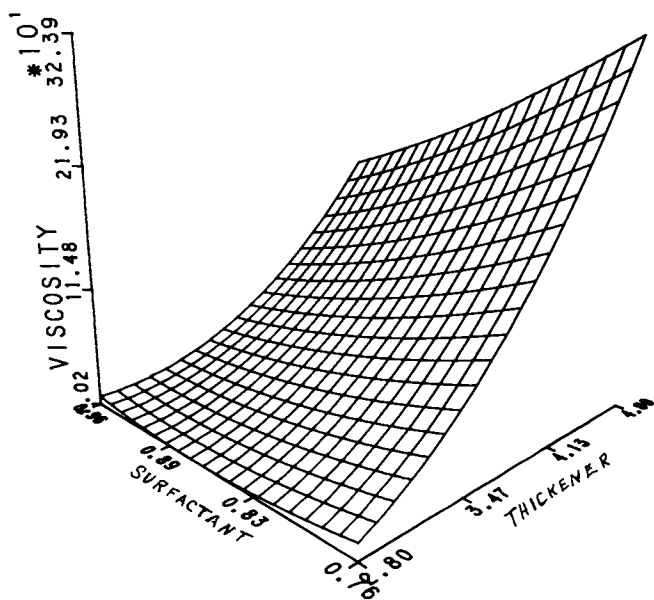


Figure 9. 3-Dimensional Perspective, Dylox 1.5 Oil Flowable.

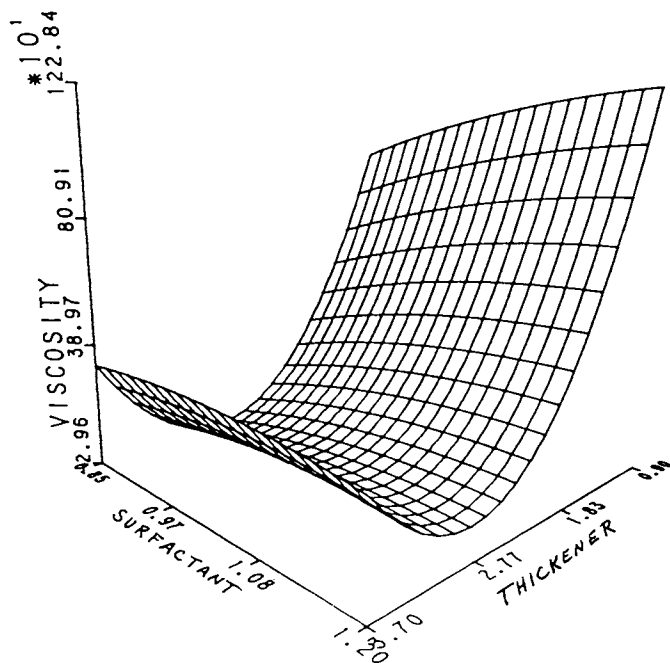


Figure 10. 3-Dimensional Perspective, Matacil 180 Oil Flowable.



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## Computer-Assisted Correlation Analysis in the Development of Pesticide Formulations

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The use of computer-assisted methods in the development of pesticide formulations has been exemplified by correlating suspensibility with composition in a set of wettable powder formulations. The concentrations of the three inert ingredients in these formulations (which contain captan fungicide, clay, dispersant and surfactant) were varied according to a composite-star experimental design to generate a set of formulations for suspensibility determinations. Regression analysis of the experimental data for 14 formulations yields an empirical equation, with 5 independent variable terms, that accounts for 91% of the variance in the experimental suspensibility values. This empirical equation has been used to generate a response-surface map, which illustrates the dependence of suspensibility on composition. The advantages and limitations of using computer-assisted methods to develop pesticide formulations are discussed.

Understanding the relationship between the composition of a mixture and its properties is fundamental to the development of formulated products. In the pesticide industry, formulation chemists seek to translate such an understanding into products that meet criteria established for properties such as suspensibility, emulsibility, storage stability, compatibility, and most importantly, biological activity. The preferable way to acquire the necessary knowledge is to deduce the properties of mixtures in terms of mechanisms that are operative at the microscopic level. However, mixtures are extremely complex systems and the available theory is usually insufficient for developing useful theoretical models. For example, we are unable quantitatively to predict, on the basis of molecular theory, the suspensibility of a wettable powder from a knowledge of its composition.

The inability to adequately understand complex systems — such as solutions and condensed phases in general — on the basis of molecular theory has made it necessary to develop alternative methods. Basically

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there are two approaches (1) that are available for this purpose. In the first, simplifying assumptions are made so that the available theory may be applied to make calculations and interpretations. Unfortunately, in most instances, the degree of approximation is so extensive that the relationship to the original theory becomes tenuous. The second approach has been to observe the macroscopic behavior of a system and interpret it in terms of an empirical model. A satisfactory model not only accounts for the experimental data, but more importantly provides predictive capability within a given system. Once an empirical model has been identified, attempts are then made to introduce appropriate amounts of molecular theory to rationalize the model. An objective of this approach, which is frequently used in chemical research, is to generate empirical equations that satisfactorily correlate experimental data. The process of generating the desired empirical equations has been facilitated by the availability of numerous computer-assisted techniques, particularly those involving multivariate statistical procedures such as regression analysis, principal components analysis, and discriminant analysis. A well-known application of statistical methodology in pesticide research is the development of quantitative structure-activity relationships (QSAR). These are empirical equations that correlate biological activity with selected structural parameters of compounds. While the correlation of structure with activity has received considerable attention, the relationship between the composition of a mixture and its properties has not been extensively investigated. Empirical equations for rocket flares (2), insecticide mixtures (3), gasoline blends (4), food products (5), and pharmaceutical formulations (6) have been reported. The last reference is one of the few that specifically concerns formulations development.

The objective of this report is to discuss with the help of an illustrative example, the applicability of computer-assisted methods to the development of pesticide formulations. The example describes the process of planning and conducting a study to obtain an empirical equation which correlates the suspensibility of a wettable powder with its composition.

### Experimental Data For Suspensibility Correlation

Wettable Powders. The compositions of the wettable powders examined in this study are indicated in Table I. The concentration of the active ingredient, captan fungicide (5.2  $\mu\text{m}$  median particle diameter), was held constant while the inert ingredients — clay, dispersant, and surfactant — were varied within a practical range. Wettable powders were prepared by mechanically blending the components, and then processing the resulting mixture through a laboratory hammer-mill.

Experimental Design. Figure 1 shows the composite-star experimental design according to which the wettable powder compositions of this study were selected. This type of experimental design has proved to be useful in correlating the properties of mixtures, in which the concentrations of

Table I. Composition Data for Wettable Powder Formulations.

Component	Description	Concentration Range ( % )
1. Captan fungicide	technical grade (92%)	55.0
2. Clay carrier	kaolin clay	43.20 - 15.00
3. Dispersant	sodium naphthalene formaldehyde condensate	0.90 - 15.00
4. Surfactant	sodium N-methyl-N-oleoyl taurate	0.90 - 15.00

the variable components have upper and lower bounds. The parallelogram 1234, defined by the concentration ranges selected for the three variable components, encloses the data space of this study. The 14 points in the parallelogram — located at the vertices and midpoints on the sides and diagonals — indicate the relative concentrations of the variable components in the corresponding wettable powder formulations. Since the variable components constitute 45% of these wettable powders, a relative concentration multiplied by 0.45 is equal to the actual concentration. As exemplified in this case, it is often convenient in mixture experiments to consider relative concentrations — sometimes referred to as pseudocomponent concentrations — rather than actual ones. The two concentrations are related by a constant multiplier. Correlation was initially attempted with the data for 13 experimental formulations. However, the inclusion of an additional formulation became necessary to obtain satisfactory statistical significance. This additional experimental point — located near vertex 1, on the diagonal — was selected to provide better representation of formulations with relatively low suspensibility. Pseudocomponent concentrations, actual compositions, and suspensibility values for the 14 experimental formulations of this study are listed in Table II. Only the three variable components appear in Table II; the fourth component captan fungicide, was maintained at a constant concentration of 55%.

**Estimation of Suspensibility.** Suspensibility was estimated in terms of a sedimentation rate. Aliquots (4 g) of accurately weighed wettable powder were dispersed in each of two portions (approximately 70 ml) of deionized water contained in 250 ml beakers. The resulting suspensions were quantitatively transferred to 100 ml graduated cylinders and made up to volume (100 ml) with deionized water. Both cylinders were agitated simultaneously by subjecting them to 30 smooth inversions in about 30

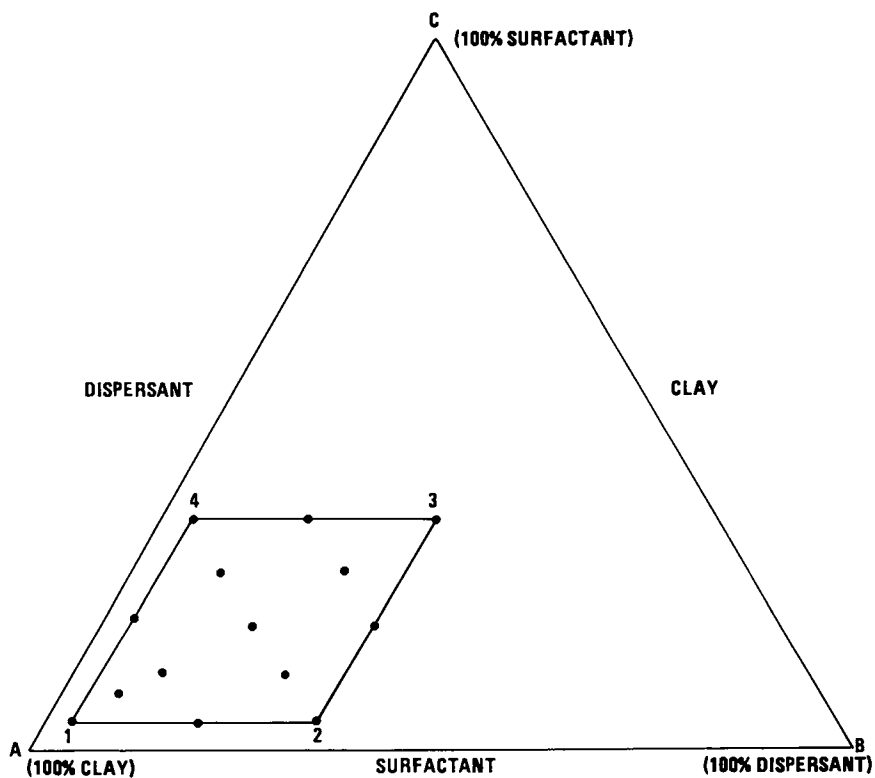


Figure 1. Experimental Design for Suspensibility Correlation.

Table II. Composition and Suspensibility Data for Wettable Powder Formulations.

FORMULA #	PSEUDOCOMPONENTS (%)			COMPONENTS (%)			SUSP (%)
	CLAY (A)	DISP (B)	SURF (C)	CLAY (X1)	DISP (X2)	SURF (X3)	
1	96.00	2.00	2.00	43.20	0.90	0.90	28.0
2	64.67	33.33	2.00	29.10	15.00	0.90	67.2
3	33.33	33.33	33.33	15.00	15.00	15.00	71.4
4	64.67	2.00	33.33	29.10	0.90	15.00	56.0
5	80.33	2.00	17.67	36.15	0.90	7.95	63.7
6	80.33	17.67	2.00	36.15	7.95	0.90	79.7
7	49.00	33.33	17.67	22.05	15.00	7.95	59.7
8	49.00	17.67	33.33	22.05	7.95	15.00	58.0
9	64.67	17.67	17.67	29.10	7.95	7.95	61.5
10	80.33	9.83	9.83	36.15	4.42	4.42	64.8
11	64.67	25.50	9.83	29.10	11.47	4.42	67.4
12	49.00	25.50	25.50	22.05	11.47	11.47	54.2
13	64.67	9.83	25.50	29.10	4.42	11.47	60.8
14	88.00	6.00	6.00	39.60	2.70	2.70	48.6

seconds. The cylinders were then placed in a 25°C water bath and allowed to equilibrate for 15 minutes. The agitation procedure was then repeated, and the top 25 ml from one cylinder was immediately transferred by pipette to a tared centrifuge tube. This sample was designated as Sample 1. During the transfer process, care was taken to keep the tip of the pipette as close to the liquid surface as possible; agitation of the suspension was kept at a minimum. The second cylinder was allowed to remain in the water bath for an additional 15 minutes and then sampled as before to obtain Sample 2. Both samples were centrifuged and the clear supernatant layers were discarded. The sediment in each tube was resuspended with deionized water and the separation procedure was repeated. The centrifuge tubes, containing sediment, were placed in a 50°C oven to obtain an essentially moisture-free residue (comprising the water insoluble components, captan and clay) in each of the tubes. These were then weighed to determine the mass of residue resulting from each sample. Equation 1 was used to provide an estimate of the per cent suspensibility (SUSP).

$$\text{SUSP} = \frac{(\text{mass of residue from Sample 2})}{(\text{mass of residue from Sample 1})} \times 100 \quad (1)$$

The experimental suspensibility values listed in Table II represent the average of two determinations. A pooled standard deviation of 3.8% was calculated for the suspensibility determinations.

Data Analysis. Unless otherwise mentioned, SAS software (7) was used to analyze suspensibility data and generate empirical equations. SAS (Statistical Analysis System) is a widely used data-analysis system that comprises a group of computer programs which are integrated in a way that allows efficient execution of numerous statistical routines.

## Results and Discussion

Additive Equations. Additive empirical equations have been widely used in chemistry to correlate numerous properties including, biological activity (8), thermodynamic parameters (9), and partition coefficients (10, 11). In an additive equation, a response variable such as suspensibility or biological activity, is expressed as a sum of contributions from other selected properties — for example concentration, partition coefficient, and refractive index. A mathematical rationale for the use of additive equations is that a complex function — such as a theoretically derived model — may be transformed to an additive form by applying a procedure known as the Taylor expansion. The resulting polynomial may then be simplified, by neglecting higher order terms, to obtain an additive equation that approximates the initial function or theoretical model. In some cases the omission of higher order terms is not valid; this is one of the reasons why the approximations sometimes fail to provide satisfactory correlations.

Equation 2 represents a type of additive equation — sometimes described as a special-cubic equation — that has been widely used to correlate properties of mixtures. In Equation 2, Y represents the value of the response variable; X1, X2, and X3 the concentrations of the variable components; and k is a constant term. In this study, fitting the experimental data by regression analysis to a modification of Equation 2 provides an empirical equation that satisfactorily correlates susceptibility with concentrations of clay, dispersant, and surfactant. The reason for modifying Equation 2, by reducing the number terms in the polynomial, is discussed in the next section.

$$Y = a_1 X_1 + a_2 X_2 + a_3 X_3 + a_{12} X_1 X_2 + a_{23} X_2 X_3 + a_{13} X_1 X_3 + a_{123} X_1 X_2 X_3 + k \quad (2)$$

Selection of Regression Equation. Before proceeding with regression analysis, it was necessary to obtain some information about the statistical significance of the independent variable terms in Equation 2. The objective was to explore whether the number of terms in Equation 2 could be reduced while maintaining an acceptable degree of correlation. This was done with this help of the RSQUARE routine of SAS. RSQUARE provides the correlation coefficients for the regression equations that result from all possible combinations of the independent variable terms. Since there are seven independent variable terms in Equation 2, the output from RSQUARE contained 127 correlation coefficients. Table III is an excerpt from the RSQUARE output which indicates the maximum correlation obtained with a given number of variable terms. Since the correlation coefficient is dependent on the number of variables, the values listed in Table III are not directly comparable. The most important outcome of an analysis of this type is the identification of the general form of empirical equations that provide an acceptable level of correlation. The RSQUARE routine provides a striking example of the efficiency of an integrated data-analysis system. Only a few years ago, a computation of this type would have been both laborious and intimidating.

From an inspection of the RSQUARE output, the five-variable equation with the highest correlation was selected for a more complete regression analysis. The five-variable equation (Equation 3) represents the best balance between high correlation and economy in the number of variable parameters. A serious disadvantage of having numerous independent variables in an empirical equation is the increased risk of a chance correlation (12). Consequently, the number of experimental observations required to establish statistical significance increases rapidly with the number of independent variables. In this study, 14 experimental determinations were required to obtain statistical significance at the 95% confidence level.

$$SUSP = a_2 X_2 + a_{12} X_1 X_2 + a_{23} X_2 X_3 + a_{13} X_1 X_3 + a_{123} X_1 X_2 X_3 + k \quad (3)$$



Table III. Excerpt from RSQUARE Output Showing Correlation Coefficients for Additive Equations Containing Selected Independent Variables

Number in Model	R Square	Variables
1	0.2898	X1X2
2	0.3812	X1X2 X1X3
3	0.4615	X3 X1X2 X1X2X3
4	0.5422	X1 X2 X3 X1X2
5	0.9085	X1 X1X2 X2X3 X1X3 X1X2X3
6	0.9248	X2 X3 X1X2 X2X3 X1X3 X1X2X3
7	0.9286	X1 X2 X3 X1X2 X2X3 X1X3 X1X2X3

**Regression Analysis.** The GLM (General Linear Models) procedure of SAS was used to fit the experimental data to Equation 3. This procedure provides estimates of coefficients and intercept; GLM also tests hypotheses and indicates the overall quality of the correlation. Output from the GLM procedure is shown in Tables IV, V, and VI; numbers, which are listed to 6 decimal places in the original output, have been rounded off to 4 places.

Table IV shows the overall analysis of variance (ANOVA) and lists some miscellaneous statistics. The ANOVA table breaks down the total sum of squares for the response variable into the portion attributable to the model, Equation 3, and the portion the model does not account for, which is attributed to error. The mean square for error is an estimate of the variance of the residuals — differences between observed values of suspensibility and those predicted by the empirical equation. The F-value provides a method for testing how well the model as a whole — after adjusting for the mean — accounts for the variation in suspensibility. A small value for the significance probability, labelled  $PR > F$  and 0.0006 in this case, indicates that the correlation is significant. The  $R^2$  (correlation coefficient) value of 0.9085 indicates that Equation 3 accounts for 91% of the experimental variation in suspensibility. The coefficient of variation (C.V.) is a measure of the amount variation in suspensibility. It is equal to the standard deviation of the response variable (STD DEV) expressed as a percentage of the mean of the response response variable (SUSP MEAN). Since the coefficient of variation is unitless, it is often preferred for estimating the goodness of fit.

Table IV. Analysis of Variance for Suspensibility Correlation

SOURCE	DF	SUM OF SQUARES	MEAN SQUARE	F VALUE
MODEL	5	1700.6168	340.1234	15.89
ERROR	8	171.2717	21.4090	PR > F
CORRECTED TOTAL	13	1871.8886		0.0006

RSQUARE	C.V.	STD DEV	SUSP MEAN
0.9085	7.7025	4.6270	60.0714

Table V lists the estimates of the intercept and the coefficients of Equation 3. The entries labelled T FOR  $H_0$ : PARAMETER = 0 are the t-values for testing the null hypothesis that any parameter equals zero. The value of each entry under PR > T answers the question, "If the parameter is really equal to zero, what is the probability of getting a larger value of t?" A small value for this probability indicates that it is unlikely that the parameter is actually equal to zero. For example, the probability-significance value for the coefficient of  $X_1X_2X_3$  is 0.0002, consequently, the hypothesis that  $a_{123} = 0$  is not acceptable. The finding that all the parameters of Equation 3 are significant confirms the results obtained from the RSQUARE procedure.

Table VI is a table of residuals, provided by the GLM procedure, that lists for each of the 14 experimental formulas the difference between the observed suspensibility and that predicted by Equation 3 (using the parameter estimates listed in Table V).

**Response-Surface Map.** A particularly useful application of an empirical equation is the construction of response-surface maps. These maps are pictorial representations — in the form of contour maps — which depict the behavior of the response variable in geometric planes defined by two of the independent variables. Figure 2 is a response-surface map, generated from Equation 3 and Table V, in a plane defined by the concentration of dispersant and clay. The contour lines connect points of equal predicted response — in this case suspensibility — and are therefore known as iso-response lines. The iso-response lines of Figure 2 were drawn with the aid of a computer routine (13) in which suspensibility values were calculated for pairs of  $X_1$  and  $X_2$  values in the experimental space. In the plotting algorithm, two nested loops are used to increment  $X_1$  and  $X_2$  in steps of 0.06%. Since  $X_3$  is specified by  $X_1$  and  $X_2$ , a suspensibility value may be calculated after each step from Equation 3 and Table V. If the calculated value at any point is  $(5n \pm 0.5)\%$  ( $n$  is an integer less than 21) then that point is plotted. A series of points corresponding to the same suspensibility value defines a contour line on the response-surface map.

Table V. Parameter Estimates for Equation 3 Obtained by Regression Analysis.

PARAMETER	ESTIMATE	T FOR H <sub>0</sub> : PARAMETER = 0	PR > /T/	STD ERROR OF ESTIMATE
k	-478.506	-5.28	0.0007	90.673
a <sub>1</sub>	10.867	5.66	0.0005	1.919
a <sub>12</sub>	0.505	6.98	0.0001	0.072
a <sub>23</sub>	1.519	6.33	0.0002	0.234
a <sub>13</sub>	0.470	6.51	0.0002	0.072
a <sub>123</sub>	-0.051	-6.68	0.0002	0.008

Table VI. Table of Residuals for Suspensibility Correlation.

FORMULA #	SUSP	PREDICTED	RESIDUAL
1	28.0	28.3	-0.3
2	67.2	70.7	-3.5
3	71.4	72.5	-1.1
4	56.0	56.6	-0.6
5	63.7	63.5	0.2
6	79.7	72.3	7.4
7	59.7	56.7	3.0
8	58.0	51.4	6.6
9	61.5	65.0	-3.5
10	64.8	63.6	1.2
11	67.4	68.1	-0.7
12	54.2	58.9	-4.7
13	60.8	61.1	-0.3
14	48.6	52.3	-3.7

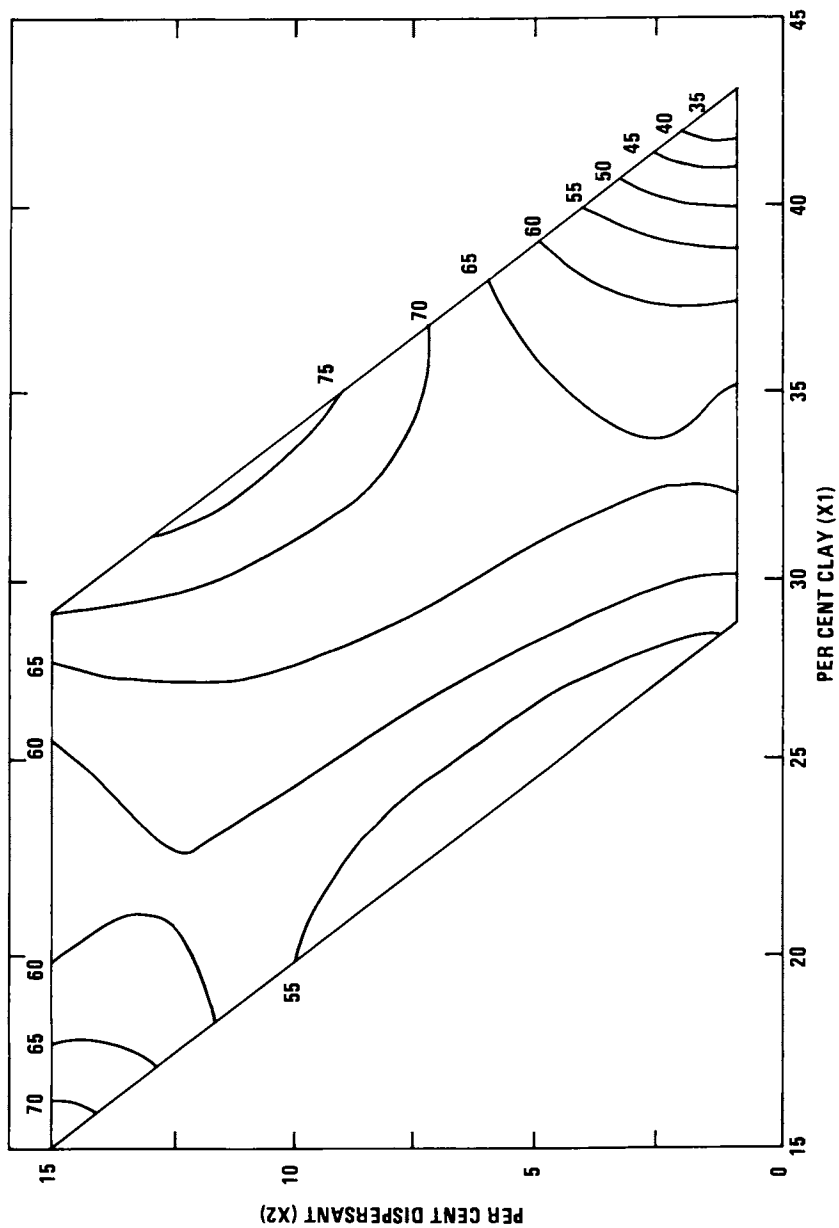


Figure 2. Response-Surface Map for Suspensibility Correlation.

Figure 2 clearly indicates that a captan wettable powder containing approximately 55% captan, 33% clay, 11% dispersant, and 1% surfactant should be evaluated if maximum suspensibility is desired. In addition to indicating regions of optimal composition, response-surface maps are extremely useful in analyzing cost vs. performance. Questions such as, "What is the most economical formulation that has 60% suspensibility?" may be answered objectively, without additional experimentation.

Advantages and Limitations of Computer-Assisted Methods. In developing formulations with the aid of computers, it is important to be aware of the limitations of such an approach. While computer methods help to render experimental data into useful forms, such as empirical equations, they are no substitute for chemical knowledge. In the illustrative example discussed in this study, the process of deriving an empirical equation could only be commenced after the components of the formulation were identified. The contribution of computer-assisted development was to provide an empirical equation that may be used to specify concentrations of the selected components in optimal formulations. While statistical techniques may be of some assistance in screening components, chemical knowledge is essential in selecting the clays, dispersants, and surfactants that might be suitable for formulating captan as a wettable powder. Computer methods are therefore valuable tools that help formulation chemists to extend their skills, not replace them.

Some other limitations are associated with the statistical methods that are used to interpret the experimental data. The primary objective of these methods is to predict the behavior of a population — within an experimental space — based on the observation of a sample. In the suspensibility correlation, the 14 experimental formulations represent the sample, while the population comprises all possible formulations within the experimental space. There are risks associated with making such predictions which could result in erroneous conclusions. These risks may be minimized by proper attention to the experimental design and the assumptions of the statistical methods being used to analyze the experimental data. Regression analysis is a preferred method for correlating mixture-data. However, not all such data are amenable to regression analysis, and a desired level of predictive capability may not be attainable. The process of generating an empirical equation by regression analysis requires a response variable that is quantitatively measurable with an appropriate degree of precision. Unfortunately, many of the response variables associated with formulations are difficult to quantify. This is evidenced by qualitative descriptions such as excellent bloom, poor compatibility, or excessive dusting for those response variables. Although there are statistical methods for dealing with qualitative and semi-quantitative variables (see Conclusions section), it is important to recognize that in some situations computer methods are not necessary and existing methods are adequate.

A major advantage of computer-assisted analysis is that it introduces the critical elements of planning and economy into a development program. While the intuitive process plays an essential role in the early stages of development, its dominance in the later stages is usually detrimental. There is perhaps nothing more damaging to the science of pesticide formulation than the unplanned, or poorly planned, mixing of ingredients until a desired mixture is obtained — or perhaps more frequently not obtained. A well-known example of a poor experimental plan, which unfortunately is all too common, is the one-at-a-time variation of independent variables. The pitfalls of such a plan, which have been well documented (14), can be readily avoided by implementing a statistically sound experimental design followed by correlation analysis of the experimental data. The ability to generate a response-surface map is a compelling reason to use regression analysis when appropriate. Another advantage is that complex mixtures, with numerous components, may be studied by correlation analysis. For the purposes of this report, it was convenient to study a relatively simple formulation; however, the same techniques may be used with formulations having more variable components. It may be rightly argued, that an experienced chemist could specify, with a minimum amount of effort, the ratios of the three variable components in a satisfactory formulation. While the intuitive route to a formulated product may be occasionally appropriate, the objectivity, efficiency, and predictive capability of the computer-assisted approach are difficult to match.

### Conclusions

This report describes how computer-assisted correlational analysis may be used in the development of pesticide formulations. In the example used to illustrate methodology, the suspensibility of a captan 50% wettable powder has been correlated with its composition. The correlation is expressed by an empirical equation, with 5 independent variable terms, that accounts for 91% of the variance in the suspensibility values of 14 experimental formulations. These formulations contain four components: captan fungicide, clay, dispersant, and surfactant. Only the concentrations of the three inert ingredients were varied, according to a composite-star design, to generate an experimental set of 14 formulations. The empirical correlation equation has been used to generate a response-surface map, that illustrates the dependence of suspensibility on composition. The map indicates regions of maximum suspensibility, and facilitates cost vs. performance evaluations.

The methods used to correlate suspensibility may be used with other response variables — such as biological activity, stability, or yield value — that are important in the development of pesticides. Also, formulations of greater complexity, which have more components, can be studied with the same correlational techniques. There are, however, many important response variables that are qualitative or semiquantitative and are not usually estimated with the precision necessary for reliable regression analysis. These include, freeze-thaw stability, bloom, compatibility, and

physical stability. There are statistical methods for handling less precise response variables; in our research program we are exploring the utility of other correlation techniques such as pattern recognition, rank correlation, discriminant analysis, and simplex-optimization. The last two techniques seem to be particularly applicable to formulation studies.

While correlation analysis is clearly a powerful technique for studying formulations, the limitations of this and other computer-assisted methods should be recognized. There are many situations where computer methods do not offer any particular benefits, and existing methods are quite adequate. Also, some aspects of formulations development will continue to be more art than science. However, there seems to be little doubt that many of the major advances in the technology of pesticide formulations will be associated with the judicious use of computer-assisted methods.

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## Computerized Optimization of Emulsifiers for Pesticide Emulsifiable Concentrates

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The art of developing emulsifiers and emulsifier blends for pesticide emulsifiable concentrates has been practiced for many years. In a large number of cases, due to the complexity of emulsion systems and the time pressure placed on the practitioner, emulsifiers are designed by empirical test data coupled with intuition and experience. This talk will discuss a logical, numeric method of a) defining an emulsification problem in terms of averaging easily understood parameters for oil mixtures, defining the water types, and emulsifier types desired; b) mathematically determining a near neighborhood "best" emulsifier combination to solve the emulsification problem; and c) a subsequent, computerization of the mathematical methods described above.

The agricultural formulation chemist is faced with myriad variables to evaluate in the development of a new product. This is an ideal type of problem environment for the employment of a suitable computer program. The computer program, based on a mathematical model, should be of such character to allow:

- 1) Ease of input data collection
- 2) Logical evaluation of all pertinent variables and data within a clear, understandable, mathematical model
- 3) Generation of output data in a sorted collection of "near-neighborhood" best results

For the development of agricultural emulsifiable concentrates the application of the principles of Cohesive Energy Density yields a mathematical model. This model, when written into a computer program, satisfies the criteria above.

To demonstrate the effectiveness of this approach, a review of the C.E.D. principles, with an example application, is given

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below. The concept of Cohesive Energy Density was first developed by Hildebrand and Scott (1,2) in their research to define a physical parameter which would predict the miscibility of solvents. They found that the square root of the heat of vaporization divided by the molar volume of a solvent gave a useful solubility parameter. Thus,

$$\delta = \left(\frac{\epsilon}{V_m}\right)^{1/2} = \left(\frac{\Delta H_V - RT}{V_m}\right)^{1/2}$$

where  $\Delta H_V$  is the heat of vaporization,  $V_m$  is the molar volume, and  $RT$  (3) is a correction factor involving the universal gas constant and temperature. This parameter squared has the physical dimensions of calories per cubic centimeter. The theory implies, when considering two solvents, that if their parameters differ by a value of less than 2, they are miscible, and if their parameters differ by more than 3.5, they are immiscible. Using these parameters, Hildebrand was able to formulate an expression to determine the energy of mixing and an approximate heat of mixing for the combination of two solvents (2)

$$\Delta H^M \approx \Delta E^M = \phi_A \phi_B (X_A V_A + X_B V_B) (\delta_A - \delta_B)^2$$

This equation uses the volume fractions of the two solvents, nominally A and B; the molar fractions of the two solvents  $\phi_A$  and  $\phi_B$ ; the molar volumes of the two solvents  $V_A$  and  $V_B$ ; and the difference between their respective C.E.D. parameters squared. This approach makes very reasonable predictions concerning the interactions of solvents.

Charles M. Hansen (4) was working in the area of paint technology. He was aware of the Hildebrand/Scott solubility parameter, and explored the use of the solubility parameter in polymer-solvent interactions. He began his research with the consideration of the thermodynamic equation for the energy of mixing

$$\Delta F_{MIX} = \Delta H_{MIX} - T\Delta S_{MIX}$$

SOLUBILITY  $\uparrow$  AS  $H_{MIX} \downarrow$

He noted that the solubility increased for the interaction of two materials as the heat of mixing decreased. He, therefore, took note of the Hildebrand expression for the approximation of the heat of mixing

$$\frac{\Delta E_{MIX}}{\phi_A \phi_B} = V_m (\delta_A - \delta_B)^2 \approx \Delta H_{MIX}$$

He found that the C.E.D. parameter differential was not accurate enough for his purposes. Further research showed that added precision could be given to the bulk parameter by considering that parameter as being composed of three distinct types of

interactive energies. He postulated that these three specific cohesive energies were attributed to the London cohesive energy, the Keesom cohesive energy, and the hydrogen bonding cohesive energy. He further postulated that these three energy contributions to the bulk cohesive energy density parameter could be described in a straightforward vector summation expression

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

He then proceeded to break up the solvent bulk parameter into respective dispersion forces: Keesom, or polarity forces; hydrogen bonding forces; and London forces. He did the same for the polymers which were under his consideration. He compared these parameters for solvents and polymers term-wise, and analyzed their differentials in order to make predictions concerning their solubility interactions. In conducting 10,000 interaction experiments involving solvents and polymers, he found that he could make accurate predictions in 97% of the cases using his C.E.D. refinements.

A. Beerbower and J.R. Dickey (5) were also concerned with the interactions of solvents and polymers as they were working in an area concerning the effects of hydraulic fluids on hoses and linings. In applying the Hansen approach to their particular set of polymers and solvents, they found that accurate predictions required the addition of a correction factor:

$$\frac{\Delta E_{MIX}}{\phi_A \phi_B V_m} = (\delta_{DA} - \delta_{DB})^2 + (\delta_{PA} - \delta_{PB})^2 + (\delta_{HA} - \delta_{HB})^2 - 2\psi$$

In their analysis of this correction factor, they found that it was a function of the Keesom force and the hydrogen bonding force used in their original equation. They found that an improvement over the original vector summation of the three forces could be made by adjusting the polarity force and the hydrogen bonding force. This adjustment involved the multiplication of these two factors by a constant. It was found that this constant was specific, depending upon the particular liquid interaction. A brief table is given below showing the values of the constant correlated with particular types of interactions(3).

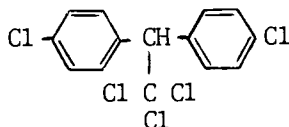
$$\psi = b \{ (\delta_{PA} - \delta_{PB})^2 + (\delta_{HA} - \delta_{HB})^2 \}^*$$

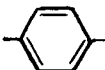
b	LIQUID INTERACTING WITH
.25	Polymers, Surfactants, Pigments
.205	Paraffins
.103	Aromatics

Several researchers such as Small, Hoy and McClellan (6-8) examined the chemical structure and chemical group contributions to the Cohesive Energy Density parameters. Through their efforts

tables have been built which contain the chemical group contributions for the molar volume, London force, Keesom force and hydrogen bonding force. Utilizing these tables, a worker has the ability to determine mathematical values for the aforementioned factors, by considering the chemical structure of a compound. For example, by examining the chemical structure of DDT, these four significant factors are determined, as below:

## C.E.D. STRUCTURAL CONTRIBUTIONS



	V	$V\delta_D$	$V\delta_P$	$V\delta_H^2$	$V_m = 261.7$
2 	2(74.7)	2(795.4)	2(50)	2(50)	$\delta_D = 9.85$
2 Cl	2(25.3)	2(161.0)	2(300)	2(100)	
1 - CH<	0	86.0	0	0	$\delta_P = 4.49$
1 >C<	-14.2	32.0	0	0	$\delta_H = 1.47$
1 Cl TWIN	50.6	342.7	175	165	
1 Cl	<u>(25.3)</u>	<u>205.1</u>	<u>300</u>	<u>100</u>	
	261.7	2578.6	1175	565	

These values can be of benefit to the researcher in selecting solvents for a compound under examination. Cohesive Energy Density parameters for solvents can be found in literature, such as a table found in the ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, Copyright 1971, by John Wiley and Sons, Inc. A mathematical comparison of various solvent parameters versus the parameters of the compound in question can be made. Those combinations which have the minimum mathematical difference are the most desirable combinations in terms of efficient solubilizing of the compound. In the DDT example, table values indicate that the chlorinated hydrocarbon solvents should be effective for solubilizing this technical material. This has been shown by experience to be the case.

Another advantage to the Cohesive Energy Density approach in defining the physical characteristics of materials is that volume fraction averaging (2) generates averages for the Cohesive Energy Density parameters. These averages work reasonably well over a broad range of molar volumes. Thus, when a technical material is combined with a solvent or solvents, an average of

all of the Cohesive Energy Density parameters may be obtained by multiplying each one of the components' parameters by its respective volume fraction in the formulation.

$$\bar{\delta}_D = \phi_1 \delta_{D_1} + \phi_2 \delta_{D_2}$$

$$\bar{\delta}_P = \phi_1 \delta_{P_1} + \phi_2 \delta_{P_2}$$

$$\bar{\delta}_H = \phi_1 \delta_{H_1} + \phi_2 \delta_{H_2}$$

In the DDT example, when it is combined in a formulation with xylene at a 30% weight-by-weight ratio, we have an estimated 18% volume-by-volume ratio of DDT to xylene. As this example demonstrates, we derive reasonable parameters for the Cohesive Energy Density parameters and molar volume using this technique.

30% w/w DDT/XYLENE  $\cong$

18% v/v DDT/XYLENE =

$$\bar{\delta}_D = .18(9.85) + .82(8.7) = 8.9$$

$$\bar{\delta}_P = .18(4.49) + .82(.5) = 1.2$$

$$\bar{\delta}_H \approx .18(1.47) + .82(1.5) = 1.5$$

$$\bar{V}_m \approx .18(261.7) + .82(121.2) = 146.5$$

At this point, we have laid the groundwork with sufficient theory to justify a test concerning its applicability to surfactants and emulsifiers. If the equations considered to this point hold up in the interactions of surfactants in water, we should be able to test their application per the nonionic cloud point phenomena encountered when using nonionic surfactants. In this test, we used the thermodynamic equation previously described, and, by curve fitting techniques, judge the accuracy of the implied fit of the experimental data versus the data generated from the proposed equation. This leads us to the consideration of the parameters and equations given below:

$$\Delta F_{\text{MIX}} = \phi_S \phi_W (X_S V_S + X_W V_W) \left[ (\delta_{D_S} - \delta_{D_W})^2 + .25 (\delta_{P_S} - \delta_{P_W})^2 + .25 (\delta_{H_S} - \delta_{H_W})^2 \right] + KRT \left[ X_S \ln X_S + X_W \ln X_W \right]$$

$$@ C_p (T), \Delta F_{\text{MIX}} = 0.0$$

WATER

$$\delta_{D_W} = 7.6, \quad \delta_{P_W} = 7.8, \quad \delta_{H_W} = 20.7$$

POLYOXYETHYLENE (9)

$$V_{\text{EO}} = (44n + 17)/1.125, \quad \delta_D = (344n - 160)/V_{\text{EO}}, \quad \delta_P = 18.3(1.5 + .1n)/V_{\text{EO}}^{1/2}, \quad \delta_H = \left[ (4650 - 660n)/V_{\text{EO}} \right]^{1/2}$$

Two types of surfactant nonionics were considered. The nonyl phenol ethoxylates and the octyl phenol ethoxylates. These two types of surfactants were chosen as they are often encountered in agricultural formulations because of their respective efficiency. The results of the evaluation are given below:

Cloud Point Temperatures Nonyl Phenol + N Moles E.O.				
N	Density gm/ml		Cp Temp. °F.	
	Actual	Calc.	Actual	Calc.
6	1.040	1.037	<32	29.3
8	1.053	1.049	70-87	86.5
12	1.068	1.066	178-182	174.7
14	1.073	1.072	202-205	206.2
Octyl Phenol + N Moles E.O.				
7.5	1.054	1.032	70	83.8
9.5	1.065	1.044	149	136.3
12.5	1.071	1.057	190	198.9

As can be noted, the correlation between the calculated and actual results, using a very simple curve fitting technique, yields good fits concerning molar volume, which is examined in terms of density, and in cloud point data, examined in terms of temperature. For those not familiar with the cloud point phenomena, nonionic surfactants exhibit inverse solubility characteristics per temperature increases, i.e., as the

temperature increases, the solubility of the nonionics in water decreases.

With the very encouraging correlation between calculated and real values for cloud points involving nonyl phenol ethoxylates and octyl phenol ethoxylates, it would seem that there is justification for proceeding with this mathematical model.

A mathematical model, which determines the type of emulsion form, was defined by Windsor in a qualitative sense, and by Beerbower in a quantitative sense, using Cohesive Energy Density parameters. In this model, the surfactant tails protruding into the aqueous phase and the oil phase are considered. This particular approach says that the surfactant, to be an effective emulsifier for the system, must accumulate at the interface between the two phases. And, once the surfactant has accumulated at the interface between the two phases, an effective swelling takes place in the hydrophilic portion of the surfactant and in the lipophilic portion of the surfactant. If more swelling occurs on the aqueous or water side of the oil/water partition, the curvature of the oil/water interface will be towards the oil. Secondly, if there is an equal amount of swelling of the hydrophilic portion and the lipophilic portion, the resultant emulsion will be a planar type, i.e., there is no tendency for curvature in the interface. Thirdly, if there is more swelling of the lipophile in the oil phase than there is of the hydrophile in the aqueous or water phase, the curvature will be towards the water.

Therefore, this approach defines three types of emulsions: 1) oil in water, or water continuous type; 2) the planar type; and 3) the water in oil invert type of emulsion, or oil continuous type. This effective swelling was quantified by Beerbower in his Cohesive Energy Ratio expression

$$R_o = \frac{V_L \delta_{*L}^2}{V_H \delta_{*H}^2} \quad \delta_{*}^2 = \delta_D^2 + (\delta_P^2 + \delta_H^2) \quad (.25)$$

In this expression, he divides the number of calories generated on the lipophile side of the surfactant by the number of calories generated by the hydrophile side of the surfactant. The amount of calories reflects or implies a proportional amount of swelling of the hydrophile and the lipophile, i.e., the greater number of calories on the lipophile side, the more tendency there is to form an oil in water type of emulsion. This definition of the C.E.R. (or Cohesive Energy Ratio) parameter leads to a direct expression which ties HLB to the Cohesive Energy Density parameter directly. The expression is:

$$\log_{10} R_o = .925 - .0963(\text{HLB})$$

A more detailed description of the relationship between HLB and Cohesive Energy Ratio is given in one of Beerbower's (10) papers. Also, this allows for a quantification of the type of emulsion per the value of the C.E.R. parameter. Thus, the quantified C.E.R. values for the three types of emulsions are given below:

$$O/W, R_o : \{.58 - .29\} \quad P, R_o : \{1.25 - .85\}$$

$$W/O, R_o : \{2.3 - 1.9\}$$

To check the validity of this approach, we considered the surfactants that we previously evaluated in the cloud point determinations. We evaluated the HLB by taking the percent of ethylene oxide per the particular surfactant and dividing it by five (5), which usually yields reliable HLB values, and comparing those results with the results found using the equation involving C.E.R. described above.

NONYL PHENOL + N MOLES ETHYLENE OXIDE

N	R	HLB [% E.O./5]	HLB
6	.6224	10.9	11.7
8	.4828	12.3	12.9
12	.3331	14.1	14.6
14	.2884	14.7	15.2

OCTYL PHENOL + N MOLES ETHYLENE OXIDE

7.5	.5458	12.3	12.3
9.5	.4405	13.4	13.3
12.5	.3415	14.5	14.5

As shown by the results found in this table, there is a reasonable correlation between the Cohesive Energy Ratio and the resultant HLBs using the relationship involving the Cohesive Energy Ratio and HLB values. Beerbower (11) extended this relationship to define the interaction between surfactants and oil/aqueous phases.

$$R_o = \frac{V_L [\delta_O^2 + \delta_L^2 - .5(\Delta\delta_{O,L})^2]}{V_H [\delta_{*W}^2 + \delta_{*H}^2 - .5(\Delta\delta_{W,H})^2]}$$

By this expression, the type of emulsion which will be formed using a particular surfactant and oil can be predetermined



mathematically, and also the converse. The expression involves the use of the molar volume of the lipophile, the molar volume of the hydrophile, the cohesive energy for the lipophile, the cohesive energy for the aqueous or water phase, the cohesive energy for the hydrophile, the differentials between the oil and the lipophile Cohesive Energy Density parameters, and the differential between the Cohesive Energy Density parameters for the hydrophile and the aqueous or water phase. The Cohesive Energy Density parameters for pure water can be found in literature, but the parameters for salt solutions have been determined by us, using laboratory tests.

This was accomplished by considering the Beerbower expression for the determination of the surface tension, using Cohesive Energy Density parameters and average molar volumes (3)

$$\gamma = .0715 V^{1/3} \left[ \delta_D^2 + .632 (\delta_P^2 + \delta_H^2) \right]$$

We, also, used the expression for the analysis of mixing (4)

$$\Delta F_m = \phi_1 \phi_2 \left[ X_1 V_1 + X_2 V_2 \right] (\delta_1 - \delta_2)^2 - T\Delta S$$

$$\delta_1 - \delta_2 \rightarrow 0 \text{ Max. Sol.}$$

Thus, by considering the apparent solubilities of water with various types of inorganic salts, and the surface tensions of these solutions, we were able to make determinations concerning the apparent associated Cohesive Energy Density parameters. In Figure 1 a comparison is made between the volume fraction of inorganic salt in the water solution and the surface tension divided by the Beerbower correction factor, divided by the cube root of the molar volume. Using this data, in addition to the data found in Table I, we are able to make reasonable approximations for the Cohesive Energy Density parameters associated with various concentrations of inorganic salt solutions.

To this point, we have considered the interaction of nonionic surfactants within the framework of the mathematical model. The activity and character of anionics in emulsification is complicated by the ionization steps which an anionic surfactant may take when exposed to salt solutions. For instance, in a dialkyl metallic salt, there are three compounds which may exist in various concentrations, depending upon the ionic strength of the salt solution which, in turn, would exhibit, at least, three different HLB numbers. To address the problem of generating Cohesive Energy Density parameters for the anionic hydrophiles, certain standardized assumptions

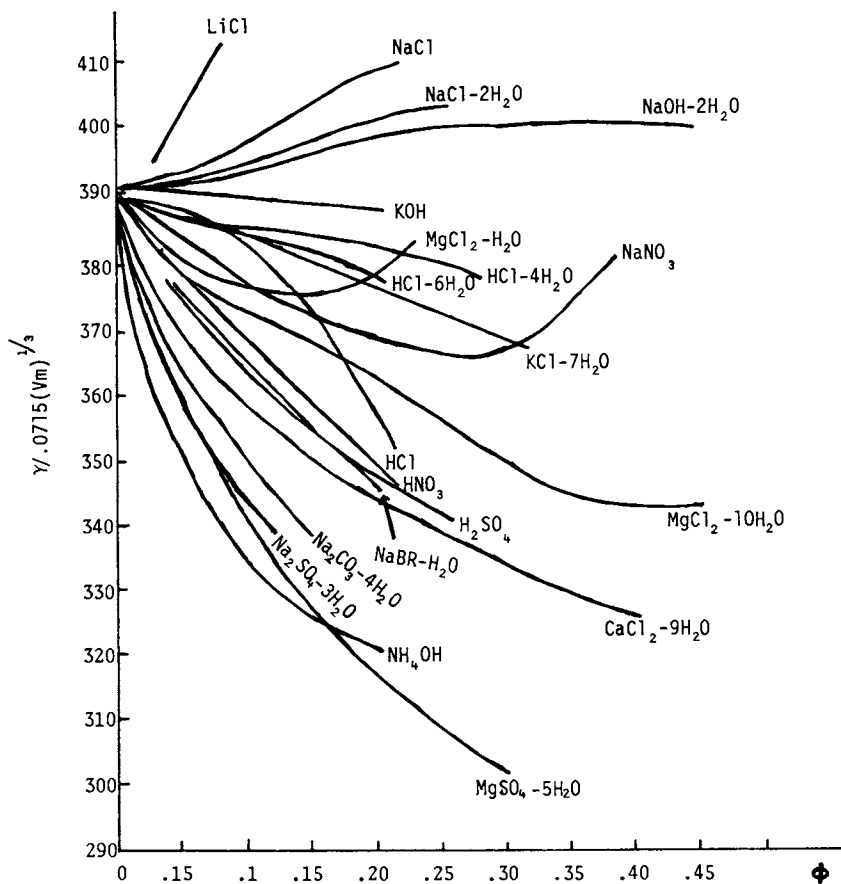


Figure 1  
C.E.D. Determination by  
Surface Tension Analysis

Table I  
C.E.D. Parameter Determination  
by Solubility Analysis

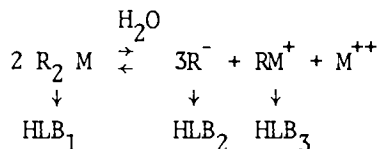
	Na <sub>2</sub> SO <sub>4</sub>	KOH	NaOH	NaCl	MgSO <sub>4</sub>	HCl	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> O	Urea	CaCl <sub>2</sub>	δ <sub>D</sub>	δ <sub>P</sub>	δ <sub>H</sub>
MeOH	SS+	S	S	S	S	S	S	S	S	S	7.4	6.0	10.9
Ethanol	SS	S	S	S	S	S	S	S	S	S	7.7	4.3	9.5
IPA	SS	S	S	SS	S	S	S	S	S	S	7.7	3.0	8.0
n-butanol	NS	NS	NS	NS	NS	NS	NS	SS-	NS	NS	7.8	2.8	7.7
Ethylene glycol	S	S	S	S	S	S	S	S	S	S	8.3	5.4	12.7
Propylene glycol	S	S	S	S	S	S	S	S	S	S	8.2	4.6	11.4
Dieth.Gly.M.Eth.	S	S	S	S	S	S	S	S	S	S	7.9	4.5	6.0
Dieth.Gly.M.But.	SS	SS	SS	SS	SS	S	S	S	S	S	7.8	2.5	6.0
Ethyl Ether	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	7.1	1.4	2.5
Dioxane	S	SS	SS	SS+	S	S	S	S	S	S	9.3	0.9	3.6
CS <sub>2</sub>	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	10.0	0.0	0.3
DMSO	S	S	S	S	S	S	S	S	S	S	9.0	8.0	5.0
Acetonitrile	SS-	SS-	SS-	SS-	S	S	S	S	S	S	7.5	8.8	3.0
Ethylene Carbona.	NS	S	NS	S	S	S	S	S	S	S	9.5	10.6	2.5
MeCl <sub>2</sub>	NS	NS	NS	S	S	S	S	S	S	S	8.9	3.1	3.0
2-Pyrrolidone	S-	S	S	S	NS	NS	NS	NS	NS	NS	8.5	8.5	5.5
N-meth-2-pyrrol.	S-	S	S	S	S	S	S	S	S	S	8.8	6.0	3.5
Cyclohexanol	NS	NS	NS	NS	NS	SS	NS	NS	NS	NS	8.5	2.0	6.6
Glycerine	S	S	S	S	S	S	S	S	S	S	8.5	5.9	14.3
Ethanol Amine	S-	S	S	S	SS	S	S	S	S	S	8.4	7.6	10.4
Formamide	S	S	S	S	S	S	S	S	S	S	8.4	12.8	9.3
Methyl Ethyl Ket.	NS	NS	NS	NS	SS	NS	NS	SS+	SS+	VSS	7.8	4.4	2.5
Epichlorohydrin	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	9.3	5.0	1.8
Nitro Benzene	NS	NS	NS	NS	NS	NS	NS	NS	NS+	NS+	9.8	4.2	2.0
Formic Acid	S	S	S	S	S	S	S	S	S	S	7.0	5.8	8.1
DMF	SS+	S	S	S	S	S	S	S	S	S	8.5	6.7	5.5
Nitromethane	NS	SS	SS	NS	VSS	NS	NS	VSS	NS	VSS	7.7	9.2	2.5

VSS=Very Slightly Soluble  
NS=Not Soluble

S=Soluble  
SS=Slightly Soluble

are needed. One is that the surfactant is exposed to pure water alone. Two, some standardized temperature will need to be used. With the standardized test conditions, it is possible to empirically determine a series of Cohesive Energy Density parameters for anionic surfactants.

#### ANIONIC IONIZATION



#### STANDARD HLB TESTS

$$\text{For HLB} = f(\text{HLB}_1, \text{HLB}_2, \text{HLB}_3,)$$

The C.E.D. parameters for anionics was addressed by Beerbower, and a series of values were determined for various anionic hydrophiles.

In the pursuit of a mathematical model to determine an optimized surfactant system, all the criteria mentioned to this point are critical. However, secondary mechanisms must be considered, such as the entropy of mixing associated with the interaction of the molar volume of the lipophile and the molar volume of the oil. This energy should be minimized as much as possible to ensure adhesion of the lipophile to the oil phase. Beerbower analyzed this entropy of mixing, using molar volumes and Cohesive Energy Density parameters. The equations associated with his mathematical approach are given below: (11)

#### ENTROPY OF MIXING

$$\Delta G = \Delta H - T\Delta S_m$$

$$\Delta G = C_{OL} - C_{OO} - C_{LL} - T\Delta S_m = 0.0$$

$$C_{OO} = \phi_o^2 V_L \delta_o^2 / \phi_L$$

$$C_{LL} = \phi_L V_L \delta_L^2$$

$$C_{OL} = 2 \phi_o V_L \delta_o \delta_L$$

$$T\Delta S_m = -RT(X_L \ln X_L + X_O \ln X_O)$$

Thus, he took the first step in producing an optimization technique for the development of surfactants and emulsifiers for a particular oil. Using a table such as Table II, showing the molar volumes and Cohesive Energy Densities for various lipophiles, one may start to make evaluations of the effectiveness of various surfactants in emulsifying oils. However, for the agricultural formulation chemist, one further optimization step should be taken. As the ag formulation chemist is concerned about the solubility of a surfactant in his formulation, he will need an optimization step which considers the solubility of the surfactant in the product.

An approach which may be taken is shown below:

#### OPTIMIZATION BY SOLUBILITY

$$V_E = V_L + V_H$$

$$\delta_{DE} = (V_L \delta_{DL} + V_H \delta_{DH})/V_E$$

$$\delta_{PE} = (V_L \delta_{PE} + V_H \delta_{PH})/V_E$$

$$\delta_{HE} = \left[ (V_L \delta_{HL} + V_H \delta_{HH})/V_E \right]^{1/2}$$

$$\Delta F_{OE} = \phi_O \phi_E (X_O V_O + X_E V_E) (\delta_E - \delta_O)^2 + \\ RT(X_O \ln X_O + X_E \ln X_E)$$

$$\text{MINIMIZE } \Delta F_{OE}$$

At this point, we have assembled a sufficient mathematical model for the selection of emulsifiers to be used in agricultural emulsifiable concentrates so that we may write a computer program which will take into consideration all the variables mentioned thus far. The mathematical model will take into consideration these variables, analyze the data in a logical systematic method, yield results which should give us a "near-neighborhood" to a "best" type of surfactant system. The computer program will require an input such as the table given below:

Table II

## C.E.D. Parameter Determinations

$\delta_D \approx$  Nonpolar Homomorph Comparison

$\delta_D \approx$  Boiling Point (Non Polar)

$\delta_D \approx$  Chemical Structure

$$\delta_P \approx \left[ \left( \frac{12.108}{V_m^2} \right) \cdot \left( \frac{\epsilon - 1}{2\epsilon + N_D^2} \right) (N_D^2 + 2) \mu^2 \right]^{1/2}$$

$$\delta_P \approx 18.3\mu / (V_m)^{1/2}$$

$\delta_P \approx$  Chemical Structure

$$\delta_H \approx (\delta^2 - \delta_D^2 - \delta_P^2)^{1/2}$$

$\delta_H \sim T_{OK}/M_W, T_{OK}$  Boiling Point

$\delta_H \approx$  Chemical Structure

## INPUT ACCOUNTING FOR ALL VARIABLES

- 1 Temperature of Emulsion
- 2 Volume Percent of Oil
- 3 Volume Percent of Emulsifier
- 4 Volume Percent of Water
- 5 Molecular Volume of Oil
- 6  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  of Oil
- 7 Molecular Volume of Water
- 8  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  of Water
- 9 Type of Emulsion
- 10 Type of Surfactant (Data Base)

In the DDT example mentioned above, calculating the parameters associated with the 30% concentration in xylene and analyzing the effectiveness of octyl phenol adducts versus nonyl phenol adducts, we see the correlation between the predicted performance and the laboratory evaluations. Thus, a flow chart of events for the calculation, using a computer program, would be as follows:

- 1) determine the Cohesive Energy Density parameters for the oil
- 2) determine lipophile differentials between the oil and lipophile parameters; minimize those values
- 3) determine the entropy of the interaction between the lipophile and the oils; minimize those values
- 4) evaluate the correct C.E.R. ratio for the desired surfactants
- 5) optimize the solubility of the particular solvent/pesticide/emulsifier combination
- 6) select the "N" best surfactants to accomplish the particular problem at hand
- 7) evaluate those "N" best surfactants in the laboratory

Using the DDT and nonionic examples cited above, we can evaluate the proposed mathematical model. This example also has the benefit of comparing two surfactants that are very similar in chemical structure and physical characteristics. Let us evaluate the model by defining the problem as follows:

1. Form an oil in water emulsion
2. Conduct emulsion test at room temperature
3. Dilute the oil at a five percent to ninety-five percent rate

4. Select the oil as the one cited above, i.e., 30% w/w DDT in xylene
5. Use five percent surfactant in the oil

The results of this test for a computer run using a program based on this model and laboratory evaluations are given below:

### I. Computer Results

- A. The first optimized selection was octyl phenol plus 8 moles of Ethylene Oxide.
  - 1) C.E.D. differential = 3.971
  - 2) Entropy factor = 0.1362
  - 3) Solubility factor = -0.015
- B. The second optimized selection was nonyl phenol plus 8 moles of Ethylene Oxide.
  - 1) C.E.D. differential factor = 4.500
  - 2) Entropy factor = .1829
  - 3) Solubility factor = 0.002

### II. Laboratory Results

- A. Octyl phenol plus N mole of Ethylene Oxide

N	% Layering in 1 hour
7.5	0
9.5	0
12.5	2-

- B. Nonyl phenol plus N moles of Ethylene Oxide

6	2
8	$\frac{1}{2}$
9.5	$\frac{1}{2}$
12.0	$1\frac{1}{2}$
14.0	$1\frac{1}{2}$

As shown by these results, very reasonable predictions can be made regarding surfactants in emulsification using the mathematical approach described.

This paper, because of its brevity, has made only a cursory examination of the details involved in the specific application of the principles described.



It has been our experience that, in the successful design and operation of a computer program of this type, all the subtleties of the theories and principles must be accounted for and incorporated into the mathematical model and subsequent workable computer program.

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## Microencapsulated Pesticides and Their Effects on Non-Target Insects

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Recent studies indicate that microencapsulated insecticides do not represent a unique or special hazard to beneficial insects, in particular bees. It has been found that not only microencapsulated methyl parathion but also emulsifiable concentrate formulations of various pesticides are carried back to hives by bees approximately in proportion to their rates of application. Field studies involving blooming crops have demonstrated that in many instances the microencapsulated methyl parathion is less hazardous to bees than the corresponding emulsifiable concentrate. This hazard can be further reduced by the addition of certain adjuvants of the "sticker" type which in experimental studies has resulted in 50 to 90 percent reductions in bee mortality. Numerous field observations on various crops have shown that microencapsulated methyl parathion frequently has a minimal adverse effect on entomophagous insects.

The widely used organophosphate insecticide methyl parathion was the first material to be formulated as a microencapsulated pesticide. This formulation, sold under the tradename PENNCAP-M Insecticide (a registered trademark of Pennwalt Corporation), consists of nylon-type microcapsules which contain the active ingredient. The capsules are suspended in water and typically have an average particle size of approximately 25 microns (fifty percent by weight of the capsules have a particle size of 25 microns or more). Upon application by conventional spray equipment the water evaporates, and the active ingredient is slowly released over an extended period of time.

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By virtue of their unique formulation, microencapsulated pesticides have significantly lower dermal and oral toxicities than the corresponding emulsifiable concentrate formulations. Microencapsulated methyl parathion (MMP) was introduced commercially in 1974; in 1976 and thereafter reports of bee kills allegedly caused by this product were published, primarily in the news media and non-refereed journals. Claims were subsequently made that MMP is carried back to the hive and is uniquely hazardous because the size of the microcapsules is in the range of many pollens.

Since many of the studies reported were after the fact of bee kills it was usually impossible to determine the conditions at the time of the application, or even which of several insecticide applications was responsible. We therefore undertook an extensive program to assess the hazard of MMP to bees. Such research was also conducted by government agencies, especially the USDA. (Note: Some of the crops and application methods reported herein are not consistent with the EPA-registered label. The crop application and methods employed were used solely to determine the nature and extent of the hazard and are not endorsed or recommended. The registered label should always be followed.)

#### Insecticide Contamination of Bee Hives

Our first objective was to determine whether microencapsulated methyl parathion is unique in its property to be carried back to the hive by bees. To that end a mixture of three commonly used insecticides along with MMP was applied to a plot of blooming rape. The agents were azinphos-methyl (Guthion), parathion, and carbaryl (Sevin). By using a mixture on a single plot the effects of variation in bee visitation were eliminated and the tendencies to be carried to the hive could be measured by the relative residue levels in the pollen samples. Five applications were made over a period of seventeen days. Pollen samples were collected from hives placed near the field after two, three, four, and five successive applications approximately two days after each application was made. The application rates were doubled for the last two applications. The data are shown in Table I.

Table I. Insecticide Residues in Rape Pollen

No. of Treatments	Residues (ppm)			
	MMP (a,b)	Parathion(b)	Azinphos- methyl(b)	Carbaryl(b)
2	0.23	0.08	0.59	0.39
3	0.13	0.04	0.33	0.35
4(c)	1.53	0.28	0.71	0.60
5(c)	0.39	0.36	0.26	1.2

a. PENNCAP-M

b. Initial application rates were 0.125, 0.36, 0.125, and 0.25 lb/acre of active ingredient for MMP, parathion, azinphos-methyl, and carbaryl, respectively.

c. Application rates were doubled.

Although the residues found cannot be correlated with the application rates, the results nevertheless demonstrate that all insecticides used in this test were absorbed on the pollen and carried back to the hive. These observations have been confirmed using other approaches by USDA and university researchers at the University of Wisconsin, who reported that foraging bees have brought back to their hives permethrin, carbaryl, and methyl parathion emulsifiable concentrate (MPEC) when applied to shedding corn.(1)

Another area of concern is the residual life of a pesticide once it is brought back to the hive. Microencapsulated methyl parathion was at one time believed to represent a special hazard because of its controlled release feature. Thus methyl parathion from MMP was reported to persist in stored pollen for up to 17 months.(2) Unfortunately, little is known about the persistence of insecticides in honey bee combs and the subsequent effects of their residues on the honey bees. Carbaryl has been shown to persist for at least eight months in colonies (4) and permethrin for at least seven months.(5) Recently, USDA researchers at the University of Wisconsin studied samples from two bee kills that apparently involved methomyl and MMP applied to sweet corn. Samples were collected to determine, among others, whether methomyl persisted in combs. Analysis demonstrated that eight months after the insecticide application, residues of 0.03 ppm of methyl parathion and 0.03 ppm of methomyl (5) remained, even though the latter is considered to be a short-residual pesticide.

In another study conducted by the Honey Bee Research Laboratory of the Agricultural Research Service in Laramie, Wyoming, pollen cake or dry pollen treated with MPEC or MMP was

fed long term at low rates in studies conducted in 1979 and 1980.(6) At rates of 0.01, 0.1, and 1.0 ppm (active ingredient, a.i.) no significant mortality differences were noted between the treated pollen and the control. At 10 ppm MMP there was significant mortality, and three out of six colonies died after 15 weeks; however, significantly higher mortality resulted when MPEC was fed at that concentration. These results are significant in that in numerous Pennwalt investigations of bee losses where MMP use was a suspected cause, the residues of methyl parathion, if found, were of the order of 1.0 ppm. The same authors conducted a similar study with carbofuran and found that all colonies died within eight days when they were fed sugar syrup containing 10 parts per million of that insecticide.(7)

#### Comparative Bee Toxicity of Insecticide-Treated Fields

To investigate the toxicity of field-applied MMP, USDA and Texas A&M researchers in 1981 near Lubbock, Texas, treated 10-acre plots of sunflowers in late full bloom with MPEC and MMP, respectively.(8) Six colonies of bees were placed near each of these fields as well as near a third untreated field which was retained as a control. Daily collections of dead bees and pollen were made to monitor the toxic effects of the insecticide and to estimate levels of foraging activity. The results are shown in Table II.

Table II. Bee Mortality - Sunflowers

	Total No. of Dead Bees (six colonies)		
	Untreated Control	MMP (a,b)	MPEC (b)
Before Treatment	116	119	126
Total for Five Days After Treatment	431	2760	11941

a. PENNCAP-M

b. Application rate 1 lb a.i./acre

Clearly, bee colonies exposed in this test to MMP suffered only about one fourth the damage experienced by the colonies exposed to MPEC. Peak mortality for MPEC-treated plots occurred on the first day and on the second day for the MMP. On the fifth day mortalities were 45, 82, and 207 dead bees for the control, MMP, and an MPEC, respectively. Similarly, the amount of pollen collected from the field treated with the MPEC was about 80% less than the amount collected from the MMP-treated plot.

Methyl parathion residues in trapped pollen before and for five days after application were also measured. No statistically significant differences were noted (Table III).

Table III. Methyl Parathion Residues in Trapped Pollen  
- Sunflowers

Day	Residues (ppm)	
	MPEC	MMP
0	0	-
1	1.94	1.62
2	0.73	0.49
3	0.19	0.06
4	0.16	0.08
5	0.08	0.04

Recently researchers at the Plant Science Research Laboratory of the USDA in Oklahoma examined the relative toxicity to honey bees of the two methyl parathion formulations when applied to flowering alfalfa. (9) Three aerial applications were made over a period of 21 days, two with MMP and one with MPEC. Bee mortality observed with MMP one day after application was only 11 percent of that observed for MPEC. Over the four-day period after application the total mortality in the MMP plot was 22 percent of that in the MPEC plot.

Table IV. Bee Mortality From Application of Methyl Parathion Formulations to Blooming Alfalfa

Days After Spray	Av. No. of Dead Bees (per hive)	
	MMP (a,b)	MPEC
Pre-Spray	15 ( 16)	21
1	287 (216)	2608
2	307 (116)	262
3	90 ( - )	219
4	65 (133)	198
5	35 ( 44)	-

a. PENNCAP-M

b. Figures in parentheses were obtained after a second application.

Studies comparing MMP with other pesticides have also shown that it does not represent an unusual hazard to bees. In Wisconsin application on pollen-shedding corn of carbaryl plus parathion

in early and standard treatments and of carbofuran all produced greater bee mortality than did MMP.(1)

Clearly, the above data indicate that microencapsulated pesticides do not necessarily represent a unique hazard to bees, but, to the contrary, there is evidence that this hazard, at least in the case of methyl parathion, is less than for the emulsifiable concentrate on many crops.

#### Reduction of Bee Mortality by Adjuvants

Studies conducted by Pennwalt Corporation in the past three years have indicated that the bee hazard of MMP may be further reduced by the addition of certain adjuvants. These additives are believed to be effective by reducing the pick-up of contaminated pollen by foraging bees. Numerous small-plot field studies were made by comparing bee mortality resulting from the application to various blooming crops of MMP alone or with a sticker formulation added to the spray. Reductions in bee mortality from 55 to 75% were noted (Table V).

Table V. Comparison of Bee Mortality in Small-Plot Tests on Blooming Crops - MMP vs. MMP Plus Sticker(a)

Crop	Av. No. of Dead Bees Per Hive(b)		
	MMP	MMP + Sticker	% Reduction
Buckwheat	413	125 (1%)(c)	70
Buckwheat	7533	1916 (2%)(c)	75
Safflower	1058	360	70
Mustard	12560	5705	55

- a. Experimental Pennwalt sticker formulation no. 1253.  
 b. Over background.  
 c. Sticker solids concentration in tank mix.

These results were confirmed in larger scale field trials using aerial applications on sunflowers and alfalfa. Tests conducted by USDA and Texas A&M researchers near Lubbock, Texas, on blooming sunflowers (10) and by E. L. Atkins of the University of California on blooming alfalfa (11) gave reductions in bee mortality versus MMP alone of 65 and 80 to 90%, respectively. A study by researchers at the USDA Honey Bee Pesticide-Diseases Research Laboratory, Laramie, Wyoming, (12) was conducted on sunflowers with bee colonies placed immediately adjacent to the fields treated with MMP and MMP Sticker combinations, respectively. A 49% reduction in bee mortality was noted in this test along with a 79% decrease in methyl parathion residues in pollen brought back from the sticker-treated field (Table VI).

Table VI. Comparison of Bee Mortality Large-Scale Tests on Blooming Crops - MMP vs. MMP Plus Sticker

Crop	Av. No. of Dead Bees Per Hive(a)		
	MMP	MMP + Sticker	% Reduction
Sunflowers (Wyoming)	765	387	49
Sunflowers (Texas)	13511	4682	65
Alfalfa (California)	508	100 (1%)(b) 29 (2%)(b)	80 94

a. Versus background.

b. Sticker solids conc. in tank mix.

#### Effect of MMP on Entomophagous Insects

The effects of MMP on entomophagous (parasitic and predatory) insect species have been evaluated primarily on alfalfa and apples, two crops where MMP is considered a standard treatment. Effects on these beneficial insect groups have also been investigated on corn and cotton, but to a lesser extent. The available data are summarized in Tables VII through IX. These data, in general, show MMP to have a minimal or no detrimental effect on most of the test species. For the most part, parasitic and predatory insect populations were reduced by less than 50% (Table VII). In several instances, the reduction approached 70% (Table VIII). Even considering the latter level of reduction, a large nucleus would be available from which beneficial insect populations could quickly rebuild.

As shown by the test data, in some areas the parasitic and predatory insect populations have even increased despite MMP applications (Table VII). In these locations phosphate resistance is suspected. However, MMP is effective against the pest species, as evidenced by its continued use.

The use of MMP at lower rates (compared to MPEC) to reduce the pest populations below the economic injury level, while

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Table VII. Impact of MMP on Entomophagous Insects: Minimal Effect (50-100% Survival of Check Population)

Crop	Species	Location	Researcher
Alfalfa	<i>Bathyplectes curculionis</i>	MO, CA	Huggins, Davis
	Spiders	UT	Davis
Apples	<i>Amblyseius fallacis</i>	PA, NY	Hull, Lienk
		MI*, OH*	Howitt, Hall
	Predacious bugs	WA	Covey
	Lady Beetles	WA	Covey
	<i>Metaseiulus occidentalis</i>	WA*	Hoyt
	<i>Stethorus punctum</i>	PA*	Hull, Asquith(1975) Asquith(1976)
			Howitt
	Predacious mites ( <i>Stigmaeidae</i> )	MI	Howitt
	Predacious mites ( <i>Typhlodromus</i> )	WA	Covey, Secondo
		WI	Davis
	Predacious mites ( <i>Zetzellia</i> )	WA, NY	Secondo, Weizes
Corn	Lacewings	MO	Keaster
	Pirate bugs	MO	Keaster
Cotton	Lady Beetles	TX	Nemec
	<i>Nabids</i> (Predacious bugs)	TX	Nemec

\* Population increased over check

Table VIII. Impact of MMP on Entomophagous Insects: Substantial Survival (30-49% of Check Population)

Crop	Species	Location	Researcher
Alfalfa	<i>Bathyplectes curculionis</i>	MO, CA	Huggins, Davis
	<i>Nabids</i> (Predacious bugs)	UT	Davis
		MO	Huggins
Corn	Lady Beetles	MO	Keaster
Cotton	Beneficials (species unknown)	AR	Kimbrough

still having the parasitic and predatory insects present to maintain the population below this threshold, is a real possibility. Obviously, development of Integrated Pest Management (IPM) programs is a complicated, time-consuming process, and determining the optimum use for MMP will take several seasons of testings on any given crop.

In some areas, parasitic and predatory insect populations appeared to be highly susceptible to MMP (Table IX).

Table IX. Impact of MMP on Entomophagous Insects: Low Survival (< 30% of Check Population)

Crop	Species	Location	Researcher
Alfalfa	<i>Coccinellids</i> (predatory beetles)	UT, NY	Davis, Gauthier
	Lady Beetles	MO*, UT*	Huggins, Davis
Apples	<i>Nabids</i> (predacious bugs)	CA*	Lamborn
	<i>Amblyseius fallacis</i> (predacious mite)	UT, MI	Davis, Ruppel
	<i>Anthocorids</i> (predacious bugs)	NY	Weires
Corn	<i>Aphelinus mali</i> (parasitic wasp)	CA	Pass
	<i>Nabids</i> (predacious bugs)	CA	Pass
Cotton	Parasitic hymenoptera	MI	Ruppel
		TX	Nemec

\* Complete Kill

There it is quite likely that no degree of resistance existed in the native population. The selection pressure most likely had not been as intense, and even with the reduced rate of active ingredient introduced by MMP (compared to MPEC), parasitic and predatory insect reduction was significant.

MMP introduces less active ingredient than MPEC into an agricultural ecosystem as a result of the reduced rates frequently possible with an encapsulated formulation. With less material being introduced, the effect on many parasitic and predatory insects is lessened, especially if a degree of tolerance already exists in their population. It is hoped that with further research on the usefulness of MMP in IPM, the insecticide will fulfill the promise which the data discussed here suggest.

### Conclusions

In summary, studies conducted by Pennwalt Corporation, USDA, and university researchers have demonstrated that microencapsulated methyl parathion does not represent an increased hazard to bees when compared to conventional formulations of methyl parathion; on the contrary, it is found to be less hazardous in controlled

tests on certain crops. In addition, studies with special additives in the spray tank suggest that the bee toxicity of this insecticide can be dramatically reduced further. This latter research is continuing.

The reduced effects on many parasitic and predatory insects suggest the careful evaluation of MMP in IPM programs. Further studies are needed to fully exploit this beneficial result of microencapsulation.

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## Development of an Aqueous-Based Controlled Release Pheromone-Pesticide System

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The state of the art of controlled released delivery systems in agriculture has advanced slowly in comparison with other areas of industry. This is especially true as compared to developments in the pharmaceutical industry. This situation has developed mainly due to the nature of the active ingredients and the associated high cost of the controlling system. Historically, agricultural chemical usage has been characterized by high dosage, low value and highly persistent active agents. Additionally, these actives must compete for market share with compounds of similar activity and price. In contrast, the pharmaceutical industry has had a distinct advantage by virtue of producing mainly low dosage, high value, non-persistent active agents. These agents are usually very specific in use and, thus, face much lower competition for market share. Also the nature of pharmaceutical applications is such that the chemicals are most effective when delivered at the action site in a controlled and precise rate. For these reasons, controlled release technology has been ideally suited for many applications in the pharmaceutical field. This is exemplified by the number of commercially available products and the new developments in basic research of biologically compatible controlled release drug delivery systems.

It now appears that the trend in the agricultural industry is toward the development of highly active and target specific chemical agents. These types of chemicals are represented by the synthetic pyrethroids, insect growth regulators, anti-juvenile hormones and pheromones. These novel chemical agents are active at very low dosage rates and are usually highly labile to environmental conditions. Successful formulations of these agents must provide ample environmental protection and precision delivery of the active to the target species. In the light of these developments, controlled release delivery systems are gaining increasing emphasis in formulation design. This is no more evident than in the use of pheromones for the control of specific insect species in economically important crops. The utility of these biologically native, single target specific chemicals, has been realized

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only through the use of well defined controlled-release delivery systems.

Controlled-release pheromone systems have found use in Integrated Pest Management programs as insect monitoring tools, in mass trapping strategies, and for mating disruption by air permeation. The latter technique has been modified so that the target species is attracted by the pheromone to a toxicant source. This 'attracticide' method offers the advantage of species specific eradication, without significant interference to beneficial predators. There are currently several systems specifically designed for insect monitoring and mass trapping techniques. Yet there are only two such systems that have been fully commercialized for large acreage mating disruption through air permeation, although several other systems are under development. The first system was introduced by Albany International's Conrel Division and consists of an impermeable hollow plastic fiber, sealed at one end and filled with a solvent solution of the pheromone(1), Figure 1. The system obtains release by evaporation of the pheromone solution from the open end with the pheromone diffusion rate being dependent upon the diameter of the fiber and the amount of pheromone initially present. This system has been shown to be useful for several pheromone types and has demonstrated its suitability for large acreage control of the Pink Bollworm, *Pectinophora Gossypiella* (Saunders), by mating disruption.

The second system was developed by the Hercon Division of Health Chem Corporation and consists of a laminated plastic chip, Figure 2. The chip is composed of a pheromone saturated polymer reservoir with a semi-permeable plastic membrane on either side. The pheromone is thus released by diffusion from the reservoir through the membrane. The rate is controlled by the membrane composition and thickness(2). The two systems are applied in a polybutene sticker to facilitate adhesion to the plant surface. For attracticide applications, an appropriate pesticide, usually a synthetic pyrethroid, is added to the sticker base. A common disadvantage of these systems is the need for specialized application equipment, which significantly limits the range of use of these systems. In the need for a more advanced system which would be self containing in pheromone and pesticide, and offer the distinct advantage of conventional application, Zoecon Corporation sought to develop an aqueous based controlled-release pheromone-pesticide system for attracticide applications. The requirements for a general formulation were the following:

- o General system for different pheromone types.
- o Aqueous based.
- o Constant and controllable release rate.
- o Extend protection from degradation to pheromone.
- o Contact toxic to insect species.
- o Cost effective compared to standard treatment.

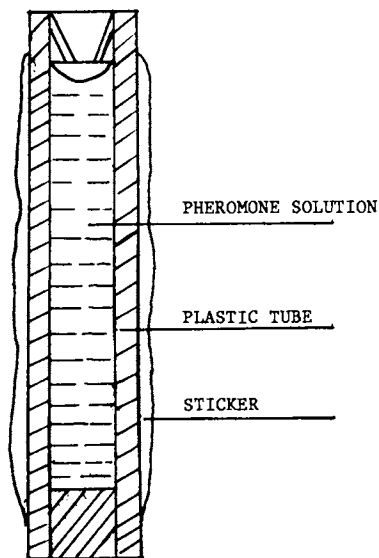


Figure 1. Conrel Hollow Fiber with Sticker

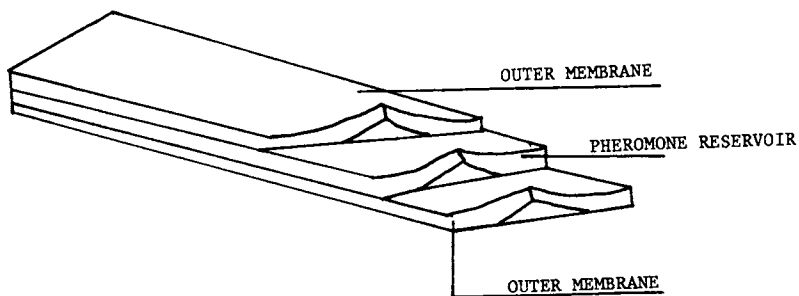


Figure 2. Hercon Laminated Chip

### Matrix Development

#### Release Rate Measurement

A dynamic flow method was used to determine the rate of pheromone release from the various matrices. A vacuum manifold was constructed for multi-sample analysis. The sample chambers were modeled after the design of Cross(3) and consisted of a glass chamber fitted with a charcoal pre-filter and absorbent column. The formulation samples were weighed onto glass cover slips and placed vertically inside the sample chambers. The entire apparatus was held at a constant temperature of 40.5 C. (105 F.) in a walk-in hot room. Air was continuously drawn through the sample chambers at a constant rate of 1.5 liters per minute. Released pheromone was collected on the columns, eluted with solvent and analyzed by GLC. Recovery rates were typically > 95%.

#### Formulation Development

The initial phase of the development was the determination of the relative solubility of the selected pheromone, ZZ and ZE-7, 11-hexadecadienyl acetate (Gossyplure, 1:1 ratio), in a suitable polymer matrix. Four different water-soluble or water-reducible resins were initially investigated: a water-soluble acrylic mixture, two latex emulsions and a natural rubber colloid. Intrinsic solubility was determined by making resin/pheromone solutions of varying concentrations and measuring the rate of pheromone diffusion from dried films. In this manner, we were able to determine the most suitable base polymer from which to begin.

The soluble acrylic system offered the most promise since the diffusion properties could be easily varied by blending of different molecular weight resins. Although composition of the polymer base was effective in partially controlling the rate of pheromone diffusion, the desired zero order release could not be obtained by this technique alone. Therefore, the pheromone was pre-formulated into a co-solubilizing oil, thus creating a liquid diffusion reservoir. By utilizing an oil that was miscible with the pheromone and partially soluble in the resin film, an effective diffusion path was established. An emulsion of the oil in the aqueous resin system was formed which resulted in the formation of a resin coated oil drop. The release rate characteristics were greatly improved over the simple mixture of resin and pheromone. The diffusion properties of the formulation could be further modified by cross-linking of the resin coat to form a permeable membrane. This was accomplished by addition to the aqueous phase of a multi-functional basic amine capable of cross-linking the resins at ambient temperature. Figure 3 shows the effect of these matrix variations upon the pheromone release rate. A small amount of highly active synthetic pyrethroid was next coated onto the membrane layer. The system was completed by the incorporation of spray modifiers to increase the cohesiveness of the solution and to aid in droplet formation.

Upon spraying, the cohesive force of the solution causes droplets of 3-5 mm diameter to be formed which are composed of up to several thousand of the oil capsules per drop. As the formulation dries, the resin crosslinks forming a continuous membrane network surrounding the capsules. Due to effects at the surface the integrity of the emulsion at the interface is destroyed which thus leads to the formation of a resin membrane surrounding the capsule network. A cross-section of the system is shown in the photomicrograph in Figure 4. This system was found to release the pheromone at a near zero order rate during the effective lifetime of the formulation. The mechanism of release is by diffusion of the pheromone from the oil solution through the membrane network. The diffusion rate was found to be dependent upon the initial pheromone concentration, the resin/oil ratio, and the degree of resin crosslinking. In each instance, the release characteristics of the system were nearly identical, that is, the amount of the pheromone released over time was constant.

Thus by determining a suitable matrix one could easily vary the parameters to obtain the desired magnitude of the release rate. Figure 5 illustrates the consistency of the release characteristics for an equivalent matrix where the only change is the initial pheromone concentration. The change in the absolute rate for equivalent pheromone concentrations is shown in Figure 6, the modification here being the resin to oil ratio. Depending upon the desired rate of pheromone release, the present system is capable of constant release for up to three weeks under the specified laboratory conditions.

### Testing and Results

In order to test the effectiveness of the various matrix bases and their formulations, a wind tunnel bioassay was performed in cooperation with researchers at the USDA-Phoenix Research Station.

The bioassay chambers were constructed of 6.4 mm plexiglass, 0.60 x 0.60 x 2.4 meters in dimension. The air inlet end was fitted with a charcoal filter through which air was drawn through the chamber by a variable velocity fan. The formulations to be tested were applied to growing cotton plants and allowed to age for the desired length of time. The treated plants were positioned at the air inlet end of the chamber and the airflow adjusted to approximately 3-5 km/hr. Male pink bollworm moths were positioned at the opposite end of the chamber, downwind of the pheromone source. Moth mortality was recorded versus an untreated control plant to compensate for any natural mortality. Table I summarizes the data from the test designed to demonstrate the 'attracticide' effect. As can be seen, significant mortality is obtained only in the case where pheromone and toxicant are both present.



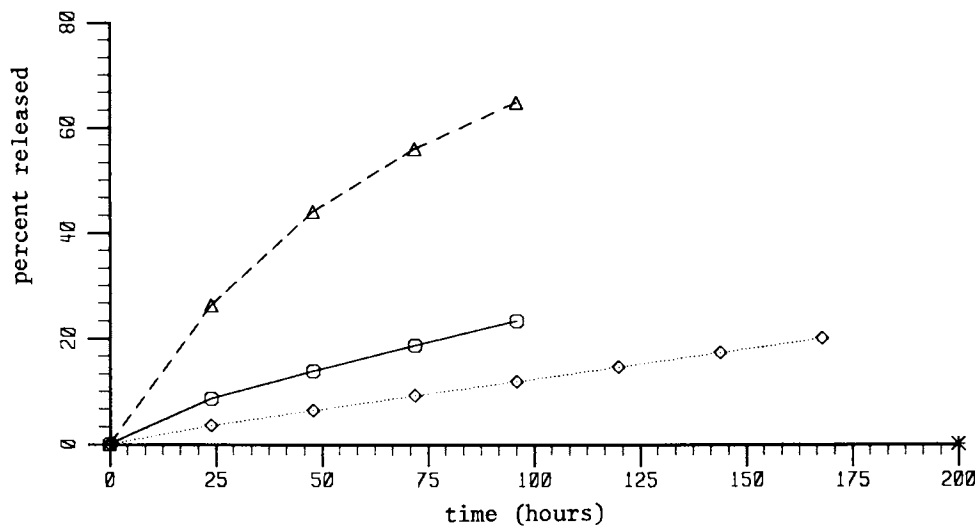


Figure 3. Effect of Matrix Variations on Release Rate

- △ Resin Only
- Resin plus Oil
- ◇ Crosslinked Resin plus Oil

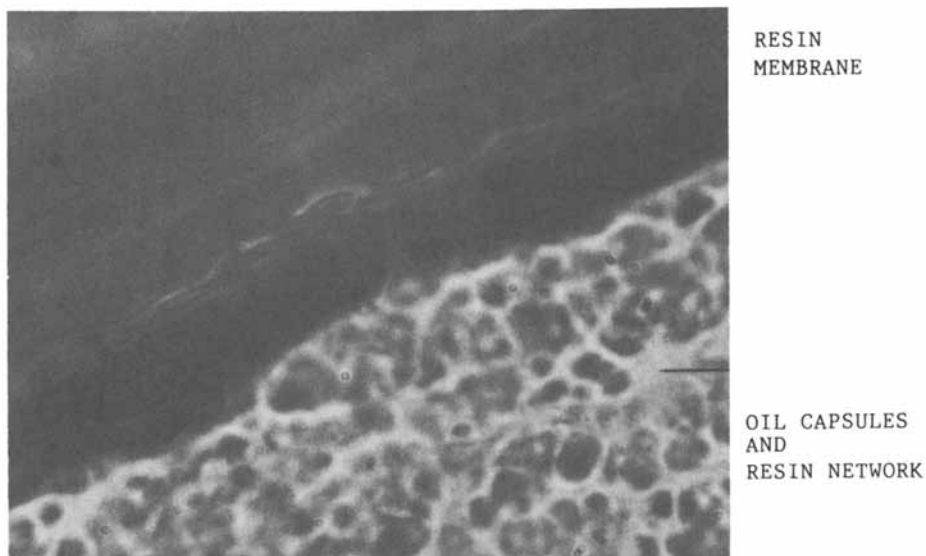


Figure 4. Photomicrograph of Resin/Oil Network 40x

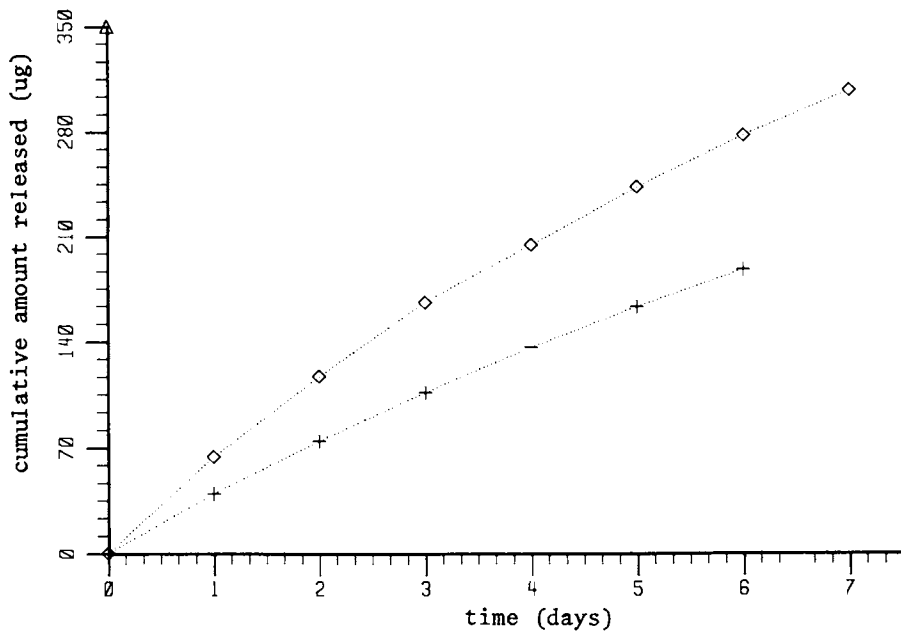


Figure 5. Effect of Pheromone Level on Equivalent Matrix  
 ◇ 750 ppm Pheromone + 500 ppm Pheromone

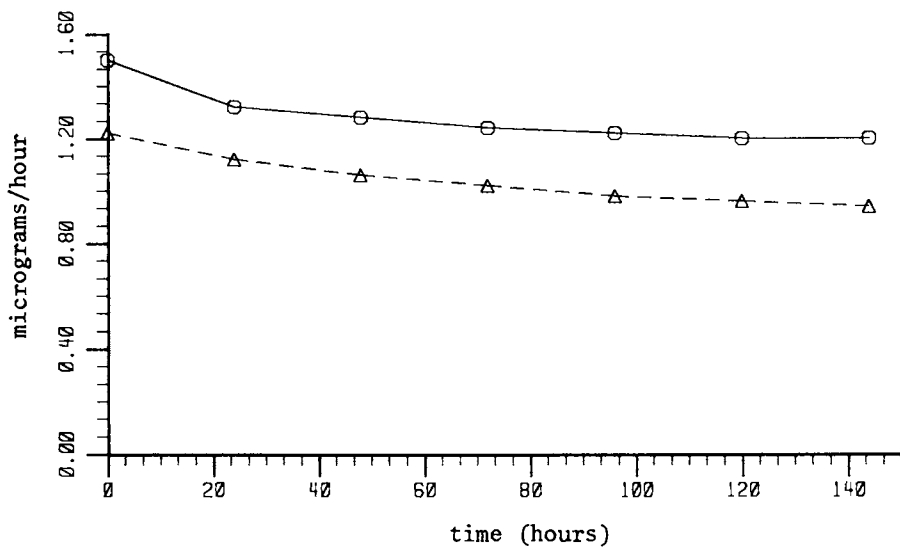


Figure 6. Effect of Resin:Oil Ratio for Equivalent Pheromone Concentration (750 ppm)  
 □ Resin:Oil = 1.0    △ Resin:Oil = 1.5

Table I. Attracticide Bioassay Data

Formulation Variation <sup>a</sup>	% Mortality	
	24 hr.	48 hr.
with pheromone & toxicant	32.0	81.4
with pheromone only	0.7	4.7
with toxicant only	4.0	6.0
blank (no toxicant or pheromone)	0.0	1.3

a = soluble acrylic base

From this stage, the most promising formulations were tested under natural field conditions for effectiveness and longevity of attraction. Since the most effective pheromone emission rate was not known, nor the long term effect of the toxicant upon moth attractiveness, a field trapping study was designed to determine the most efficacious formulation. The selected formulations were applied to growing cotton plants in the field. Daily, a treated leaf was placed in a funnel type trap designed to capture live moths(4). Table II shows the formulation variations tested and the resulting moth catch. The results of this test were significant in that they clearly demonstrated the superiority of the soluble acrylic system. Also it was possible to determine an effective field concentration of pheromone, in the presence of toxicant, that would be attractive and not disruptive to the male moths. [The effects of the toxicant needed to be tested since it had previously been reported that synthetic pyrethroids have repellent effects on some species of moths.](5) In contrast to the laboratory data, the effect of the pyrethroid upon the consistency of the pheromone release is evident. It appears that in outdoor exposure situations the chemicals are instrumental in the stabilization of the pheromone or in the mediation of its release.

### Results and Discussion

On the basis of laboratory and field results, the soluble acrylic system was chosen for further field trials. The formulation (code #1692) was tested on 210 hectares, 13 separate fields in Arizona and California during the 1982 growing season. Each test field was compared to a standard field, treated either with a chemical regime or a commercial pheromone product, located in the immediate vicinity. The efficacy assessment was based on trap catch reduction and boll infestation control. The treatment rate was 6.9 liters of formulation per hectare. This represented a rate of 3.7 grams pheromone and 36.9 grams pyrethroid per hectare. Treatment intervals were approximately ten days apart and the applications

Table II. Pink Bollworm Field Trapping Data

Formulation Base	Toxicant	%	% Pheromone	Average <sup>a</sup> Catch per day
Acrylic Emulsion	Permethrin	0.60	0.075	21.5
" "	"	0.60	0.040	11.4
" "	"	0.40	0.075	28.4
" "	"	0.40	0.040	13.8
" "	Mavrik	0.50	0.040	16.6
" "	---	--	0.075	12.7
Soluble Acrylic	Permethrin	0.60	0.075	37.4
" "	"	0.60	0.040	28.1
" "	"	0.40	0.075	36.0
" "	"	0.40	0.040	28.7
" "	Mavrik	0.50	0.050	21.1
" "	---	--	0.075	19.1
Leaf Control	---	--	---	0.0

a = 15 day average

continued throughout the normal pink bollworm season. Figure 7 shows the effect of the formulation upon the trap catch as compared to an untreated field. The data given in Table III compares the treatment regimes on a field by field basis. Unfortunately absolute comparisons to the current state of the art pheromone systems could not be made since in all cases these fields were also treated with various chemical agents. However, the data can still be compared on overall efficacy and performance. The comparative data does indicate that in the majority of the cases the boll infestation levels were kept to below 5%, which would be considered the economic threshold level(6). The data also clearly demonstrates that a considerable reduction in conventional pesticide usage can be achieved by use of this system. It is important to note that in several tests the percent infestation in comparable fields is considerably higher than the acceptable threshold level. This data exemplifies one of the more serious deficiencies of pheromones when used as chemical control agents. Many investigators have found that pheromones are most effective at relatively low to moderate population pressures, and tend to be highly ineffective at population densities above a certain threshold(7). Thus the utility of pheromone usage may be more compatible with Integrated Pest Management practices.

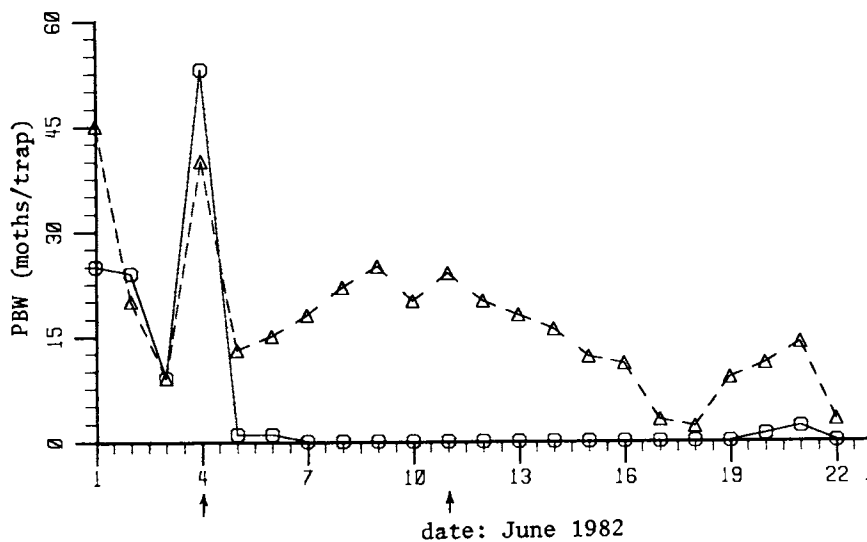


Figure 7. Trap Catch Comparison; Treated vs Untreated Field

□ Pheromone Treated at ↑  
△ Untreated

Table III. Efficacy Comparison for 1982 Field Trials

Test no.	Test Plot			Reference Plot					Cost: \$ per d hectare
	No. of Appl. Zoecon	% Infested bolls	Cost: \$ per d hectare	Insecticides	No. of Applications	Nomate	% Infested bolls	Cost: \$ per d hectare	
215	9	5.3	183.47	13	-	-	16.4	162.47	
216	6	1.7	122.31	7	-	-	2.2	92.29	
217	9	13.4	183.47	13	-	-	20.2	166.52	
220	3	1.3	61.16	7	-	-	2.0	126.61	
221	6	2.5	122.31	6	-	-	0.8	78.43	
223	6	0.0	122.31	6	-	-	2.3	96.02	
218	7	0.0	142.70	3	5 <sup>a</sup>	-	1.4	93.97	
219	8	0.4	163.09	3	5 <sup>a</sup>	-	0.4	93.97	
222	5	33.0	101.93	11	3 <sup>b</sup>	-	13.0	214.01	
224	5	2.4	101.93	3	-	3c	0.0	95.60	
225	6	0.0	122.31	3	-	3c	0.0	95.60	
226	6	1.0	122.31	3	5 <sup>b</sup>	-	3.8	118.61	
227	8	0.2	163.09	3	5 <sup>b</sup>	-	1.5	118.61	

a = Hercon Div., NY, NY; flakes containing pheromone + Pydrin

b = Hercon Div., NY, NY; flakes containing pheromone + Ambush

c = Conrel Div., Needham, MA; fibers containing pheromone

d = Represents total chemical cost. Application cost not included.

### Conclusion

An aqueous based controlled-release pheromone system was developed for control of insect species in large acreage field crops. The system was shown to be efficacious for the control of the pink bollworm, when compared to standard insecticide usage and state of the art solid release matrices. The system has the distinct advantage of being conventionally applied and containing both pheromone and toxicant. The system also allows a significant reduction in conventional pesticide usage, while limiting boll infestation to levels comparable to standard chemical usage and state of the art pheromone systems. It now remains to be seen if the system can be adapted on a general basis to the pheromones of other economically important insects species.

### Acknowledgments

The kindest thanks to Dr. Louis Bariola for conducting the bioassay studies. To Mr. David Rhoades for performing the release data measurements and Mrs. Marie Saunders for her invaluable assistance with the formulation development.

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## Reduction of Propargite Phytotoxicity Through Spray Drying

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The phytotoxicity of propargite, a sulfite acaricide, can be greatly reduced, while essentially maintaining miticidal activity, by absorbing the propargite on a carrier, adding a polymer latex, and spray drying the resulting mixture. Scanning electron microscope photographs show this process to result in an irregular, incomplete shell which prevents contact of the phytotoxic liquid with the plant, yet allows escape of propargite vapor in sufficient quantity to control mites.

Propargite, a sulfite acaricide, was commercialized by Uniroyal in 1968 under the trade name of Omite and is useful in the control of many species of mites. (1,2) The structure of propargite and some of its physical properties are given in Table I.

Propargite is a specific acaricide, which is relatively nontoxic to honeybees and many parasitic insects. In addition, predacious mites are not eliminated from treated areas. A list of important mite species controlled by propargite is given in Table II.

Use of propargite, however, is limited by its phytotoxicity to certain crops when used at acaricidal concentrations. Table III lists important sensitive and non-sensitive crops.

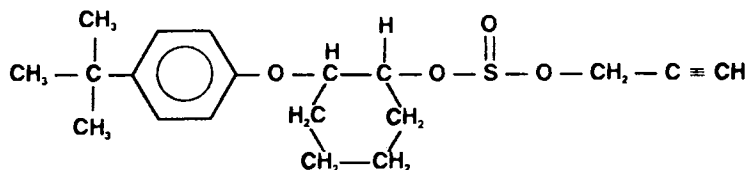
<sup>1</sup>Current address: Rohm & Haas, Inc., Norristown and McKean Roads, Spring House, PA 19477

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Table I

## Chemical and Physical Properties of Propargite



Molecular weight	350
Form	Light to dark brown viscous liquid
Odor	Faint solvent odor
Vapor pressure	Less than 1 mm at 20°C
Specific gravity	1.085 - 1.115
Flash point	20°C Pinsky-Martens
Water, maximum	Less than 0.1%
Miscibility	Immiscible with water Miscible with organic solvents
Acute Oral LD <sub>50</sub> -rats	2200 mg/kg
Eye irritation-rabbits	Severe
Ames Test	Negative

Table II

## Mite Species Controlled by PROPARGITE

apple rust mite	<i>Aculus schlechtendali</i> (Nalepa)
Banks grass mite	<i>Oligonychus pratensis</i> (Banks)
brown mite	<i>Bryobia arborea</i> (Morgan & Anderson)
citrus red mite	<i>Panonychus citri</i> (McGregor)
citrus rust mite	<i>Phyllocoptruta oleivora</i> (Ashmead)
clover mite	<i>Bryobia praetiosa</i> (Koch)
cyclamen mite	<i>Steneotarsonemus pallidus</i> (Banks)
European red mite	<i>Panonychus ulmi</i> (Koch)
McDaniel spider mite	<i>Tetranychus medanieli</i> (McGregor)
Pacific spider mite	<i>Tetranychus pacificus</i> (McGregor)
peach silver mite	<i>Aculus cornutus</i> (Banks)
six-spotted mite	<i>Eotetranychus sexmaculatus</i> (Riley)
Southern red mite	<i>Oligonychus ilicis</i>
strawberry spider mite	<i>Tetranychus atlanticus</i> (McGregor)
Texas citrus mite	<i>Eutetranychus banksi</i> (McGregor)
two-spotted spider mite	<i>Tetranychus urticae</i> (Koch)
Willamette mite	<i>Eotetranychus willamettei</i> (McGregor)

Table III

## Phytotoxicity of PROPARGITE

Sensitive crops	Non-sensitive crops
Pears	Walnuts
Citrus	Almonds
Cotton (smaller than 12-14")	Cotton (larger than 12-14")
Strawberries	Field corn
Hops	Apples
Cantaloupe	Peanuts

Table III is meant as a guide but does show that phytotoxicity is dependent not just on plant species but also on the time of application. Young cotton has an unacceptable level of crop damage; the same plants, treated later in the growing season, are much less sensitive. Citrus is listed as a sensitive crop because a very low level of phytotoxicity on the fruit itself results in a reduction in quality and hence in the price paid for the fruit. This phenomenon has kept propargite from sales on citrus in spite of its excellent activity against the mites found in citrus.

The acaricidal activity of propargite occurs primarily through vapor action, while the phytotoxic effects seem to arise only from direct contact with the plant leaf or fruiting body. Conceptually, therefore, a delivery system which could prevent contact with the plant, yet allow the acaricidal vapor to escape, would prevent phytotoxicity and allow use on sensitive crops.

Scher (3) has reviewed the microencapsulation of pesticides and discussed some of the possible ways of achieving such a delivery system.

Spray drying, one of these methods, is very suitable for the production of microcapsules. In a spray dryer, an atomizer is used to form a spray of small droplets, which then mix with hot gases to evaporate the liquid from the droplets to form a dispersed, dry product. This dry product must then be separated from the exhaust gases. Figure I shows a schematic diagram of a spray dryer.

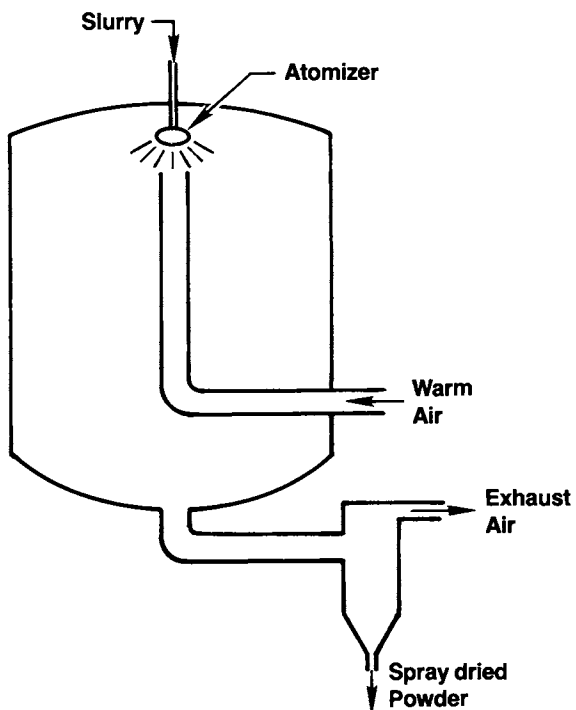


Figure 1. Spray drying system

Materials and Methods

The following materials were obtained from the sources listed and used without further purification.

Material	Trade Name	Source
Propargite	Omite	Uniroyal Chemical
Diatomaceous earth	Microcel E	Johns-Manville
Sodium lignosulfonate	Marasperse CBOS-3	American Can Co.
Octyl phenol polyoxyethanol, adsorbed on magnesium carbonate	Triton AG 120	Rohm & Haas
Polymerized sodium salt of alkyl naphthalene- sulfonic acid	Daxad 11	W. R. Grace
Diocetyl ester of sodium sulfosuccinic acid	Aerosol OTB	American Cyanamid
Polyvinyl acetate (latex)	Polyco 117-SS	Borden Co.

A 3-1/2 foot diameter "Laboratory Spray Dryer" made by Bowen Engineering, Somerville, NJ, equipped with a centrifugal atomization nozzle, was used for these experiments.

Table IV gives our procedure for the preparation of spray dried propargite.

Table IV

Preparation of Encapsulated Propargite

Step	Ingredients	Equipment
1	Propargite Diatomaceous earth Wetting and dispersing surfactants	Ribbon blender
2	Product of step 1  Polyvinyl acetate latex Water Wetting and dispersing surfactants	Slurry tank (with agitator)
3	Product of step 2	Spray dryer

Results and Discussion

The phytotoxicity and acaricidal activity of this new formulation is shown in Table V. A commercial wettable powder formulation of propargite, Omite 30W, was used for comparison purposes.

Table V

## Phytotoxicity and Acaricidal Activity

Rate of propargite, parts per million (ppm)					
	8000	2000	500	100	20
Phytotoxicity (a) of spray dried formulation	15	2	0	--	--
Phytotoxicity (a) of wetttable powder	95	20	1	--	--
% control of mites (b) spray dried formulation	--	--	100	77	69
% control of mites (b) wetttable powder	--	--	100	89	50

(a) Phytotoxicity: % of damaged tissue on primary leaves of cowpeas (*Vigna sinensis*) 7 days after treatment

(b) % control of mites: Mites loaded 1 day after spraying, scored (using Abbott's formula) one week later. Test species: *Tetranychus urticae* (Koch).

As the table shows, phytotoxicity of the spray dried formulation is much lower than the conventional formulation, while acaricidal activity is not significantly reduced.

Figure 2 shows scanning electron microscope pictures, at 300X magnification, of the two formulations. The spray dry formulation shows an irregular, incomplete shell around the particle.

The atomization system of the spray dryer produces droplets containing polyvinyl acetate micelles in water, surrounding the particles of propargite absorbed on carrier. As the droplet dries in the hot, turbulent gases of the spray dryer, the water is lost (4) and the polyvinyl acetate dries to an irregular coating around the carrier, as seen in the photomicrograph. The conditions of spray drying are optimized so as to provide the least possible degree of agglomeration, so that the particle size of the resulting powder is kept as small as possible.

We believe that the shell acts as a physical barrier preventing contact of propargite with the leaf; thus, the presence of a shell reduces phytotoxicity. Because the shell is porous and incomplete, the polyvinylacetate shell does not prevent the

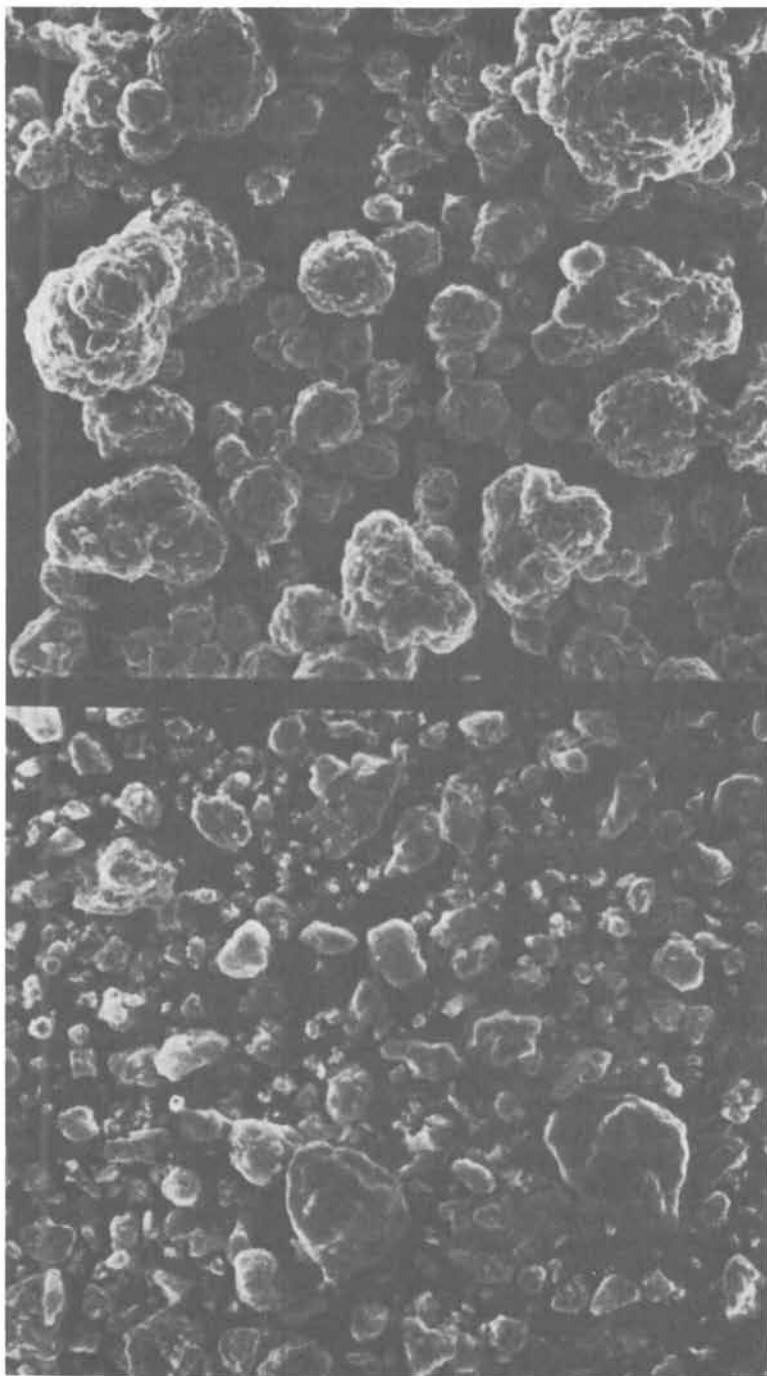


Figure 2. Propargite formulations (300X): right, spray dried; left, wetttable powder

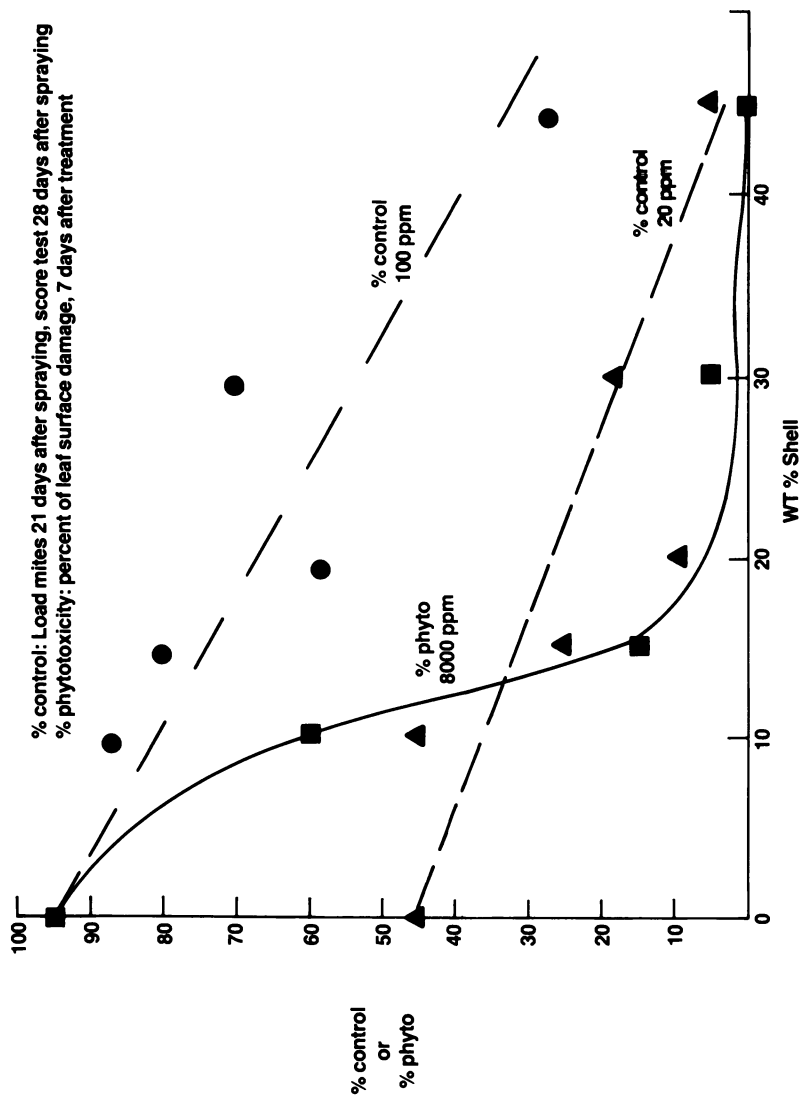


Figure 3. Effect of shell weight on propargite efficacy and phytotoxicity

escape of propargite vapor. Mite control, then, is no different than for conventional formulations of propargite. The spray dry formulation is therefore not a "controlled release" formulation as we have seen no increase in the length of control provided by a given amount of propargite.

The effect of increasing shell weight on efficacy and phytotoxicity is shown in Table VI. The test plant was cowpeas (*Vigna sinensis*).

Table VI

## Effect of Shell Weight

Weight of shell, %	% control	% control	% phyto	% phyto
	100 ppm	20 ppm	8000 ppm	2000 ppm
0 (conventional WP)	55	45	95	45
10	87	45	60	15
15	80	25	15	3
20	58	7	0	1
30	70	18	5	0
45	27	5	0	0

These data points are shown graphically in Figure 3.

The reduction in % control with increasing shell weight is almost linear. In contrast, there is a sharp drop in phytotoxicity between 10% and 20% by weight polyvinyl acetate. Evidently, 10% by weight of polyvinyl acetate is not enough to surround the particle in sufficient amount to prevent contact of propargite with the leaf surface, while a 20% shell is thick enough to prevent contact, hence lowering phytotoxicity.

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## Formulation of Biological Insecticides

### Surfactant and Diluent Selection

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The improper selection of surfactants and diluents decreases shelf life and the effectiveness of biological insecticides. The diluent's physical structure, buffering capacity, surface charge and particle size are all factors that will be reviewed as influencing physical and chemical incompatibilities. Storage tests up to 2½ years with mycoinsecticide/diluent mixtures demonstrate that differences can occur. Surfactant selection is also critical in maintaining viability and virulence of active ingredient. Mycoinsecticides exposed to surfactants of differing hydrophilic-lipophilic values, concentrations, and chemical type may be sensitive to surfactant chemical structure.

In a pesticide formulation everyone is quite aware of the chemical or biological activity of the active ingredients. However, the success of the formulation is dependent on the correct selection of the inert components. The formulation of a microbial pesticide presents unique problems that are not encountered in a standard chemical formulation. The first and obvious one is the maintenance of biological activity during storage and application. In order to avoid loss of activity of the microbial organism, a careful assessment of the chemical and physical parameters must be completed. Once the requirements of the microbial organism are defined, selection of the formulation type and ingredients can be undertaken.

The inert components, even though termed "inert", are quite chemically active. They are inert toward the target pest

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but possess qualities that enhance storage, handling, and application. The major inert component found in dusts, wettable powders and granulars is the diluent, also termed "carrier", in some formulation types, depending on the material's absorbent capacity. The diluent of a formulation can be any material, organic or inorganic, that dilutes the active ingredient to a concentration that can be managed and applied by accepted agricultural practices (1). Table I exemplifies some of the types of materials that can be used as diluents.

Table I. Types of Diluents and Carriers Used in Agricultural Formulations

Inert Type	Classification	Examples	
ORGANIC	Botanical	Corn cobs, soybean-wheat flour, rice hulls, walnut shell, wood flour	
	Synthetics	Cellulose	
INORGANIC	Silicates	Palygorskite Kaolinite Montmorillonite	
		Attapulgitite Kaolin Montmorillonite Bentonite	
		Illite Vermiculite Ca Silicate	
	Oxides	Calcium Carbonates	Lime Dolomite
		Sulfates	Gypsum
Silicon Synthetics		Diatomite Ca carbonate/ Silicon dioxide	

Phyllosilicates (clay) are the most commonly used diluents because they are relatively inert, available in large quantities at a low cost, and are easily handled during manufacturing and application. Van Olphen (2) defines clays or clay materials as fine-grained, crystalline, hydrous silicates. The structures of clays impart a certain degree of reactivity upon the microbial formulated with them. Several

different methods for classification of clays have been developed. A generalized discussion of the agriculturally important clays will be reviewed.

### Clay Structure

Three major types of clays are predominantly used for pesticide formulations. These, Grim (3) classified by their crystalline structure: two layer, three layer, and chain clays. The layers are sheet structures composed of minerals consisting of cations and anions that group to form the basic units that make up a sheet. The two-layer clays (1:1) are composed of one layer of silicon oxide tetrahedrons and one layer of aluminum oxide octahedrons. This group is termed the kaolinite group, with kaolin being the important diluent member. The montmorillonite group, a three-layer type (2:1), is composed of two layers of silicon oxide tetrahedrons and one central aluminum oxide dioctahedral or trioctahedral layer. The sheets or lattices of montmorillonite clay are loosely held together by van der Waal's force. This weak association of layers permits the crystal lattice to expand or contract in the presence or absence of water. This group contains the montmorillonites, prophybitite, talc, bentonite, vermiculite and mica. The third commercially important group, in terms of agricultural formulations, forms chains instead of alternately stacked layers. The chains form sheets of silicon oxide tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing aluminum and magnesium cations. The major representative of this type is attapulgite clay.

A great variation occurs within each type of clay. If the cation, which is the central portion of the tetrahedron and octahedron, is in the pure state, it will be silicon or aluminum. However, these elements can be replaced by sodium, calcium, magnesium, or any other elements acting as a cation. The anions of the structures are oxygen and/or hydroxyl. This replacement (isomorphic substitution) is the mechanism responsible for the differential charge at the layer's surface (4). It should be noted that due to their structure talc, pyrophyllite, and kaolinite do not undergo isomorphic substitution. The differences in the kaolinite group are, therefore, the result of hydration and variations in the stacking of layers.

The variations in structures of these clays are responsible for the differences in buffering capacity, surface charge, and other physico-chemical properties.

### Physico-chemical Properties that Influence Microbial/Diluent Compatability

The physico-chemical properties of clays are derived from their structures, and are responsible for the performance of the formulation. The survival of microbials can be directly affected by these physico-chemical properties. The importance of clays to microorganisms was summarized by Stotzky (5), "The clay or clay mineral probably exerts the greatest influence on microorganisms because of high surface activity of clays resulting from their large surface area and chemical and minerological composition." The proper selection of the diluent clay will increase the shelf life and the overall compatability of the biological insecticide by three mechanisms: maintenance of favorable pH, absorption of suppressive chemicals, and modification of the microclimate.

Maintenance of a Favorable pH. The fluctuations of pH are considered to be a major environmental stress to microbial populations (6). The compatability and, ultimately, the survival of an organism in a formulation is dependent upon the initial pH and the buffering capacity of the clay diluent.

The initial pH of clays varies widely as shown in Table II. It is quite obvious how incompatibilities between the biological

Table II. Physico-Chemical Properties of Silicate Groups<sup>1</sup>

Clay Type	pH (10% Slurry)	CEC (meg/100g)
Attapulgit	7.5 - 8	120 - 130
Kaolinite	4 - 7	2 - 10
Montmorillonite	6 - 9.5	80 - 120
Vermiculite	6.5 - 7.5	130 - 170
Talc	8 - 10	2 - 6
Silica Gel	see footnote <sup>2</sup>	62

<sup>1</sup> Data given as a range of the commonly used agricultural diluents. Source: (4), (6), (7).

<sup>2</sup> Dependent upon treatment by manufacturer.

organism and the diluent can occur when the initial pH ranges from 10 to 4. The buffering capacity is a function of the structure and ion complex of the clay. The buffering capacity

is expressed numerically as the cation exchange capacity (CEC). Clays which possess a high CEC can replace a greater number of hydrogen ions with basic cations than clays with a low CEC. The type of cation present also affects the buffering capacity. In decreasing order, the cations with the greatest exchange capacity are sodium, calcium, magnesium, potassium, and hydrogen (8).

Montmorillonite clay's degree of isomorphous substitution and the ability to expand and contract in the presence of water impart a high CEC. The expanding of the crystal lattice allows the ions between the crystal edges to become available for exchange. This gives montmorillonite clay a 17 to 20 times higher CEC than that of kaolinite clay (5). Therefore, montmorillonite clays have a much greater potential to buffer the pH of organisms during storage. Examples of cation exchange capacity for different types of clay and silica gel are shown in Table II.

The effect of the buffering capacity of clays with microorganisms was shown in the study of *Fusarium* wilt *Fusarium oxysporum* (f. sp. cubense) of the banana, and the human pathogenic fungi, *Histoplasma capsulatum* (Darling) (9) (10). Both fungi spread and were found in geographical areas that contained non-swelling clays, predominantly kaolinite. Stotzky (8) explained that areas with high buffering capacity were able to maintain a healthy flora of bacteria, thereby preventing the fungi from establishing.

The importance of buffering capacity was exhibited in the entomopathogen formulations of *Metarhizium anisopliae* (11) (12). The conidia of *M. anisopliae* were stored for six months at 20° C as mixtures of conidia/silica gel, conidia/silica gel/kaolinite clay, and conidia with the silica gel separate. The conidia mixed with silica gel decreased in viability rapidly, probably as a result of the low initial pH of the silica gel. However, the mixture of conidia/silica gel/kaolinite clay retained 20% greater viability than the mixture where the silica gel was not present to buffer the pH.

Storage tests conducted for 2 years with the mycoinsecticide *Beauveria bassiana* (Bals.) and clay diluents clearly demonstrate the differences in viability believed to be due to the buffering capacity of the diluent. Table III is a summation of the storage of *B. bassiana* conidia mixed with commercial diluent clays (Ward, unpublished).

Table III. The Effect of Clay Diluents on B. bassiana Stored Two Years at 4° C and 26° C

Clay Type	PERCENT VIABILITY <sup>1</sup>	
	4° C	26° C
Attapulgite	82%	19%
Bentonite	86%	5%
Vermiculite	65%	<1%
Kaolinite	25%	<1%
Control <sup>2</sup>	<1%	<1%

<sup>1</sup> Initial viability was 98%.

<sup>2</sup> No diluent was added.

Conidia/attapulgite mixtures exhibited the greatest longevity. The storage of these mixtures was under dry conditions, therefore, montmorillonite clay was unable to swell and buffer to its greatest potential. Given the initial rate of decline at 4° C, the conidia/attapulgite mixture is calculated to be reduced to 50% viability after a period of 102 months. The present study indicates that B. bassiana conidia, with the proper diluent, will be conserved about three years longer than conidia without a diluent, or the improper diluent. Other tests with formulations of B. bassiana and Entomophthora virulenta support the mechanism of pH maintenance by clay diluents (13-15).

Absorption of Suppressive Chemicals. The organism must continue to metabolize during storage, even at a reduced rate. The by-products of metabolism, if allowed to accumulate, will eventually inhibit the organism itself. The diluent within a formulation should adsorb many of the suppressive metabolites. Survival of B. bassiana conidia in nonsterile soils was proposed to be the result of the clay inactivating some fungistatic factor (16). Tests with mixed bacterial population including Streptomyces albidoflavus, exemplify the difference between the adsorption properties of kaolinite and montmorillonite clay (17). Even though the antibiotic streptomycin was produced in both clays, the population in the montmorillonite was unchanged.

There is no doubt that diluents impart a beneficial effect on microbial/diluent by the adsorption of detrimental components.

Modification of the microclimate. The various conditions encountered during lengthy storage allow for complex interactions between organism and diluent in a biological insecticide. Clay diluents provide a modifying influence on the microclimate of the entomopathogen. Swelling clays' (montmorillonite) ability to retain a greater amount of water enhances the moisture available to the organism at low relative vapor pressure. The swelling or expansion provides an external and internal surface area for retention of water. This provides a reservoir of moisture to dampen the cycles of wetting and drying. The electrostatic attraction of clay particles promotes the flocculation of the colloidal particles into aggregates. Bacteria, fungi, or viruses have net negative surface charges that attract them to the highly charged clay surfaces (7). The microbials become entrapped within the clay aggregates. The aggregates reduce the susceptibility of the organism to desiccation and other environmental parameters which are physically damaging (18). Marshall (17) found that formulations of *Rhizobium trifolii* containing montmorillonite clay were more tolerant to desiccation and heating. *B. bassiana* conidia mixed with bentonite (montmorillonite) clay tolerated dehydration and heating more favorably than conidia without bentonite clay over a 30-month period (19-21). Organisms surrounded by clay platelets receive physical protection from ultraviolet light and x-rays as a result of the clay's light absorption and scattering qualities (17) (22).

### Surfactant Selection

A wettable powder formulation of a biological insecticide requires a surface active agent (surfactant). This allows the organism to easily penetrate and disperse in the liquid which is to be sprayed. The surfactant enables the spray liquid, generally water, to wet the organism more effectively. In order to accomplish this, the surfactant must be in contact chemically with the organism's surface. This chemical association of anionic, cationic or nonionic, surfactants with the membrane of the biological insecticide can cause incompatibility and loss of viability. Surfactants that have been tested for compatibility with bacteria, fungi, and viruses in the field and laboratory have been reviewed by Angus (23) and Couch (24). The selection of a surfactant to optimize the physical characteristics of the formulation is accomplished by several methods reviewed in depth (25) (26). However, the majority of preceding literature leaves little explanation of how incompatibility can be determined, other than by experimental trial and error.

Cell suspension tests can indicate which type of surfactant could be potentially incompatible after long periods of storage. Three basic types of surfactants exist: anionic, cationic, and non-ionic. Parr (27) surmised that anionic surfactants are the least phytotoxic, but the results of Ernst (28) do not confirm that all anionic surfactants are harmless. Surfactants with short, aliphatic, carbon chains may also be more toxic than those with larger molecular groups (29). The surfactant's influence *in vitro* may exaggerate the effect in dry, wettable powder formulations, and thus provide an accelerated test of compatibility.

### Summary

Clays are the predominant diluents in agricultural formulations. Their structural differences arise from the anion-cation arrangement, composition, and number. Montmorillonite and attapulgite clays exhibit a greater degree of congruity with microbial organisms than kaolinite clays. The presence of a compatible diluent with the biological insecticide will increase the shelf life by decreasing the percentage of viability lost during storage. Clay diluents function by buffering pH shifts, adsorbing suppressive metabolites (including antibiotics), and physically sheltering the organism against harsh environmental stress.

Currently, there are more than 4000 surfactants available for use in the formulation of biological insecticides (30). The correct selection of the surfactant or surfactants required involves long-term storage tests in order to predict appropriateness. Tests with organisms other than entomopathogens indicate that surfactant chemical type, concentration, and hydrophilic, lipophilic values assist in determining compatibility with the organism.

The commercialization of biological insecticides has been a recent development. The primary problem with their formulation is the severe lack of compatibility information. The physical performance data for the formula components are available, although further research must be performed in order to predict their effect on biological activity.

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## Steps of Water Dispersible Granule Development

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The development and marketing of water dispersible granule (WDG) or dry flowable (DF) formulations is on the increase. Unique physical parameters are required in a delicate balance of formulation excipients. Development activities need to stress physical stability under a variety of storage conditions and packaging considerations. An experienced formulation chemist prepares viable prototype formulations on a laboratory scale basis. The pilot plant processing requires extensive trial runs to pinpoint a potential commercial formulation and manufacturing procedure. After this, the strengths and weaknesses of the formulation need to be highlighted to the consumer in how to properly use this formulation type.

The purpose of this paper is to discuss the other side of water dispersible granules or WDG's, also known as dry flowables usually not presented in discussions with respect to preparing WDG's. I am referring to the side that deals with the development of these easy to make, readily dispersible products. As you can tell by my comments, there are some factors to consider in making WDG's. This form of product is relatively new to the agricultural market, the major impact being registered in the last 5 years. An examination of the literature during this

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time yields mostly empirical recipes indicating how a few key pesticides can be formulated into acceptable WDG's. Such discussions often avoid any mention of the problems or the difficulty of getting from the lab where anything seems to work to the production step where everything must work. Therefore the purpose of this paper is to discuss what happens from the time a lab trial is initiated to a plant trial is made. What must the formulator, product manager and production supervisor consider in examining or testing this product? Needless to say, the work will be general in nature and descriptive at best. I will attempt to use photographs to graphically illustrate what can go wrong and what can go right in making WDG's.

Before I set out in our discussions one needs first to define the characteristics of the WDG so that we will be operating with the same definition. A water dispersible granule formulation consists of hard, uniform in size, free flowing, low dust granules which readily disintegrate in water and under minimal agitation forms a homogeneous sprayable suspension. If one analyzes each characteristic, a dependent relationship develops among the characteristics. The quality of each characteristic is directly related to processing parameters. The most noticeable attribute of a WDG is its bloom or rapid disintegration in water. The aesthetic value of this property is highly visible in the advertising literature. At times, too much emphasis is placed here, and the consumer looks for it under all types of use patterns.

Before examining the preparation of WDG's, let's try to understand why they have grown in user acceptance and what problems can be associated with their use. The importance of each advantage or disadvantage of the WDG's varies for each toxicant but are generally listed as:

#### Advantages:

- Free flowing, empties completely from container
- Easy to measure
- Low dust
- More concentrated
- Greater density
- Reduced transportation and warehousing costs
- Eliminates physical problems of flowables, i.e., settling, thickening, etc.
- Easier to handle than wettable powder, less chance to spill and easier to clean up
- Novel, generates consumer interest.

With every set of advantages there is a corresponding set of disadvantages. These are key to point out and have impact on the overall development cost.

**Disadvantages:**

- Formulation is sensitive to process variables and raw materials
- Requires capital expenditures
- Employs skilled operators
- Need to educate the consumer on how to use properly.

**Development of the Water Dispersible Granules**

Several general references on WDG formulations are available in the literature (1-3). In developing a good foundation, it is also recommended that one visit the various surfactant suppliers and get a hands on view of their product in action. This forms an excellent starting point. But it is just that, a starting point. Unless you plan to merely scale up what you saw, the task becomes much more involved. As a starting point, let's review a general, all purpose finished formulation in Table I.

---

Table I. Typical WDG Formulation

---

<u>Components</u>	<u>% w/w</u>
Toxicant	50-95
Dispersant	1-7
Binder	0-2
Diluent	0-45
Wetting agent	0-2

---

The dry components are uniformly blended and ground to appropriate particle size required for biological efficacy and suspension characteristics. The material is conditioned, agglomerated, dried, and sieved to desired mesh range. Wettable powder formulations are not generally suited for granulation due to presence of diluents such as amorphous silicates, which significantly increase the amount of water required for granulation. In addition, its presence effects the integrity of the granules. In reality, it is better to start from the technical, than any formulated goods when designing WDG formulations.

Proper wettability of the formulation is crucial if one is to achieve good agglomeration and subsequent performance under field conditions. The type and level of wetting agent used in

the system is determined by matching the solid surface tension  $\gamma_s$  of the toxicant with the liquid surface tension  $\gamma_l$  of the wetting agent at the field dilution rate.

The solid surface tension  $\gamma_s$  of the toxicant can be determined by:

- 1) transfer behavior of particles in two immiscible liquids having two different known surface tensions, i.e.,

$$\gamma_{l1} < \gamma_s < \gamma_{l2} \text{ or (4)}$$

- 2) measuring contact angle between a liquid of known surface tension and solid on a Goniometer (Rome-Hart Inc.), i.e.,

$$\gamma_s = \frac{(\gamma_l - \frac{\rho}{8}) (\cos \theta - 1)}{2} \text{ where } \theta = \text{contact angle.}$$

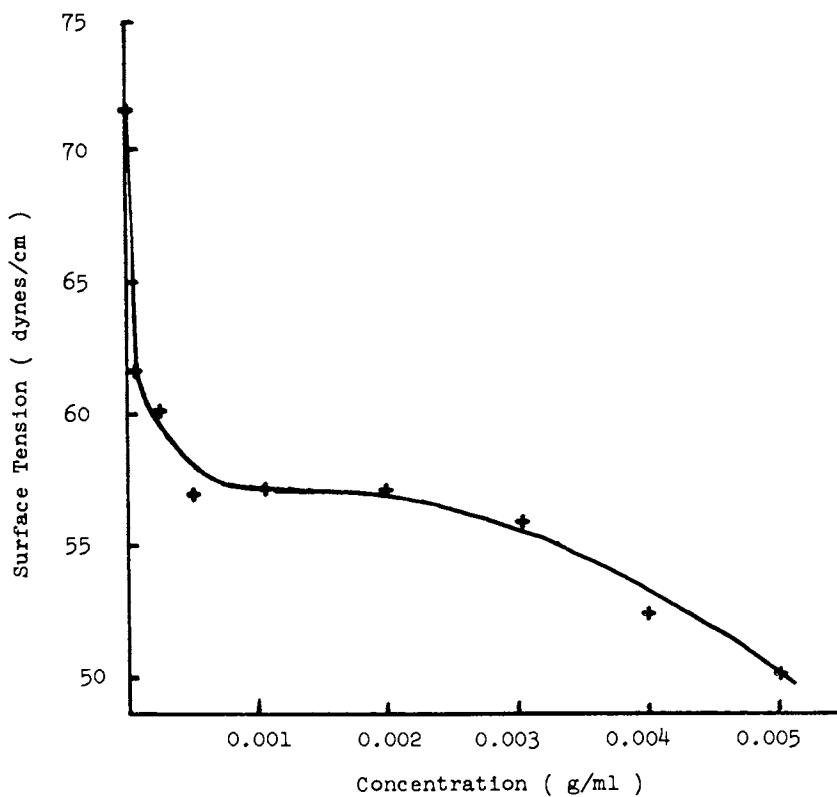
The type and concentration of the wetting agent in the formulation is determined from graphs of aqueous surface tension values of the various wetting agents  $\gamma_l$  vs. concentration where the  $\gamma_l$  value is slightly less than the solid surface tension  $\gamma_s$  of the toxicant and the change in  $\gamma_l$  as a function of concentration approaches zero, i.e.,  $d(\gamma_l)/d(\text{conc.}) \cong 0$ . The major assumption is that the wetting agent is the only inert in the formulation with significant surface tension activity. As an example, the captan  $\gamma_s$  value equals 58.7 dynes/cm and the wetting agent in Graph 1 meets the stated criteria at the concentration of 0.001g/ml. At the normal end use field dilution, this equates to 0.5% w/w wetting agent in the formulation.

The next key component deals with the selection of a binder or adhesive system. In addition to the adhesive characteristic offered by the wetting agents and dispersants it is generally necessary to incorporate a synthetic or natural gum to provide good green strength and integrity in the finish product. The selection process is a trial and error procedure.

Having therefore described the major functional ingredients, the next question is: How does one go about preparing the WDG?

### Fundamentals of Granulation

Particle size enlargement can occur either by the collision and successful adherence of the primary feed into a granule or by the continual growth of a small layer of solids around a nucleus, e.g., like an onion skin. In this latter case, the main attractive force is still the initial particle collision but growth is a slow and uniform process. Therefore purity of the



Graph 1: Plot of Surface Tension (dynes/cm) of the wetting agent vs concentration (g/100 ml) which meets the criteria for captan.

pesticide, its particle size distribution and how the solid particles adhere to each other, all influence the quality of the end use material.

The equipment and procedure we shall address in discussing agglomeration is not an all inclusive list nor does it represent an endorsement by FMC. Equipment suppliers are all willing to assist the newcomer (5-7). However, for the sake of brevity, only a few manufacturers are listed.

### Laboratory Scale

A wide variety of processing equipment is available including disc, pan and drum agglomerators. One could also utilize a PK blender with impregnation bar, fluidized bed units or compactors. The 16" granulation pan, however, offers a simple tool for small laboratory scale preparation. A batch size of 1000 gms is usually adequate for experimental work. Control of the moisture level spray is critical for proper granulation in the laboratory. In production, it becomes extremely critical. The droplet size of the spray is of equal interest. Under proper conditions, nucleation takes place then agglomeration. This is followed by the transition period in which the liquid bridges binding mechanism changes gradually from the pendular to the capillary state due to the continuous liquid addition and the consolidation of the agglomerates caused by the mechanical stress. Further liquid addition will result in granules coalescence and should be avoided (8). Therefore, how the liquid is applied becomes very critical and great attention must be paid to spray patterns and spray rates.

The pan is not a densifying system, but rather a layering system. Therefore, the end results may not meet marketing requirements or duplicate the final production product. There are ways to increase the density of the green granules, but you can be too successful and end up with a product which will not disperse or break up, at application.

After the green granules are prepared, they are dried in a convection oven. Rate of drying and drying temperature are also critical to the quality of the finished product. Low drying temperatures will result in soft granules. High drying temperatures will produce hard non-dispersible products. Usually the temperature range of 50-60°C is good. Drying is critical since final WDG moisture impacts the physical storage stability in addition to the chemical shelf life of the product.

### Scale Up

The scale up operation in WDG is a different experience when compared to other types of formulations. All the factors mentioned before in the laboratory process remain critical but even more factors are introduced. An example is the particle



size of the finished goods. For the small pan, off-size particles may range 15-20%. In scale up, the range can be as high as 40-45%. This means in order to produce 1 lb of product, you need 2 lbs of preblend. What will you do with the off-size? How can you handle it economically? This is a very serious issue, much more so than just forming granules. The major impact is plant capacity and recycle.

If you can not readily address this problem or are not prepared for it you are in trouble. The impact of these factors can be reduced but all companies handle such information as proprietary.

#### Evaluation Program and Storage Stability

For WDG evaluations specific attention must be given to dispersibility, suspensibility, particle hardness and dust properties. The following is a test procedure which has been utilized to measure the tendency of a granular to abraid thus generating dust. A standard weight of granules is placed in the glass bulb, rotated for a certain period of time while subjected to a controlled airflow. The dust is collected on the filter paper, determined and reported as mg dust/20 gm granules. Another test to evaluate the granules integrity and measure the attrition rate, is to place the samples on a railroad simulator and determine the percentage increase of - 50 mesh particles after a given time. For initial screening purposes, a criteria of a dust rate below 100 mg/20g and attrition values of less than 2% increase in -50 mesh material can be employed. In the data listed in Table II, one can see that sample C is an acceptable formulation.

Table II. Physical Evaluations of Experimental WDG Formulation versus Standard

<u>Samples</u>	<u>Dust</u> <u>mg/20g</u>	<u>Attrition</u> <u>Δ% - 50 mesh</u>
Sample A	103	5.0
Sample B	65	2.5
Sample C	30	1.2
Commercial Standard	171	2.2

Another test which is definitive is to ship a sample of granules by a commercial carrier in different types of containers to determine how the package and the physical handling

affect the granules integrity. Obviously, crushed granules are an indication of a poor product.

In the storage stability monitoring program, dispersability of the granules, particle size (before and after shipping and storage) and particle hardness should be evaluated. In addition, chemical stability must be evaluated.

### Field Test Program and Results

FMC has successfully field tested a wide range of pesticides in a WDG form on a large scale, gaining customers acceptance, and developing the knowledge to granulate any form of pesticide. Recently, FMC received a registration label for Dichlone 50 WDG, with two others, captan and ziram pending.

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# Analysis of Pesticide Formulations

## Establishment of Methods and Collaborative Testing

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The analysis of pesticide formulations is linked to specifications based on the requirements of the user. Methods of analysis for many pesticides purchased by international organizations are developed through collaborative studies initiated by the Collaborative International Pesticides Analytical Council and the Association of Official Analytical Chemists. The producer is not only concerned with analytical techniques needed for quality control but also with regulatory requirements that have imposed greater demands for analytical information in recent years. Improved analytical capabilities for detection of contaminants of potential toxicological significance, such as chlorodioxins and nitrosamines, have generated continued demands for data by regulatory agencies. Novel formulations, such as controlled-release formulations, require special analytical techniques to ensure satisfactory performance.

The majority of publications on pesticide analysis deal with terminal residues and their determination. From a practical standpoint, the determination of the active ingredient in a technical pesticide or a formulation is equally important, if not always apparently so scientifically challenging. In recent years, new dimensions have been added to the problem by regulatory requirements, and it has been recognized that certain contaminants, present in manufactured products, might present potential risks to man and the environment. From a practical standpoint, the manufacture and sale of pesticide products must be linked at all times to an analytical control system capable of adequately measuring active ingredients, since fluctuations

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in their content or quality will influence the economics of production and the performance of the formulated product.

The first consideration is the content of active ingredient, because the biological activity and application rates must be based on this figure.

Specifications require a statement as to the content of the active ingredient. It is also important that the content of impurities be defined if these interfere with the active ingredient, or are phytotoxic, such as *p*-nitrophenol in parathion; or are corrosive to packages or machinery; or induce chemical degradation; or are unduly hazardous to man or the environment, such as chlorinated dioxins or nitrosamines.

The specification must guarantee the identity and quantity of active ingredient and set limits for undesirable impurities.

The specification serves to guide buyers; it serves for comparison of batches; to recommend analytical procedures for active ingredient or impurities; to provide methods and criteria for identity of the active ingredient; and to provide chemical and physical parameters as additional tests for judging the suitability of formulations. It ensures that the product is satisfactory for the use for which it was intended by requiring that the product possess defined chemical and physical characteristics that can be verified by test methods.

The producer is concerned to ensure that his product performs consistently and meets the requirements of the user and usually provides specifications, but in many cases, national and international bodies have developed specifications, particularly for those products for which patents no longer exist, to meet their own needs for purchase of pesticides.

Specifications may refer to technical or formulated pesticides.

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TABLE I. FAO Specifications

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- |    |  |
|----|--|
| a) | origin                                     |
| b) | details of methods referred to             |
| c) | statement of scope                         |
| d) | information on the method of analysis      |
| e) | laboratory work to establish specification |
| f) | comparative laboratory work                |
| g) | other relevant information                 |
- 

The development of specifications cannot be effectively accomplished without proper analytical methodology. This also includes physical tests to ensure suitability as well as chemical analyses. Recognition of this need has led to international cooperation and coordination of effort. In this respect the Collaborative International Pesticides Analytical

Council (CIPAC) and the Association of Official Analytical Chemists (AOAC) have provided a lead through the preparation of collaborative methods.

### FAO Specifications

Following a series of meetings that began in 1965, a manual on the use of FAO specifications for plant protection products was published in 1971 (1). The FAO development of pesticides was on similar lines to those previously established by WHO and published in the handbook "Specifications for Pesticides Used in Public Health" (1967) (2). The preparation of separate FAO specifications was deemed necessary because the pesticides used for control of vectors of human health are not necessarily suitable for plant protection.

The specifications are prepared by a Working Party consisting of official governmental scientists assisted by a technical representative from the World Health Organization and by technical observers from the secretariats of international pesticide organizations which have liaison status with FAO. Industrial scientists may be consulted or invited as advisers to deal with particular items.

Draft specifications are prepared and submitted for review by the Working Party. Table I. shows the type of information to be submitted as a draft specification. If suitable, drafts are circulated and sent out for comment by industry and cooperating government agencies. After comment they are recirculated, and, subject to recommendations of the group, are adopted as:

**TENTATIVE:** based on minimum requirements, manufacturers method of analysis, not collaboratively studied;

**PROVISIONAL:** some collaborative study of analytical method or **FULL FAO specifications:** all necessary requirements and CIPAC method of analysis.

These specifications are subsequently published. The Working Party discusses patented products directly with the manufacturer and any experts the Working Party may wish to consult. In the case of commodity products, where patents have expired, worldwide consultation is necessary to ensure that all interested parties may comment.

World industry conveniently interacts with the working Party through the Groupement International de Fabricants de Pesticides (GIFAP). However, non-members of GIFAP may also be involved in consultation.

The Working Party agreed that collaboratively tested methods of analysis would be used and both CIPAC and the AOAC have made available methods which they adopted after collaborative testing. CIPAC is international in composition, but

many of its reports have originated from the Pesticides Analytical Advisory Committee (PAC) of the Ministry of Agriculture of the United Kingdom, which undertakes preparation of CIPAC methods of analysis for technical and formulated pesticides and prepares specifications where required.

The U.K. effort to control pesticides through proposed specifications and methods of analysis began shortly after World War I. Subsequently, there were continued efforts by the Ministry of Agriculture and the Association of British Insecticide Manufacturers to produce specifications and methods of analysis, but the flow of new pesticides made this task almost insurmountable. Since other countries were engaged in wasteful duplication of these efforts, it was proposed in 1957 by Dr. R. deB. Ashworth (3) that a national committee should be appointed by each country to be responsible for methods of analysis of technical and formulated pesticides. Collaborative methods would be tested and coordinated by an international committee, the Collaborative International Pesticides Analytical Council (CIPAC).

The U.K. national committee, PAC, has its counterparts in other European countries. At the first meeting of CIPAC in 1957, in addition to the U.K., representatives from the Netherlands, Federal Republic of Germany, and France participated. European representation subsequently increased and agreement was reached with FAO that the analytical methods would be published in the "FAO Plant Protection Bulletin". At about the same time WHO and CIPAC also agreed to collaborate in the preparation of methods. Representation increased at subsequent meetings, and there are now Members from 21 countries; correspondents (Associate Members) from the Official Association of Analytical Chemists (AOAC), the Food and Agricultural Organization of the United Nations (FAO), the World Health Organization (WHO), and from six more countries. Observers from other countries and the European Economic Community also attend. There is close cooperation with GIFAP and with official and industrial laboratories concerned with development of analytical methods (4).

The aims of CIPAC include the following:

- "a) to promote international agreement on:
  - (i) methods for the analysis of pesticide products and of such other substances as the Council may, from time to time, determine;
  - (ii) methods for the physio-chemical evaluation of technical pesticides and formulations;
  - (iii) methods for correlating biological efficacy with physical and chemical properties of pesticide.
- b) to foster inter-laboratory collaborative analysis among interested laboratories."

Additional aims include sponsoring symposia on methods of analysis, publishing agreed methods, proceedings of symposia, etc. and collaborating with other organizations (3).

Although the evolution of analytical methodology in the United States has differed from that in Europe, there has been close cooperation between the AOAC and CIPAC. Collaboration was proposed at the 7th meeting of CIPAC in 1963, and in 1971 CIPAC met in Washington, and it was agreed that to avoid duplication of effort CIPAC and AOAC would work closely together, and a document "Guidelines for Collaboration Between AOAC and CIPAC" was prepared (5).

This liaison had led to joint work on the development of methods, so that AOAC, CIPAC, and WHO, where appropriate, adopt each other's methods. This is indicated by the designation of a method as CIPAC-AOAC or AOAC-CIPAC to indicate the organization responsible for development of the method. In the CIPAC Handbook, methods designated CIPAC methods have been collaboratively investigated; those classified as "provisional" have been less thoroughly studied or may be less satisfactory.

#### Need for Collaborative Study

In the United States, the Association of Official Analytical Chemists has been recognized as an organization that primarily serves the needs of government regulatory and research agencies for analytical methods and it is now attempting to extend that role to the international scene. Through its efforts, the collaborative study has become a most important tool for validation of analytical methods and for determining their reliability. In the collaborative study, a number of laboratories are provided with identical sets of samples that lie within the range of the selected method. The objective of the collaborative study is to examine the accuracy, precision, sensitivity, range, limit of detection and other characteristics of the method.

This is accomplished under the direction of an Associate Referee, who, as a specialist, is in turn operating under the guidance and administrative supervision of a General Referee. The procedural details have been described (6-7). A minimum of six samples are sent to not fewer than five laboratories to be studied by the selected method. The agreed definition of Collaborative Study (AOAC - CIPAC) is "An analytical study involving a number of laboratories analyzing the same sample(s) by the same method(s) for the purpose of validating the performance of the method(s) (5).

### The Need for Harmonization

This paper has been concerned primarily with the role of CIPAC and AOAC in the preparation of analytical methods for pesticide formulations. The legal enforcement of standards makes it important to use validated procedures for determination of pesticides. To avoid duplication of effort and also to facilitate international commerce, the acceptance and validation of methods should be an international activity and the role of CIPAC internationally has corresponded to that of national committees or organizations. As the role of international bodies becomes increasingly more important, it is appropriate to focus on their activities in relation to analytical chemistry. Although there is a common basis for analytical operations, it has been recognized that some agreement is now essential among international organizations as to the development of standard methods on a collaborative basis.

In a paper presented in 1981 at the Symposium on Harmonization of Collaborative Analytical Studies in Helsinki, Finland, Dr. H. Egan called for discussion of the various philosophies adopted for establishment of standard methods of analysis and emphasized the need to examine criteria used for validation of methods, with particular reference to the international position (8). Problems arise through the absence of systematic coordination among the various bodies involved. Even though a method may have been collaboratively studied, possibly on an international basis, other organizations not involved in the study may have no means of determining whether the method meets their needs. There is need for recognition of and agreement as to the definition of a number of common analytical parameters such as accuracy, precision, repeatability, reproducibility and limit of detection and a common understanding as to where the values of the various parameters should lie for the acceptance of a method or for the agreement as to the equivalence of methods. The following definitions were suggested for important analytical terms (8):

"Limit of Detection: The smallest concentration of (or amount) of substances which can be reported with a specified degree of certainty by a definite, complete analytical procedure.

Sensitivity: The change in measured value resulting from a concentration change of one unit.

Precision (Reproducibility): The closeness of agreement between the results obtained by applying the experimental procedure several times under prescribed conditions in an inter-laboratory study.

Accuracy: The closeness of agreement between the true value and the mean results obtained by applying the experi-



mental procedure a very large number of times. In practice this should involve as many results as possible, the total number being stated."

A further philosophical problem that must be raised is that of the description of analytical methods. The collaborative studies used by the AOAC to support methods of analysis have been based generally on methods prepared in standardized format in which apparatus, reagents and procedures are rigidly prescribed. During the past two decades, laboratories have acquired increasingly complex and expensive instrumentation obtained with regard to the tasks to be performed and resources available. This diversity has made it more difficult to conduct collaborative studies based on rigid prescriptions of equipment and components, such as chromatographic columns, etc. Within recent years there have been efforts within AOAC to write analytical methods in generic terms and conduct collaborative studies of such methods. The methods are detailed in terms of performance parameters rather than in terms of specific instruments or components, thus the analyst may choose particular instrumental configurations or operating conditions as long as performance criteria are satisfied. Several methods of this type have been described, and the rapid adoption of automated or semi-automated analytical procedures, which differ from laboratory to laboratory, makes it important to examine method validation by collaborative study in the broader context of the generic description of methods (9-10).

#### Methods of Analysis and Tolerances

Non-specific methods that employ simple methods and reagents have been frequently employed for determination of active ingredients. Total chlorine and acid content may, for example, be used to measure phenoxyalkanoic acids. These methods have been largely displaced by more specific methods, such as gas chromatography, but where specific methods are unavailable, as in the case of maneb, zineb, and other complex organometallic ethylene dithiocarbamate derivatives, indirect methods are used.

The importance of specific methods can be realized by consideration of biological activity. Analysis of malathion content by total phosphorus or a colorimetric method may give a significantly higher figure than analysis by gas chromatography. This is particularly important in terms of biological activity and indicates the necessity of indicating the method of analysis when the content of active ingredient is specified by the purchaser.

Allowance must be made for variation from the true content of active ingredient because analytical methods are subject to error and variations in conditions during manufacture may also cause heterogenities of product composition. The allowance is known as a tolerance and represents the permissible departure from the declared figure. It is influenced by:

- a) the reproducibility of the analysis;
- b) sampling error of the product;
- c) demands of the buyer.

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TABLE II. Trace Contaminants in Technical Pesticides and Formulations

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CHLORINATED DIOXINS AND DIBENZOFURANS  
ISOMALATHION  
NITROSAMINES  
CHLORINATED AZOBENZENES AND AZOXYBENZENES  
ETHYLENE THIOUREA

---

#### Contaminants and Environmental Problems

The question of pesticide residues and their environmental implications must be considered in the context of the active ingredient and its accompanying trace materials. The IUPAC definition of a pesticide residue is "any substance or mixture of substances in or on any substrate resulting from the use of a pesticide and includes any derivatives, such as degradation and conversion products, metabolites, reaction products and impurities" (11). The significance of that residue depends on the toxicological properties of the substance and the degree of exposure. Thus, by definition, materials associated with the pesticide in the formulation must necessarily be considered as "pesticide residues".

It is therefore important that sufficient information be available to determine whether use of a pesticide might result in the occurrence of residues in a crop or a commodity, not only in the case of the active ingredient and its alteration products, but also for by-products of manufacture and contaminants.

In recent years, there have been a number of examples of such problems (Table II.). The proposed data requirements for pesticide registration prepared by the U.S. Environmental Protection Agency address this topic. This has been an extremely controversial regulatory problem. It is clearly important to know the composition of applied pesticides including the major associated contaminants in order to assess their potential for environmental impact, but as the quantitative significance of

contaminants decreases, a corresponding increase in toxicological significance would seem to be a pre-requisite if quantitative analysis is to be required for low-level components.

The regulations state that the "Agency is proposing that all impurities occurring in manufacturing use products end-use products in quantities greater than 0.1 percent of the product (by weight) be identified. In addition, the Agency will require further chemical analysis on a case-by-case basis when the manufacturing process or other product chemistry data suggests the presence of low-level, yet highly-toxic impurities" (12).

This approach was adopted because *in vitro* microbial assays to screen pesticide products for potentially genotoxic low-level components appeared to give a substantial proportion of false positive or false negative results.

A number of practical problems led to the development of these recommendations. Adverse effects, such as unpredicted phytotoxicity, led to the recognition that some products were likely to contain manufacturing impurities or contaminants that affected their margin of selectivity when applied to crops or their potential for damage to neighbouring crops, as in the case of phenoxy herbicides in which esterification with alcohols of low molecular weights gave volatile esters.

The recognition of the adverse consequences of contaminants has been accompanied by significant advances in analytical methodology. In fact, recognition of the problems and the development of techniques for their solutions have proceeded hand-in-hand, as is exemplified by the chlorinated dioxins and the nitrosamines.

Chlorinated dioxins are chlorine substituted dibenzo-p-dioxins. The most toxic of the large number of possible isomers is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Chlorinated dioxins, chlorinated dibenzofurans, and their precursors have been found in many chlorinated phenols, depending on their origin and conditions of synthesis. Extensive literature now deals with the problem of the dioxins and the lower limits of their detection are continually extended. The major pesticides of concern are pentachlorophenol and 2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid]. Pentachlorophenol (PCP), an important wood preservative, has been the focus of a great deal of attention as a source of toxic contaminants. Long and painstaking investigations into the composition of "toxic fats" in chicken feed revealed links between the use of pentachlorophenol for hide preservation and the deaths of large numbers of chickens when the highly toxic halogenated dioxin, 1,2,3,6,7,8-hexa-chlorodi-benzo-p-dioxin, was isolated from toxic fats (13).

Some formation of TCDD may occur during the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene to 2,4,5-trichlorophenol, (the precursor of 2,4,5-T) because the reaction is conducted at elevated temperatures under pressure. In 1972, analysis of 2,4,5-T samples by gas chromatography indicated that 23 of the 42 samples tested contained up to 10 ppm TCDD (14). A report that 2,4,5-T caused birth defects in mammals had drawn attention to the problem of 2,4,5-T and the samples used in the tests were found to contain 27±8 ppm of TCDD as a contaminant (15). The possibility that TCDD might enter the environment led the regulatory agencies in 1971 to enforce a maximum content of 0.1 ppm TCDD in manufacturing specifications for 2,4,5-T. However, improved manufacturing practices had reduced the TCDD content in most commercial grades of 2,4,5-T generally to 0.01 ppm or lower by 1980.

Malathion (O,O-dimethylphosphorodithioate of diethyl mercaptosuccinate) is used extensively throughout the world as an insecticide. It is particularly useful for control of insect vectors responsible for the spread of malaria and has replaced DDT [1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane] and benzene hexachloride as resistance to these insecticides has increased. It is generally regarded as one of the safest organophosphate insecticides, but in 1976 there was an outbreak of poisoning among 7500 workers in the malaria control programme in Pakistan (16). The symptoms were typically those of organophosphate poisoning and were observed with 3 formulations. However, incidence of poisoning was greatest with the products that contained the greatest amount of isomalathion, a toxic degradation product. Poor work practices resulted in excessive skin contact and absorption of pesticide, but the unanticipated toxicity provoked detailed investigation of the properties of the formulations and their stability in storage under tropical conditions. Analysis showed that these 2 formulations had an isomalathion content greater than 2 percent and showed high mammalian toxicity (16).

The stability of malathion and fenitrothion (O,O-dimethyl O-(4-nitro-m-tolyl) phosphorothioate formulations has been investigated (17). A number of products are formed when malathion formulations are stored at elevated temperatures. However, the quantity of S-methyl isomer (isomalathion) formed appeared to correlate best with increased mammalian toxicity and the rate of isomerization was dependent on "inert" ingredients in the formulation. Although there was some formation of the S-methyl isomer of fenitrothion, an increase in toxicity was not observed after storage at elevated temperatures. Isomalathion may be quantitatively determined by gas chromatography and the World Health Organization has specified that the isomalathion content of a 50 percent powder be no greater than 0.9 percent after 6 days at 55°C.

Several nitrosamines are known to act as mutagens or carcinogens in laboratory animals; therefore, there has been a considerable effort to identify environmental sources of nitrosamines. Nitrosamines may be formed by the action of nitrous acid on secondary amines. Thus, there are a wide variety of potential substrates, because nitrous acid, as nitrite, and secondary amines, are almost ubiquitous. The presence of nitrosamines in pesticide formulations usually results from the byproducts of a nitrosation step or a reaction between amine salts of certain pesticides and nitrite used as a corrosion inhibitor in the formulated product.

Fluorinated trifluralin ( $\alpha, \alpha, \alpha$ -trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) was found to contain nitrosamines, and it seems likely that these arose by the nitrosation of the amine used in the condensation with the nitrated chlorobenzene intermediate in the synthesis or by nitration of the product, trifluralin itself. Nitrosamines have also been found in other pesticides prepared by similar nitration processes.

The nitrosamines associated with phenoxy or benzoic acids formulated as amine salts probably arise by nitrosation of the amine when nitrite is used as a corrosion inhibitor. However, the finding of nitrosodimethylamine in batches of dimethylamine used for formulations indicates that the question of sources may be complex. Although N-nitroso compounds may be analyzed by gas-chromatography using a number of types of detector types, a specific and sensitive method is available. The thermal energy analyser (TEA) depends on the measurement of infrared emission generated by the decay of excited NO<sub>2</sub> molecules to the ground state. The pyrolytic rupture of N-NO bonds generates nitrosyl radicals (NO·) which are reacted with ozone, prepared by an electric discharge, to give the excited NO<sub>2</sub> molecules (18).

The azo compound, 3,3',4,4'-tetrachloroazobenzene, bears a steric resemblance to TCDD. It induces aryl hydrocarbon hydrolase activity in mice and chick embryos. It may be acnegenic and it is a potential carcinogen (19). It has been detected as a contaminant in formulations of the herbicide, propanil (3,4-dichloropropionanilide). Azobenzenes have also been detected in commercial samples of the urea herbicides, diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea] and linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] (20), but the amounts detected in propanil were hundreds of times greater than those found in the dichlorophenylurea herbicides. This problem probably arises in manufacture and, as in the case of the chlorodioxins, is associated with the technical product.

Ethylene bisdithiocarbamate fungicides (mancozeb, maneb, nabam, zineb, etc.) may break down in aqueous solution to produce ethylene thiourea and other degradation products. Ethylene thiourea (ETU) produces thyroid tumours in experimental animals and it is also teratogenic and mutagenic (21). Analyses of fungicide formulations for ETU content revealed that it was present as a manufacturing impurity and it also arose as a degradation product in some formulations during storage and handling (22-23).

Thus, contaminants present in technical products may be produced by reactions with formulation ingredients or by changes that occur under conditions of storage. Specifications, therefore, must take into account such eventualities and include suitable procedures for analysis or performance tests.

### Conclusion

Specifications for formulated or technical pesticides must be based on satisfactory analytical methods. Collaborative study methods that are acceptable to a number of international organizations are available through CIPAC-AOAC cooperation. Internationally, more effective use of current analytical methodology could result from increased efforts towards harmonization of methods and terminology.

Although relatively simple analytical methods are sometimes useful for formulation analysis, it is important to recognize the problems inherent in non-specific methods and also the need to detect and measure potentially harmful contaminants in technical pesticides or formulations.

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## Identification of Glucosylated Conjugates and Oxygenated Metabolites of Nonionic Surfactants in Barley and Rice Leaf Tissues

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Homogeneous  $^{14}\text{C}$ -ethoxylates (EO) of *p*-(1,1,3,3-tetramethylbutyl)phenol were investigated as model pesticide formulating agents in barley and rice leaf tissues. Polar metabolites of the 6EO or 9EO surfactants accumulated in both species. Rice tissues also contained additional  $^{14}\text{C}$ -products (>10%) that were not extracted readily with methanol. Most of the polar, water-soluble metabolites from excised barley tissues were glycosidase-resistant anionic conjugates. Mild basic hydrolysis converted up to 50% of them to neutral conjugates that were hydrolyzed by  $\beta$ -glucosidase. The major  $^{14}\text{C}$ -aglycones were identified and some conjugates of greatest polarity were characterized.

Many pesticides are of low solubility in water and field applications as true solutions may not be feasible under conditions of normal practice (1). In Table I, for example, the solution volume necessary to apply 1 lb/ac of trifluralin represents a 4-inch rainfall. This emphasizes the need for and the value of formulation techniques such as cosolvents, dispersed powders, emulsions, solubilizing surfactants, *etc.* The work of Temple and Hilton (2) suggested that up to 20-fold increases in herbicide solubility were attainable by using an appropriate surfactant. Besides having an adequate pesticide concentration, another requirement of any formulation is that the droplets produced upon spraying have adequate wetting and retention after they impinge on target foliar surfaces. The contact angle,  $\theta$ , between a spray droplet and the surface it contacts can be used to estimate formulation performance. When  $\theta$  is large, there is poor contact with the foliage and droplet retention may be limited. When  $\theta$  is

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small, droplets tend to spread on the foliage and the potential for uptake is increased (3). The decreases in  $\theta$  may be achieved by adding moderate amounts of certain organic solvents to an aqueous medium or with low concentrations of an appropriate surfactant. Considerations of cost, flammability and phytotoxicity often favor the use of surfactants.

Table I. Herbicide Solubilities and Dilution Requirements in Aqueous Media.

Compound	Molecular Weight	Solubility in H <sub>2</sub> O ( $\sim 25^{\circ}\text{C}$ )	Spray Volume for 1 lb ai in Solution
Amitrole	84.1	$\sim 28\%$	$\leq 1$ gal
2,4-D (acid)	221.0	0.09%	130 gal
Atrazine	215.7	33 ppm	3600 gal
Trifluralin	335.3	$\leq 1$ ppm	$> 100,000$ gal

(Adapted from Ref. 1 with permission.)

### Surfactant Behavior in Plants

Reports about the fate and behavior of any pesticide applied in different kinds of formulations to plants are rather limited. This is true even more so for the other constituents of formulations including surfactants. McWhorter (4) has estimated that considerable quantities of surfactants are applied to plants with pesticides. The general assumption is that these constituents present lesser environmental hazards than the pesticides. Parr (5) has discussed some aspects of surfactant toxicology.

Solutions (250 ppm) of Triton X-100, a commercial ethoxylated nonionic surfactant, were administered to excised barley leaves. Partial inhibition of photosynthetic oxygen evolution occurred in tissue segments taken from the leaves after 5 h of exposure, but there was a partial recovery of activity by the excised leaves during the next 18 h. In contrast, treatments with 2 ppm atrazine caused nearly complete and irreversible inhibition (6).

Homogeneous ethoxylated nonionic surfactants incorporating  $^{14}\text{C}$ -label were synthesized by Tanaka *et al.* (7,8). The derivatives of purified *p*-(1,1,3,3-tetramethylbutyl)phenol with either 6 or 9 ethylene oxide (EO) units, analogs of Triton X-100 were used in this work. The hydrophobe, called tert-octylphenol (tOPh-OH), was converted to ethoxylates with the  $^{14}\text{C}$ -label at the outer carbon of the innermost EO group (Example: [ $^{14}\text{C}$ -1EO]tOPh-6EO). Studies by Stolzenberg *et al.* (6) with the homogeneous tOPh[ $^{14}\text{C}$ ]-ethoxylates showed that uptake occurred through the upper surface of barley leaves into intact plants. Translocation throughout the plants was limited, and there was rapid metabolism of the

surfactants near the site of application. Metabolites with similar chromatographic profiles were formed when the *t*OPh-ethoxylates were administered to excised barley leaves. Surfactant concentrations within the excised leaves ranged from 4-80 ppm (fresh weight basis).

**Metabolite Profiles.** Preliminary trials with *t*OPh·6EO yielded surfactant metabolism rates similar to those for barley in excised leaves of a variety of monocot species (9) although there were qualitative and quantitative differences in the <sup>14</sup>C-metabolites found. Under equivalent conditions, however, metabolism of the parent surfactant was slower in excised rice leaves. Table II compares the metabolic fate of <sup>14</sup>C-*t*OPh·6EO in excised leaves of barley and two rice cultivars. Recoveries of <sup>14</sup>C were high with barley tissues and only limited quantities occurred as methanol-insoluble metabolites or as volatiles. The <sup>14</sup>C recoveries from rice were lower and up to 20% was present as methanol-insoluble residues (combusted to <sup>14</sup>CO<sub>2</sub>). Exhaustive methanol extraction decreased the amount of insoluble <sup>14</sup>C to about 15% (9).

Table II. Uptake and Fate of Surfactant in Excised Seedling Leaves Treated (1 mL/g fr wt) with 12 ppm Solutions of <sup>14</sup>C-*t*OPh·6EO and then Held in Water.

Tissue	Surfactant Uptake (ppm) <sup>a</sup>	Elapsed Time (h) <sup>b</sup>	Distribution (%) <sup>c</sup>	
			Parent	Insolubles
Barley	7.3 ± 0.7	4 + 0	82	
(cv. Dickson)		4 + 3	58	
		4 + 8	29	↳
Rice (cv. Nato)	10.5 ± 0.8	6 + 0	84	
		6 + 16	41	17
(cv. Star-bonnet)	10.1 ± 0.9	6 + 0	82	
		6 + 16	43	14

a From <sup>14</sup>C assays: (original amount)-(solution not absorbed).

b (Treatment)+(Time in water).

c Assays by TLC and combustion, respectively; methods in Ref. 6.

Polar metabolites accumulated with longer time periods and at lower surfactant concentrations in excised tissues of both species (9). Analyses of the methanolic tissue extracts showed that some of the polar metabolites were unstable, yielding yet other polar materials (6). Although some characterizations were achieved by TLC techniques, detailed analyses were not possible until the polar metabolites were isolated more rapidly by solvent partitioning (10). This permitted removal of most of the unme-

tabolized parent surfactant ( $t\text{OPh}\cdot 6\text{EO}$ ) and plant pigments in hexane. Some additional pigments and traces of surfactant were removed with ethyl acetate, while the polar surfactant metabolites remained in the aqueous phase.

Nonpolar Metabolites. In excised barley tissues 10-20% of the  $^{14}\text{C}$  was present as hexane-soluble metabolites that were less polar than the parent surfactant. This also was true for excised rice leaves. Analyses of the nonpolar metabolites of both species showed that these were predominantly lower ethoxylates derived from the parent surfactant by EO losses. Structural examples are given in Figure 1 ( $R_1=\text{H}$ ). The 2EO ( $n=1$ ) metabolite was most abundant in barley (6) and the 1EO ( $n=0$ ) product was next. In rice the 1EO material was typically 40% of the nonpolar  $^{14}\text{C}$  metabolites, the 5EO ( $n=4$ ) up to 20%, and there were essentially equal amounts of the 2-, 3-, and 4EO materials (9). The site of  $^{14}\text{C}$ -labeling (see Figure 1) precluded identification of the free phenol ( $t\text{OPh}\cdot\text{OH}$ ), but it was not detected in similar trials with barley using a [ $^{14}\text{C}$ -phenyl] $t\text{OPh}\cdot 6\text{EO}$  surfactant (6).

With both species, small quantities of other hexane-soluble, nonpolar metabolites were isolated. Some were hydrolyzed in alkali and yielded the respective parent  $^{14}\text{C}$ -surfactants. These metabolites also had very low mobility in reversed-phase (RP) chromatography systems. This suggested they were equivalent to the surfactant fatty acid esters (Figure 1;  $R_1=\text{fatty acyl}$ ,  $n=5$  or 8) whose formation by cell-free homogenates from corn tissues was reported by Frear *et al.* (11).

#### Analysis of Polar Metabolites

Cleavage of the innermost EO unit from the  $t\text{OPh}$ -moiety (see Figure 1) could yield oligomeric  $^{14}\text{C}$ -polyethylene glycols (6). Solvent partitioning and RP TLC procedures were developed to show that neither the water-soluble metabolites from barley nor their acid hydrolysis products contained more than trace quantities of these materials (12).

Preliminary TLC analyses showed that methanolic extracts from surfactant-treated excised barley tissues contained some unstable polar metabolites. These water-soluble metabolites were assumed to retain the  $t\text{OPh}$ -group because typically 95% of the  $^{14}\text{C}$  was retained by Sep-Pak C18 cartridges (6). Solvent partitioning procedures were applied to the methanolic extracts. After removal of the ethyl acetate-extractables, the water-soluble polar conjugates were analyzed. About 90% of the  $^{14}\text{C}$  in this fraction was retained by anion exchange resins. A portion of these metabolites reverted to neutral polar conjugates during subsequent cleanups, and overnight exposure to 1-2 N  $\text{NH}_4\text{OH}$  caused similar conversions (10). About 50% of the  $^{14}\text{C}$ -materials still were acidic (anionic) and all components of these  $\text{NH}_3$ -treated samples seemed to be stable during subsequent analyses. Although the

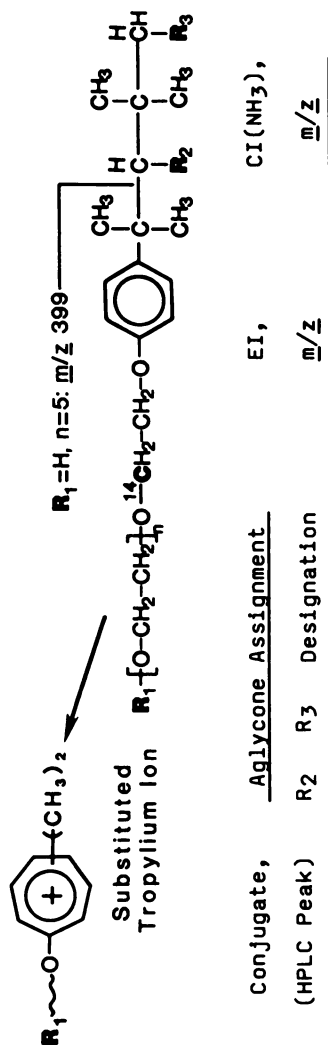


Figure 1. Structural features and mass spectral fragments of tOPh-ethoxylates and some deethoxylated, oxygenated and/or conjugated metabolites (6). Isolation as glucosylated conjugates (C,D) is represented in Figure 2. For the MS data, ( $\overline{m/z}$ )=presumed molecular ion was not observed.

polar (anionic) conjugates were resistant to  $\beta$ -glucosidase at the time of isolation, after  $\text{NH}_3$ -treatment about 35% of the  $^{14}\text{C}$ -materials were hydrolyzed by this enzyme. Only about 40% of the polar water-soluble metabolites of  $t\text{OPh}\cdot 6\text{EO}$  or  $\cdot 9\text{EO}$  isolated from treated rice tissues by solvent partitioning were anionic. Exposure to  $\text{NH}_4\text{OH}$  did not substantially alter the proportion retained on anion exchangers.

Glucosylated Parent Compound. Figure 1 also depicts other known sites of metabolic transformations for the  $t\text{OPh}$ -ethoxylates in plant tissues. The first polar conjugate identified was isolated by direct TLC of the methanolic extracts of barley tissues and was purified by repeated TLC and by HPLC (C18). Acid hydrolysis released the parent surfactant (with 6EO or 9EO) as did enzymatic hydrolysis with  $\beta$ -glucosidase (6). Thus,  $\text{R}_2=\text{R}_3=\text{H}$  and the glycosidic bond formed at the existing  $-\text{OH}$  ( $\text{R}_1=\beta\text{-D-glucosyl}$ ) in the poly(oxyethylene) chain ( $n=5$  or  $8$ ). This conjugate was also found in the ethyl acetate phase when the solvent partitioning steps described earlier were applied to extracts from excised barley tissues. Extracts from surfactant-treated excised rice tissues did not contain the glucosylated parent compound in appreciable quantities.

Separation of Glucosides on RP HPLC Columns. Gradient elution of a C18 column for surfactant metabolite characterization was reported (6). Separation and purification of the  $\text{NH}_3$ -treated polar metabolites from barley treated with  $t\text{OPh}\cdot 6\text{EO}$  was achieved on similar columns (10), and typical profiles are shown in Figure 2. The solvent compositions are given in Figure 2. Peak A from the methanol gradient consisted of the  $\text{NH}_3$ -resistant anionic materials [eluted from Cellex-T using procedures like those reported by Tanaka *et al.* (8)] and were present at the previously-found levels of up to 50%. The other peaks were not retained on anion exchange resins. Peak B was heterogeneous and was not analyzed in detail. Peak D had a retention time (RP) similar to that for the parent surfactant, but TLC on silica confirmed that it was a polar conjugate (6); and acid hydrolysis or  $\beta$ -glucosidase treatment released the parent surfactant. Thus,  $\text{NH}_3$ -treatment of an anionic conjugate yielded the glycosylated parent compound ( $\text{R}_1=\beta\text{-D-glucosyl}$  in Figure 1).

Because hydrolysis of Peak C released several products, this abundant fraction was rechromatographed in an acetonitrile gradient (10) and at least three peaks resulted (Figure 2). The structures of the metabolites associated with the fractions from Peak C are discussed in later sections of this report. Conjugate fraction C-1 was a mixture that, upon  $\beta$ -glucosidase treatment, released a material assigned as a  $1^\circ$  alcohol ( $\text{R}_2=\text{OH}$  in Figure 1). Fraction C-2 was cleaved nearly quantitatively by  $\beta$ -glucosidase to release a  $2^\circ$  alcohol ( $\text{R}_2=\text{OH}$ ). Fraction C-3 was cleaved extensively by  $\beta$ -glucosidase and one of the major hydrolysis products

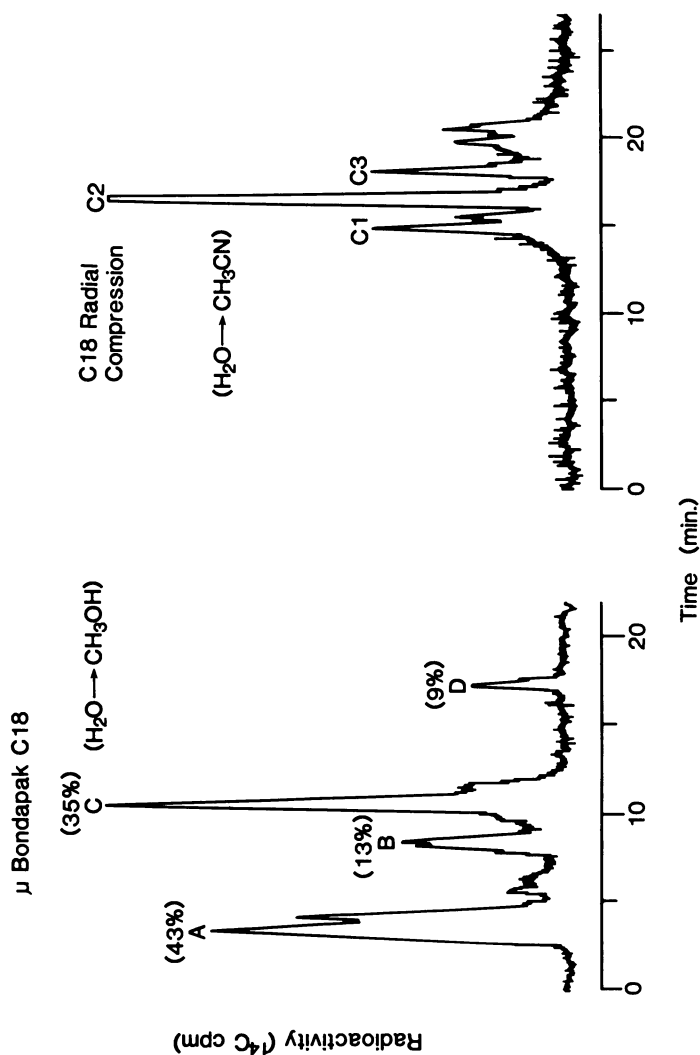


Figure 2. Radiochromatograms for  $^{14}\text{C}$ -metabolites of tOPH·6EO eluted from RP-HPLC columns with linear gradients (25 min): left, water-soluble  $\text{NH}_3$ -treated fraction from excised barley leaves [50-100%  $\text{CH}_3\text{OH}$  at 2.0 mL/min (6)]; right, purification of peak C' (8 mm cartridge, 25-100%  $\text{CH}_3\text{CN}$  at 2.5 mL/min).

parent surfactant from peak D gave  $m/z$  488, and the 1° alcohol from peak C-1 gave 504. The 2° alcohol from peak C-2 gave  $m/z$  504, and the species from peak C-3 presumed to contain a carbonyl group in the neopentyl moiety gave  $m/z$  502.

Acid-labile Oxygenated Metabolite. The 2° alcohol metabolite (Figure 1, R<sub>2</sub>=OH) was first isolated in moderate yield from the ethyl acetate phase after solvent partitioning (6). Because yields of the free 2° alcohol in this phase sometimes were observed to increase when the partitioning steps were delayed, decomposition of an unstable polar metabolite may release this oxygenated material.

Earlier analyses of the polar, water-soluble conjugates from excised barley tissues had involved acidic hydrolyses (1-2 N HCl) and the 2° alcohol was not isolated in significant amounts (6). A few percent of the <sup>14</sup>C was a product similar chromatographically to the parent surfactant, tOPh·6EO. Its EI-MS, however, had no  $m/z$  399 tropylium ion; an intense  $m/z$  411 suggested that another alkyl substituent was present (Figure 3). This was interpreted as the result of a rearranged carbonium ion (14) from the 2° alcohol in acidic media (10). Mild acidic hydrolysis (aqueous HCl in CH<sub>3</sub>OH) successfully released the 2° alcohol from the major HPLC peak C-2.

Silica HPLC of Neutral Conjugates. Bürger (15) showed that silica TLC resolved nonionics with respect to their EO content. Available RP systems resolved the hydrophobic groups in these surfactants but were rather insensitive to their EO content (12). McGinnis and Fang (16) used polar solvents to separate glycosides on silica HPLC columns. Some solvent systems employed by the authors are given in Table III. Retention times have been reasonably reproducible and various aglycones or glycosyl residues of model conjugates (purchased from Sigma or U.S. Biochemical) and of surfactant metabolites could be resolved. Silica columns have been used to purify some of the metabolites isolated in these metabolism studies.

Ammonia-resistant Anionic Metabolites. Peak A from HPLC (see Figure 2) contained up to one-half of the conjugates in barley tissues after long time periods. These metabolites resisted alkaline hydrolysis, but 1.0-1.5 N HCl released many neutral materials of reduced polarity. This suggested the presence of glycosidic linkages. Silica and RP chromatography and preliminary EI-MS suggested that most of the hydrolysis products have lost several EO units and have been oxygenated in the tertoctyl group.

The post-ammonia acidic conjugate fraction from rice is similarly complex by RP-TLC and further analyses are pending. The relatively lower abundance of polar, water-soluble metabolites from rice may be offset by formation of a methanol-insoluble

appeared to be a carbonyl-containing material. Thus, Peak C contained several neutral glucosides of oxygenated surfactant metabolites.

Methanolic extracts from surfactant-treated rice tissues were subjected to solvent partitioning and to ion exchange chroma-

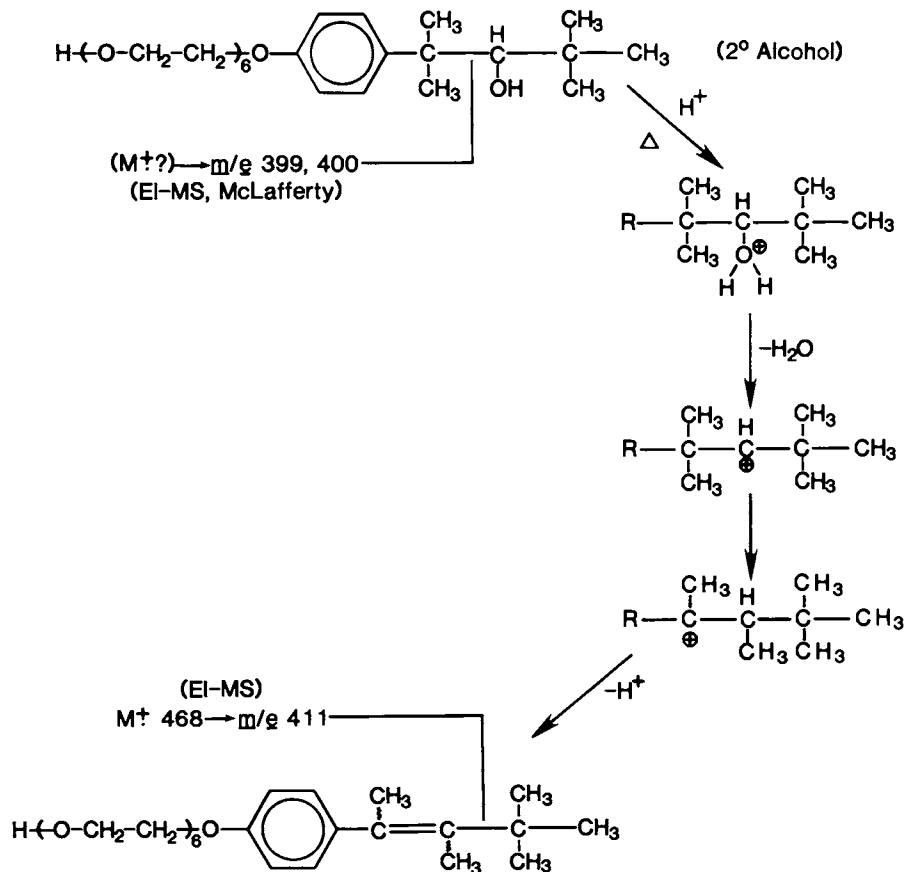


Figure 3. Conversion of an acid-hydrolyzed conjugate from a 2° alcohol by dehydration and carbonium ion rearrangement to a species yielding  $m/z$  411 ( $\text{R} = -\text{Ph} \cdot 6\text{EO}$ ).



tography. The neutral fraction gave mostly peak C (see Figure 2) on HPLC with a  $\text{CH}_3\text{OH}$  gradient. Glycosides were indicated because mild acid hydrolysis released several less polar  $^{14}\text{C}$ -materials nearly quantitatively.

#### Mass Spectrometric Characterization of Surfactant Metabolites.

The electron impact mass spectra (EI-MS) of ethoxylated alkylphenols and some surfactant metabolites from barley have been described (6). More recent samples were analyzed on a Varian-MAT 112S instrument with a dual EI/chemical ionization (CI) source using a solid sample probe. The analysis of carbohydrate materials using ammonia reagent gas [CI( $\text{NH}_3$ )-MS] has been described (13). In EI-MS these nonionic surfactants undergo cleavage of an  $\alpha\text{-}\beta\text{C}$  linkage (see Figure 1) in the molecular ion ( $\text{M}^+$ ), usually losing the largest  $\alpha$ -substituent (here the  $\text{C}_5$  neopentyl group) as a neutral fragment (6). This intense ion is attributed to a substituted 7-membered cyclic species, a tropylium ion (see Figure 1); the  $\text{tOPh}\cdot 6\text{EO}$  surfactant ( $n=5$ ) yields  $\underline{m/z}$  399 and  $\text{tOPh}\cdot 9\text{EO}$  ( $n=8$ ) gives  $\underline{m/z}$  531. Metabolism within the EO chain would shift these intense ions to other values. The failure to observe a tropylium ion at  $\underline{m/z}$  415 (vs. 399) was presumed to exclude ring hydroxylation or hydroxylation at an  $\alpha$ -methyl group in  $\text{tOPh}\cdot 6\text{EO}$  (6). An identical tropylium ion results when the neutral fragment has substituent groups at  $\text{R}_2$  and/or  $\text{R}_3 \neq \text{H}$  (see Figure 1). Thus, information about  $\text{R}_2$  or  $\text{R}_3$  was lost unless the  $\text{M}^+$  was observed.

The major product of  $\beta$ -glucosidase hydrolysis from sub-fraction C-1 (Figure 2) gave a  $\text{M}^+$  (486); this is characteristic of  $1^\circ$  alcohols and  $\text{R}_3=\text{OH}$  was assigned. The  $^{14}\text{C}$ -material released by  $\beta$ -glucosidase from the major peak C-2 gave no  $\text{M}^+$ ; this is typical of  $2^\circ$  alcohols and  $\text{R}_2=\text{OH}$  was assigned. Its enhanced  $\underline{m/z}$  400 (relative to the  $\underline{m/z}$  399 tropylium ion) was attributed to a McLafferty-type rearrangement of a hydrogen on a  $\gamma$ -hetero atom back into the ring through a 6-membered transition state with a loss of a neutral carbonyl-containing fragment (6). The major enzymatic hydrolysis product from C-3 gave no  $\text{M}^+$ ; its intense  $\underline{m/z}$  399 tropylium ion lacked a  $\underline{m/z}$  400 rearrangement peak. The strongest evidence for oxygenation (presumably at the 2C or 4C positions) was that the  $^{14}\text{C}$ -aglycones from peaks C-1, C-2 and C-3 had very similar retentions on C18 columns with  $\text{CH}_3\text{OH}$  (10). These three aglycones eluted with  $\text{CH}_3\text{CN}$  in the same sequence as their respective neutral conjugates (C-1, C-2, and C-3).

The CI( $\text{NH}_3$ )-MS data supported the assignments given in Figure 1 (10). With  $\text{NH}_3$  reagent gas (13) all four materials gave rather intense molecular ion species shifted by 18 mass units. The fraction. Mild acid hydrolysis released over 50% of the insoluble  $^{14}\text{C}$  as neutral products. Silica and RP-TLC suggested that most of the products are oxygenated and have lost EO units.

Table III. Chromatography of Glycosidic Conjugates and Some Ethoxylated Compounds on Silica.

Compound	CH <sub>3</sub> CN-H <sub>2</sub> O (91:9)		CH <sub>2</sub> Cl <sub>2</sub> -CH <sub>3</sub> OH-H <sub>2</sub> O (65:15:1)	
	TLC <sup>a</sup> Rf	HPLC <sup>b</sup> min	TLC <sup>a</sup> Rf	HPLC <sup>b</sup> min
Ph-β-D-glucoside	.63	2.3	.63	3.3
<u>p</u> NO <sub>2</sub> -Ph-D-glycosides:				
-β-galactoside	.62	2.7	.58	4.3
-α-glucoside	.56	2.3	.58	4.0
-β-glucoside	.63	2.5	.62	3.0
-β-lactoside	.33	6.0	.25	~16
<u>t</u> OPh-derivatives:				
-Free-OH's				
•6EO	.71		.97	
•9EO	.57	3.7	.96	3.5
-β-D-glucosides				
•6EO	.45			
•9EO	.34	9.0		7.5

<sup>a</sup> HLF Silica (0.25 mm layer), Analtech, Newark, DE.

<sup>b</sup> Silica (10μ) cartridge, 8 mm i.d.; Radial Compression Module (2.5 mL/min); Waters Assoc., Milford, MA.  
(Adapted from Ref. 1 with permission.)

### General Discussion

The behavior and fate of surfactants applied with pesticides to crops and weeds has not been studied extensively. Alkylphenol ethoxylates have been shown to undergo methyl and methylene oxygenation, O-glucosylation, and formation of other conjugates in barley tissues. Data for excised rice leaves are less complete at this time. Numerous pesticides undergo oxygenation and glucosylation in plant tissues (17) and it is possible that various metabolic interactions occur when these surfactants are present.

Anionic water-soluble conjugates are formed in both rice and barley. The structural changes caused in NH<sub>3</sub>-labile anionic conjugates from barley to form the neutral glucosides (Peaks C and D in Figure 2) have not been identified. Frear (17) has reviewed reports of acylated glycosides in plant tissues. For most examples that were adequately characterized, acidity was imparted by a 6-O-malonyl hemiester substituent that was labile in mild alkali. The aglycones reported were both naturally occurring and xenobiotic.

The sites of O-glucosylation in the oxygenated surfactant metabolites are not known (see Figure 1). More details may come from MS of the conjugates or from nuclear magnetic resonance spectra of the conjugates and their aglycones.

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## Physical Properties Determining Chargeability of Pesticide Sprays

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From a formulation viewpoint, the several technical approaches to the droplet-charging phase of the electrostatic pesticide-spraying process are shown to depend primarily upon liquid electrical resistivity and dielectric constant. Ionized-field charging of low permittivity oil-based sprays theoretically attains at least half the charge level of that imparted to aqueous-based pesticide spray having ca. a 40-fold greater dielectric constant. Theoretically, electrostatic induction is shown to satisfactorily charge spray liquids exhibiting resistivity values over a  $10^6$ -fold range from ca.  $10^6$  ohm m downward. For direct electrostatic atomization and charging of hydrocarbon liquids by 2-electrode systems, precise formulation to assure that resistivity values lie within a comparatively narrow  $10^6 - 10^8$  ohm m region is required. Experimentally measured resistivity values for common commercial pesticide formulations were typically found to range from ca.  $10^5$  to 1 ohm m for water: pesticide dilutions of 0:1 to 80:1, respectively.

Incorporation of electric force fields into pesticide spray application has been shown to greatly increase the mass-transfer efficiency of the basic droplet deposition process (1-3). The most elementary statement of the conditions necessary for such electric-force augmentation is

$$\vec{F}_p = q_p \vec{E} \quad (1)$$

where  $\vec{F}_p$  is the electrical force in newtons acting upon a spray droplet  $p$  having net free charge of  $q_p$  coulombs, and  $\vec{E}$  is the electric field in volts per meter  $p$  experienced at the droplet location. Previous studies have considered the technical

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requirements and relative magnitudes of the electric fields  $\vec{E}$  associated with image charges induced into target boundaries, with externally applied electrodes, and with the space charge delivered by the airborne spray cloud itself (4). Additional laboratory studies using tracer-tagged sprays have documented that droplet charge levels corresponding to 1 mC/kg or greater acting in conjunction with such electric fields generally provide very significant increases in spray deposition efficiency (5,6). The objective of this paper is to briefly review droplet-charging methods and, hence, to define for the pesticide formulator those physical properties which determine the degree of electrical chargeability of liquids for use in the electrostatic spraying process.

### Theoretical Limitations

In the technical approaches described below for imparting droplet charge  $q_p$ , their levels of performance can be ascertained by comparison with theoretical limits on the maximum charge which can exist on an isolated particulate. Two such limits are established by: (a) dielectric breakdown of the air at the highly curved surface of the charged solid or liquid particulate with subsequent gaseous discharge, *i.e.*, the ion emission limit; and (b) hydrodynamic instability due to electrical forces active within the periphery of a charged liquid droplet exceeding surface tension forces, with subsequent ejection of appreciable charge and mass, *i.e.*, the Rayleigh limit (7). As seen in Figure 1, the Rayleigh charge limit as calculated by the equation

$$q_{\text{Ral.}} = 8\pi \sqrt{\epsilon_o \Gamma} r_p^{3/2} \quad (2)$$

is dominant for droplets of liquid having surface tension values  $\Gamma$  typical of aqueous and oil-based pesticide sprays. As surface tension ranges to a low value of, say, 20 mN/m for surfactant-laden liquids, the stability limit on droplet charge reduces to approximately 52% of its common value for water ( $\Gamma \approx 72$  mN/m). Thus, for tank preparations of any given pesticide formulation, Equation 2 theoretically establishes the maximum attainable level of chargeability as a function of liquid surface tension.

### Droplet Charging Methods

Field-proven methods for imparting charge  $q_p$  to pesticide sprays are: (a) ionized-field droplet charging of both conductive and non-conductive liquids; (b) electrostatic-induction droplet charging of conductive liquids; and (c) direct electrostatic atomization and charging of non-conductive liquids. When considered in relation to technical requirements of the vastly differing pesticide-application situations encountered in

agriculture, each droplet-charging method possesses its unique advantages as well as disadvantages; they are complementary approaches.

Figure 2 illustrates in concept these droplet-charging methods. Shown in axially symmetrical geometry is a continuous jet J of liquid issuing at a velocity v from a fluid nozzle N and directed toward an outlet end near which a sharply pointed discharge electrode P is located. By interaction of externally applied energy the continuous liquid jet J may be disrupted into discrete airborne droplets within a droplet-production zone Z intermediate in location to the nozzle N and the point P. Coaxial with this jet and zone is a cylindrical electrode C which can influence the electric-field direction and intensity in the neighborhoods of zone Z and point P. By the connection of the conductors L<sub>1</sub>, L<sub>2</sub> and L<sub>3</sub> to various combinations of electrical potential, the three charging methods can be effected as described below.

Ionized Field Droplet Charging. When conductors L<sub>1</sub> and L<sub>2</sub> are grounded and a sufficiently high d.c. potential is applied to conductor L<sub>3</sub>, dielectric breakdown of the air immediately surrounding the metal point P will result. For the cylindrical geometry shown, a self-sustaining corona discharge current will, thus, flow between P and C such that the major portion of the cylindrical gap is occupied by unipolar air ions traveling outward along the radial electric-field lines to the non-ionizing electrode C. Either solid or liquid particulates of diameters larger than approximately 0.5 μm traveling through this ionized-field region can theoretically acquire by ion attachment a saturation charge dependent upon the particulate's dielectric constant K, its surface area, and the electrical characteristics of the corona discharge. (Diffusion-charging theory appropriately applies for particulates smaller than 0.5 μm here, but this size realm is of little consequence for pesticide spray-charging development.) The fraction f of the saturation charge actually attained by the particulate depends upon the residence time t<sub>r</sub>, and the concentration N and mobility k<sub>i</sub> of the ions in the charging field. Ionized-field particulate-charging theory has been developed mathematically (8) and is summarized by the following equations

$$q_p = f \left[ 1 + 2 \frac{K-1}{K+2} \right] 4\pi\epsilon_o E_o r_p^2 \quad (3)$$

$$f = \frac{(Nek_i/4\epsilon_o)t_r}{(Nek_i/4\epsilon_o)t_r + 1} \quad (4)$$

As a practical matter, fractional charge values of f = 0.5 saturation may be imparted in one particle-charging time constant of t<sub>r</sub> = 4ε<sub>o</sub>/Nek<sub>i</sub> typically of several milliseconds duration. For

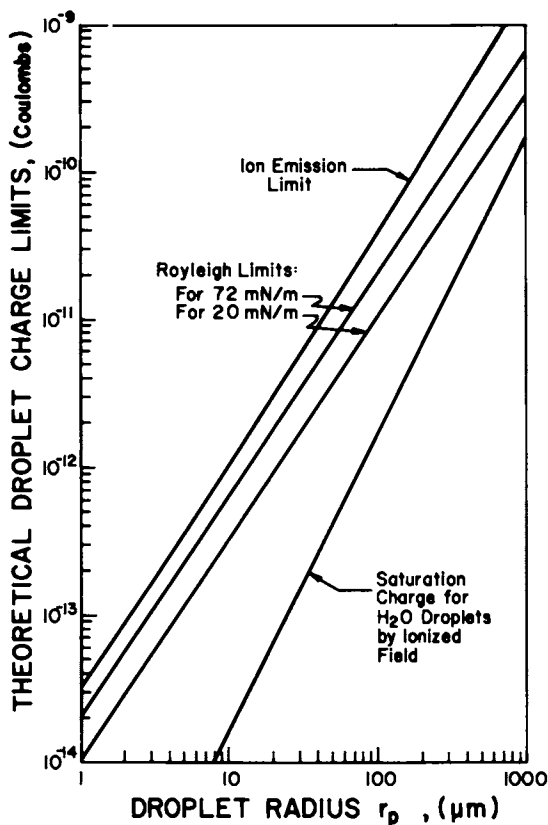


Figure 1. Theoretical charge limits for airborne pesticide droplets as functions of droplet radius and liquid surface tension ( $25^\circ\text{C}$ ).

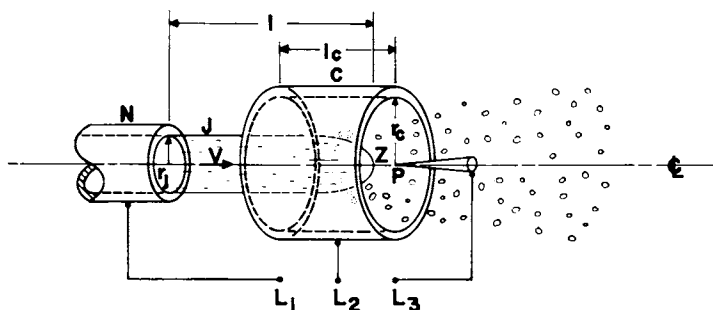


Figure 2. Conceptual representation of spray-droplet charging methods. (Reproduced with permission from Ref. 10. Copyright 1978, American Society of Agricultural Engineers.)

typical corona charging conditions, the magnitude of droplet saturation charge is plotted in Figure 1 as a function of droplet radius  $r_p$  for aqueous spray ( $K = 80$ ).

As far as the physical properties of a pesticide material are concerned in this charging process, the liquid's dielectric constant  $K$  is the main factor which determines droplet charge transfer. The bracketed  $K$  expression in Equation 3 is a measure of the degree to which the ionic charging electric-field lines are concentrated onto the airborne particulates. As seen in Figure 3, the expression ranges in value from approximately 1.5 for good dielectrics such as oils to a maximum value of 3 for conducting particles. Thus, theoretically even droplets of a liquid dielectric material (such as many undiluted pesticide formulations) could be charged at least half as well as highly conductive metallic particles or water droplets by this ionized-field charging process.

Induction Droplet Charging. If the gaseous-discharge electrode is removed and if a positive potential is applied to the cylindrical electrode C in Figure 2 by connection of a voltage source between conductors  $L_1$  and  $L_2$ , then theoretically for any liquid having non-zero electrical conductivity an excess negative charge will accumulate on the grounded liquid jet J. This charge transfer results from the electrostatic induction of electrons onto the axial jet in order to maintain it at ground potential in the presence of the nearby charged cylindrical electrode. Individual droplets formed from the surface of this negatively charged continuous jet will depart with a net negative charge provided that the droplet-formation zone Z is subject to the inducing electric field acting between the cylinder and the jet. Gauss' law indicates that maximum droplet charging should occur for the droplet-production zone located at the region which provides maximum field strength at the terminal surface of the jet.

In theory, the level of droplet charge imparted by the electrostatic-induction process depends heavily upon the relative time rate of charge transfer to the droplet-formation zone as compared with the time required for droplet formation. The charge-transfer capability by conduction from the grounded metal fluid nozzle N through the liquid jet J depends upon the electrical properties of the liquid forming the continuous jet. For the pesticide formulator, this spray-liquid characteristic may be specified by the charge-transfer time constant (9) or charge relaxation time  $\tau$  which is a function of the electrical conductivity  $\sigma$  and the permittivity  $\epsilon$  of the liquid as

$$\tau = \epsilon/\sigma \quad (5)$$

In terms of the spray liquid's dielectric constant  $K$  and resistivity  $\rho$ , this time constant becomes



$$\tau = K \rho \epsilon_0 \quad (6)$$

Theoretically spray liquids having charge-transfer time constants  $\tau$  less than the length of time  $t_f$  which characterizes droplet formation should be compatible with the electrostatic-induction charging process, while liquids having  $\tau > t_f$  could not be satisfactorily charged by this method. For the generalized charger arrangement of Figure 2, the characteristic droplet-formation time is estimated to be approximately 1.6 msec (10). This available charging time is more than  $22 \times 10^3$  longer than the  $\tau \approx 70$  nsec value calculated by Equation 6 for aqueous sprays (e.g.,  $K \approx 80$ ,  $\rho \approx 10^2$  ohm m). A period of five time constants is generally considered adequate to effect greater than 99% of the charge transfer attainable by electrostatic induction for a given spray liquid. Thus, for water-based sprays Figure 4 indicates that charge-transfer limitation (as defined by  $t_f < 5\tau$ ) would be encountered for resistivities of  $\rho > 4.5 \times 10^5$  ohm m. The corresponding value for oil-based sprays (e.g.,  $K \approx 5$ ) would be  $\rho > 7.2 \times 10^6$  ohm m. Spray liquids less resistive than these values should charge satisfactorily by the electrostatic-induction method.

It should be mentioned that it is possible to also effect the electrostatic-induction charging process in a reverse manner to that described above; that is, a negative potential may be directly applied to  $L_1$  while  $L_2$  is grounded to permit the cylinder C to serve as a field intensifying electrode (11). This variation of the electrostatic-induction method necessitates a high degree of isolation of the electrified nozzle and its liquid. However, all other formulation criteria are as previously stated.

Electrostatic Atomization. If the following modifications are made in the apparatus of Figure 2, then electrical forces can be utilized to stress a jet of low-conductivity liquid sufficiently to atomize (and charge) the liquid with no additional energy input (12): (a) remove point P; (b) reduce the length  $\ell_c$  of the earthed field-intensifying electrode C and position it upstream from the droplet-production zone Z; (c) let the jet approach capillary dimensions by reducing jet-orifice radius  $r_j$  or by altering it to an annulus; and (d) apply a high d.c. potential to the liquid jet through  $L_1$ . This device then essentially becomes a 2-electrode electrostatic atomizer appropriate for use with oil formulations. Successful exploitation of this droplet atomization and charging method requires very rigorous specifications regarding the liquid's electrical and viscoelastic properties. For the type spray-charging device described, pesticide-liquid resistivity is generally limited to the fairly narrow  $10^6 - 10^8$  ohm m region of values.

A somewhat more recent approach to electrostatic atomization and charging has been developed for hydrocarbon fuels in various combustion systems (13). This method employs direct charge injection into the continuous stream of hydrocarbon liquid by means of

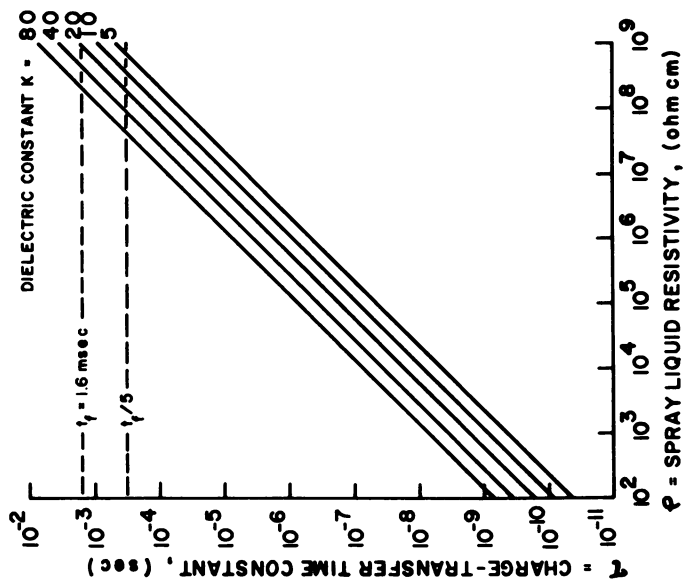


Figure 4. Charge-transfer time constants characterizing spray liquids as functions of liquid electrical resistivity and dielectric constant. (Reproduced with permission from Ref. 10. Copyright 1978, American Society of Agricultural Engineers.)

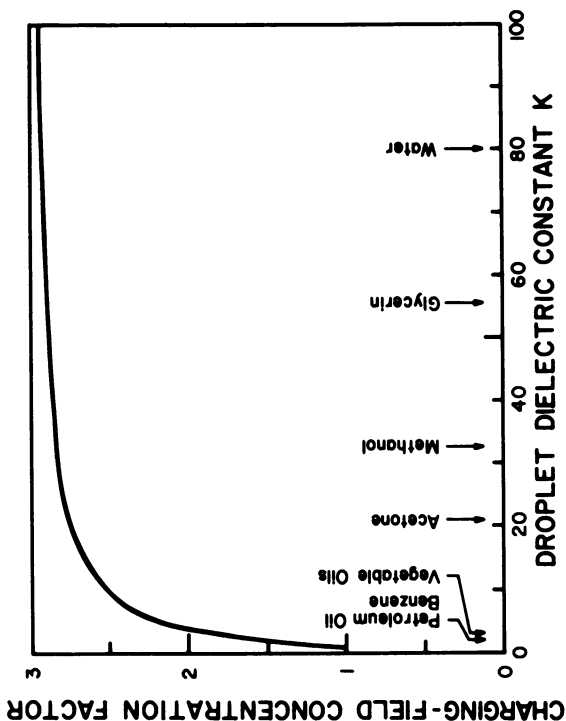


Figure 3. Effect of spray-liquid dielectric constant upon charging-field concentration factor  $\left[ \frac{1+2(K-1)}{K+2} \right]$  associated with ionized-field droplet charging.

a submerged field-emission electron gun incorporating a setaceous electron-emitter surface of  $\frac{1}{2}$   $\mu\text{m}$  tungsten fibers developed in a  $\text{UO}_2$  matrix at an area density of approximately  $4 \times 10^6/\text{cm}^2$ . With this "Spray Triode" class of electrostatic-atomizing device, Kelly (14) reports that spray-liquid electrical conductivity does not fundamentally determine the characteristics of the charged spray subsequently generated, and that theoretically no minimum liquid conductivity limit is associated with the operation of such electrostatic atomizers based upon the direct charge-injection method:

"Universal spray behavior occurs for all fluids having viscosities  $\eta < 1.5 \times 10^{-5} \sqrt{\delta/\Gamma^2}$  and droplet diameters  $d(\mu\text{m}) > 0.1/\Gamma$ . In this spray regime droplet size distribution is narrow ( $\pm 3\mu\text{m}$  about the mean) and scales with liquid density, surface tension and, most sensitively, viscosity. However, the mean (*i.e.*, distribution peak  $d_p$ ) droplet size depends only on the volume charge density  $\rho_e$  of the spray liquid as  $d_p(\mu\text{m}) = 84/\sqrt{\rho_e}$ . All liquids will spray the same, that is they will have the same mean droplet size independent of fluid properties, if they are charged to the same level. For instance, for oils of interest having viscosities less than approximately 200 centipoise, uniform spray charging to  $4 \text{ C/m}^3$  will result in the electrostatic atomization of a  $42 \pm 2\frac{1}{2} \mu\text{m}$  diameter spray."

### Experimental Measurements

For pesticide formulations, dielectric-constant values generally exhibit less than a 40-fold variation. In contrast, electrical resistivity values encountered may range over 10-12 orders of magnitude. Thus, this latter physical property is of prime interest in predicting spray chargeability by the various technical methods other than direct charge injection.

Resistivity measurements were conducted on a number of representative insecticides selected from several major formulation categories as listed in Table I. Readings were taken at room temperature ( $\approx 20^\circ\text{C}$ ) and 1000 Hz using a dip-type conductivity cell ( $0.10 \text{ cm}^{-1}$  constant) operated in conjunction with an auto-balance digital impedance meter. All test liquids were measured at 16 dilution ratios (*i.e.*, distilled water:commercial formulation) ranging from 0:1 to 80:1 on a volume basis.

Figure 5 depicts the typical resistivity response measured as a function of dilution ratio. Maximum values for each material tested were obtained for the undiluted formulation, with minimum values occurring immediately upon small dilutions at ratios of typically 1:2 to 4:1. Additional dilution resulted in a gradual increase in the resistivity of the test liquids. It appears that initial dilution with the distilled water caused molecular

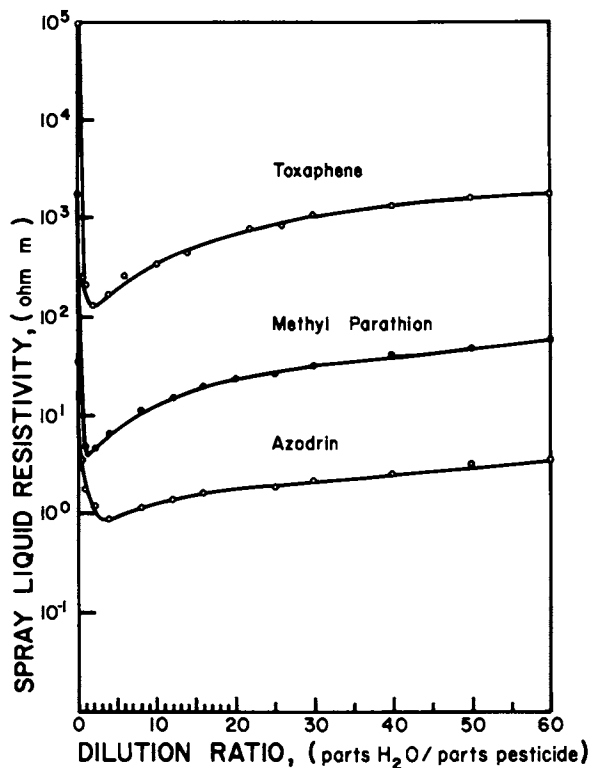


Figure 5. Electrical resistivity measurements for selected insecticide formulations as a function of aqueous dilution (1000 Hz, 20°C).

Table I. Electrical resistivity characteristics of representative insecticide formulations at stated dilutions.†

Type insecticide	Active ingredient	Electrical resistivity values $\rho$ , (ohm m @ 1000 Hz)				
		Max. $\rho$ @0:1	min. $\rho$ @ 4:1	$\rho$ @12:1	$\rho$ @20:1	$\rho$ @80:1
Azodrin	55%	38	0.99 @ 4:1	1.34	1.70	4.59
Methyl parathion	45%	$1.70 \times 10^3$	4.2 @ 1:1	15.3	23.4	74.6
Malathion	56%	$5.60 \times 10^4$	8.0 @ 4:1	14.0	21.0	53.0
Guthion	22%	$6.20 \times 10^4$	18.1 @ 1:1	44.0	73.0	187
Toxaphene	59%	$1.28 \times 10^5$	130 @ 2:1	400	715	2240
Pydrin	2.4 E	$2.10 \times 10^4$	48.3 @ 1:1	166	195	395
Lannate	1.8 E	$1.55 \times 10^4$	19.8 @ 1:2	92.2	133	400
Lorsban	4.0 E	$1.13 \times 10^4$	14.2 @ 1:1	76.3	92.9	222
Ambush	2 E	$2.37 \times 10^4$	23.6 @ 1:2	96.8	129	306

† Vol.:Vol. dilutions of (distilled H<sub>2</sub>O:commercial insecticide formulation) at 20°C.

dissociation of certain constituents of the pesticide formulation which increased the charge carrier population of the test liquid. Increased dilutions may have merely reduced the numerical density of these introduced charge carriers.

Table I summarizes the experimentally determined resistivity characteristics for the nine formulations investigated. On the basis of Equation 6 and these data, a high degree of spray chargeability by the electrostatic induction process could be predicted for all the pesticide samples tested. For these particular pesticide formulations, laboratory spray tests confirmed excellent droplet charging to greater than 10 mC/kg. Similar electrical resistivity measurements will serve as a suitable predictor of the chargeability of other formulations of interest in the electrostatic pesticide-spraying process.

### Acknowledgments

The contribution of unpublished material related to direct charge injection of hydrocarbon liquids by Arnold J. Kelly, Department of Mechanical and Aerospace Engineering, Princeton University is gratefully acknowledged.

### Legend of Symbols

$E$	= electric field strength, V/m
$E_o$	= corona-discharge field strength, V/m
$e$	= electronic charge = $1.60 \times 10^{-19}$ C
$F_p$	= electric force on charged particulate, N
$f$	= fractional charge attained, unitless
$K$	= particulate dielectric constant, unitless
$k_i$	= charging-ion mobility, $m^2/Vs$
$N$	= charging-ion concentration, ions/ $m^3$
$q_p$	= particulate charge, C
$q_{Ral.}$	= Rayleigh limit on droplet charge, C
$r_p$	= particulate radius, m
$t_f$	= droplet formation time, s
$t_r$	= charging residence time, s
$\Gamma$	= spray-liquid surface tension, N/m
$\delta$	= liquid density, $kg/m^3$
$\epsilon$	= spray-liquid electrical permittivity, $C^2/Nm^2$
$\epsilon_o$	= permittivity of air $\approx 8.85 \times 10^{-12}$ $C^2/Nm^2$
$\eta$	= liquid viscosity, $kg/m \cdot s$

- $\rho$  = spray-liquid electrical resistivity, ohm m  
 $\rho_e$  = volume charge density in liquid, C/m<sup>3</sup>  
 $\sigma$  = spray-liquid electrical conductivity, mho/m  
 $\tau$  = spray-liquid charge-relaxation time, s

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## Compatibility and Tank-Mix Testing of Pesticides

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The suitability of a newly developed agrichemical formulation for use in existing agrichemical application equipment is a critical parameter in the market acceptance of the new product. This suitability is more critical, and more difficult to determine, in those cases when two or more herbicides are combined in the spray tank (i.e., a tank mix).

Static laboratory tests and dynamic laboratory methods, with the formulation alone and in combination with other pesticides, may be used to predict compatibility or to identify potential problems. These data may then be related to testing in actual field application equipment. Due to the differences in application equipment and in actual use practices, these data are not absolute but are predictive and are most useful in avoiding problems in the field.

The acceptance by a user of a new pesticide formulation is determined by several factors:

1. The efficacy of the product (for example, as a herbicide),
2. The cost of the product, and
3. The handling properties of the formulation in the field. Examples of handling properties are the amount of dust in the product (in the case of dry formulations), the manner in which the product dilutes with water (or other carrier liquid), the way in which the product sprays through an agricultural spraying system, and the manner in which the product will tank mix with other pesticide formulations.

This paper is addressed to this last concern.

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There are two principal reasons for tank mixing pesticides:

- 1) By using two or more pesticides, the farmer can obtain a spectrum of activity unavailable with a single product, and
- 2) By combining two or more pesticides into a single application tank, the user can avoid several trips across the field and thereby make savings in both time and money. Pesticide tank mix applications were the subject of a symposium in 1980 (1).

Formulation scientists usually formulate their product to be used alone in water. The potential of tank mixes or the use of liquid fertilizers as a carrier liquid is considered later in the formulation development process. Obviously, the environment a formulation will encounter in use is very different when it is mixed with one or more agrichemicals as compared to the formulation being mixed in pure water. Rather than having one active ingredient present with surfactants carefully selected to disperse that formulation, two or three active materials with six or eight different surfactants may be present in the spray tank. No wonder there are incompatibilities!

Incompatibility of pesticides when tank mixed can cause substantial problems. There are two potential types of incompatibility:

1. Chemical Incompatibility in which formulations react chemically with each other. An example of this type of incompatibility is when two active ingredients, which are organic materials, react with each other. Another example would be if two surfactants react with each other. Incompatibilities of this sort are rare. If this occurs, there is little one can do to avoid the problem short of totally reformulating the product.
2. Physical Incompatibility in which the formulations form sediment, agglomerates, or oily material and cannot be delivered by the sprayer. This can cause several problems:
  - a. Lack of weed control or areas of crop phytotoxicity because the pesticide has not been delivered uniformly to the site of action.
  - b. Clogging of the spray equipment (which is troublesome to the user).

The second type of incompatibility described, physical incompatibility, may be more difficult to determine, due to the time required for incompatibility to become obvious. Often several hours, overnight standing, or repeated tanks of a mixture are necessary before problems are apparent.

Physical incompatibilities when different types of formulations are tank mixed are often a particular problem. An example is a tank mix of an emulsifiable concentrate with a wettable powder. Another example is an emulsifiable concentrate mixed with an aqueous suspension (or a flowable). In these mixtures the solvent in the emulsifiable concentrate will "gather" the wettable powder product and form oily agglomerates. The reason for this may be the solid surfactant

in the wettable powder formulation allowing the organic solvent to wet the wettable powder. This can result in the wettable powder being "waterproofed" by a layer of organic solvent. Once these agglomerates are formed, it is almost impossible to cause them to disperse. When using different types of formulations, the order of addition of the products to the spray tank may be critical to obtaining a useful mixture. The order of addition of the products may actually determine whether or not a tank mix is useful. One suggested order of addition is:

1. First, dry flowables (or water dispersible granules) then
2. Wettable powders then
3. Aqueous suspensions (or flowables) then
4. Solutions and finally
5. Emulsifiable concentrates

This order of addition usually minimizes the potential of incompatibilities by allowing each formulation to be fully dispersed in water before the next formulation is added. Dry flowables are added first so that the product can be fully dispersed to the primary particle size before the next formulation is added. Wettable powders and aqueous suspensions follow in sequence and must be fully dispersed prior to addition of solvents. Emulsifiable concentrates are added last so that the solvent has the least possible chance of contacting clumps of unwetted solid organic material from the powder formulations.

Occurrence of physical incompatibility and the magnitude of the problem is also dependent on the type of spray equipment and the duration of spraying. For example, some tank mixes which may form an oily residue or a light precipitate under static conditions may be applied with sprayers having vigorous agitation systems. Another example is that certain mixtures, which form a residue upon standing, may be applied if the mixture is prepared and then sprayed quickly.

This spring Elanco Products Company (a Division of Eli Lilly and Company) introduced a 60% dry flowable (or water dispersible granule) formulation of BALAN. BALAN is a preemergence, dinitroaniline herbicide used on peanuts and lettuce. BALAN Dry Flowable is an addition to formulations of BALAN which are produced and sold by Elanco. BALAN LC, a 1.5 lb/gal emulsifiable concentrate which has been on the market for several years, is often tank mixed with several other agrichemicals. Therefore, it was critical to evaluate this new product form for tank mix performance with all agrichemicals with which it could be tank mixed.

This paper describes three different types of testing completed with BALAN Dry Flowable as an example of the type of testing which may be necessary: A) testing under static conditions, B) testing in a spray-rig simulator, and C) testing in actual spray rigs. Other company's products were evaluated

as tank mixes with BALAN Dry Flowable. However, the products are not identified. They will only be referred to as formulation types.

### Compatibility Testing Under Static Conditions

This evaluation allows the formulations to be mixed at the actual use rate in either water or liquid fertilizers. It is simple to run, involves no special equipment, allows observation of the nature of any incompatibilities which form, and is a long enough test that the formation of incompatibilities after different periods of time may be determined. A disadvantage is that the evaluations are done under static conditions and, therefore, do not simulate the continuous mixing of a herbicide spray rig.

Evaluations with Water as the Carrier Liquid. The BALAN Dry Flowable was first dispersed in water (328 ppm hardness with iron), the other chemical was added next, and the mixture agitated. After the mixture was allowed to stand at room temperature overnight, three types of observations were made.

- a. Evidence of flocculation, agglomeration, crystallization, or sedimentation (determined by visual examination).
- b. Ease of resuspension - determined by measuring the number of inversions necessary to resuspend any sediment.
- c. The particle size of any sediment - determined by filtering the mixture through wire screens of 50-, 100-, and 325-mesh size. The 50- and 100-mesh screens are used because these are the smallest mesh sizes which would be used in spray rigs. The 325-mesh screen is used to obtain all sediment which has formed.

Each sample was evaluated at recommended field use dilutions for both the herbicides and carrier liquid. Table I gives the number of inversions necessary to resuspend the mixtures after standing for 20 hours. These data indicate that no sediment was formed which would not resuspend. Table II gives the data for material retained on 50-, 100-, and 325-mesh screens, as well as the average percent solids retained.

Table I. Physical Compatibility of BALAN Dry Flowable with  
with Several Registered Commercial Herbicides

Formulation	Number of Inversions to Resuspend after 20 Hours		
	R1	R2	R3
BALAN DF Alone	3	3	3
BALAN DF + a Wettable Powder	9	9	9
BALAN DF + EC A	7	5	5
BALAN DF + EC B	3	3	2
BALAN DF + EC C	5	6	6
BALAN DF + EC D	3	4	4

R = Replicate

EC = emulsifiable concentrate

Table II. Physical Compatibility of BALAN Dry Flowable with  
Several Registered Commercial Herbicides

Formulation	Retained on Screens Avg of 3 Reps, g			Average Percent Retained
	50	100	325	
BALAN DF Alone	tr	tr	0.13	2.9
BALAN DF + a Wettable Powder	0	tr	0.03	0.3
BALAN DF + EC A	tr	tr	0.33	2.2
BALAN DF + EC B	0	0	tr	0.0
BALAN DF + EC C	tr	tr	0.06	1.1
BALAN DF + EC D	tr	tr	0.30	5.2

tr = Trace

Based on these data, BALAN Dry Flowable appears to be compatible with each of the agrichemicals with which it may be tank mixed, since there was little residue retained on the 50-, 100-, and 325-mesh screens.

#### Evaluations with Liquid Fertilizer as the Carrier Liquid.

Liquid fertilizers are often used as the carrier liquid to apply BALAN and also BALAN tank mixes.

In this evaluation, BALAN Dry Flowable was dispersed in the liquid fertilizer. If a compatibility agent was used, it was added next. This allows the compatibility agent, which is a strong surfactant, to be dispersed in the liquid fertilizer before the next product is added. The agent was added at a rate equivalent to 2 pt/ton. If the compatibility of BALAN Dry Flowable with another herbicide in liquid fertilizer was evaluated, that herbicide was added next. Of course, a compatibility agent is used in the field only when necessary. Therefore, one tests these agents only if they are required to provide a uniform mixture. A compatibility agent functions by providing extra surfactant capability. The strong ionic nature of liquid fertilizers may actually deactivate the surfactants which are present in the formulation. Also, pesticide formulations are usually developed to disperse in pure water. The ionic nature of a liquid fertilizer is much different, and therefore, more surfactant (and possibly more effective surfactants) are required.

The observations made were: 1) the uniformity of the mixture after certain time intervals and 2) the number of inversions required to resuspend the settled material. This gives an indication of the utility of a mixture after being left in a spray tank for an extended period of time. These data are given in Tables III and IV. These data indicate that BALAN Dry Flowable is compatible with the three liquid fertilizers tested and that no compatibility agent is required when BALAN Dry Flowable is used alone. In the case of tank mixes with other herbicides, the compatibility agents sometimes increase the uniformity of the mixture. For an example, see BALAN/Emulsifiable Concentrate D with and without Compatt (Table IV).

Table III. Compatibility of BALAN Dry Flowable in Liquid Fertilizers

Product	Observations			Number of Inversions After 20 hr
	15 m	After		
		2 hr	20 hr	
BALAN DF in 10-34-0	U	F	F	1
BALAN DF in 3-9-12	F	F	F	5
BALAN DF in 3-10-30	U	F	F	1

U = uniform mixture, F = Flocc, a flocculent mass formed by the aggregation of a number of fine suspended particles.

Table IV. Tank Mix Compatibility of BALAN Dry Flowable with Herbicide D in Liquid Fertilizers

Product	Fertilizer, 10-34-0			Number of Inversions After 20 hr
	Observations			
	15 m	After		
		2 hr	20 hr	
BALAN + EC D	U	F	F	1
BALAN + EC D, Sponto 168D	U	F	F	1
BALAN + EC D, Spraymate	U	O	O	3
BALAN + EC D, Unite	U	F	F	3
BALAN + EC D, T-Mulz 734-2	U	U	U	1
BALAN + EC D, Compatt	U	U	U	1
BALAN + EC D, Kem Link	U	U	U	1

U = Uniform mixture, O = Oil ring, F = Flocc, a flocculent mass formed by the aggregation of a number of fine suspended particles.

Compatibility agents are often a problem to identify and test. There are many different products available and many are regional brands available only in limited areas. The best approach is usually to test only the major brands of compatibility agents unless a regional product use pattern is likely.

### Testing in a Spray-Rig Simulator

This evaluation allows the product to be evaluated under dynamic conditions similar to actual spray equipment. It is simple to run and does not involve special equipment which allows evaluations to be run under a variety of conditions. For example, different agitation systems, spray nozzles, screens, and pumps may be evaluated.

For this testing, a spray rig simulator was equipped with a centrifugal pump operating at 30 psig. The agitation system was either a sparger pipe or a jet agitator. A sparger is a pipe or hose with small holes drilled along its length and installed lengthwise in the tank. This offers the advantage of providing agitation over the entire length of the tank. A jet agitator is a restricted orifice device which is fitted in the bottom of the spray tank. As spray solution is pumped through the restricted orifice, the high pressure jet of moving solution provides agitation. The jet agitator is usually installed so that the jet of solution moves down the length of the tank.

When tank mixes were evaluated, the BALAN Dry Flowable was first dispersed in the spray water (328 ppm hardness with iron) and then the other product was added. Table V describes the details of testing at a rate of 2.5 lb/acre at 20 gal/acre with sparger-pipe agitation. After four repetitive evaluations in which the contents were sprayed out and in which there was no clean out between tankfuls, the screens were clear and there was no residue in the bottom of the tank. The system was not cleaned out between runs to better simulate continuous spraying in actual use. Table V also describes the same type of evaluation with a jet agitator rather than a sparger pipe. This resulted in little residue in the in-line screens and none on the bottom of the tank.

The product was also tested with both sparger pipe and jet agitation at a rate of 5 gal/acre (Table VI). These conditions resulted in some residue but the herbicide did spray satisfactorily. Obviously, more vigorous agitation would more fully suspend the product and would result in less residue.

Table V. Spray Rig Simulator Testing of BALAN Dry Flowable  
(2.5 lb/acre at 20 gal/acre)

Run Number	Type of Agitation and Percent of Tank Volume*	Screens		Tank Residue	Suitable for Use
		Primary	Secondary		
1	Sparger (10.8 <sup>0</sup> /o)	Not observed		Not observed	--
2	" "	Not observed		Not observed	--
3	" "	Not observed		Not observed	--
4	" "	Clear	Clear	Clean	Yes
1	Jet (10.6 <sup>0</sup> /o)	Not observed		Not observed	--
2	" "	Not observed		Not observed	--
3	" "	Clear	Clear	Clean	Yes

\*Percent of tank volume recirculated through the agitator.

Table VI. Spray Rig Simulator Testing of BALAN Dry Flowable  
(2.5 lb/acre at 5 gal/acre)

Type of Agitation and Percent of Tank Volume	Screens		Tank Residue	Suitable for Use
	Primary	Secondary		
Sparger (10.8 <sup>0</sup> /o)	Slight residue	Clear	Slight residue	Yes
Jet (10.6 <sup>0</sup> /o)	Residue	Clear	Clean	Yes



When BALAN/Emulsifiable Concentrate D tank mix was tested at a rate of 5 gal/acre, the system was unsuitable for application (Table VII). However, when the spray volume was increased to 10 gal/acre, the tank mix was compatible. As a result, the the BALAN Dry Flowable label recommends that tank mixes be applied at a minimum of 10 gallons/acre.

Table VII. Spray Rig Simulator Testing of BALAN Dry Flowable with Herbicide D (2.5 lb with 3.0 pt/acre)

Gal/ Acre	Type of Agitation and Percent of Tank Volume	Screens		Tank Residue	Suit- able for Use
		Primary Floc	Secondary Floc		
5	Sparger (10.8 <sup>o</sup> /o)			Floc	No
10	Sparger (10.8 <sup>o</sup> /o)	Slight residue		Slight residue	Yes

When tank mixes of two products are evaluated, and when each of the products require a different volume of spray solution when the product is used alone, it is usually necessary to use the larger volume of the two. For example, the label for Emulsifiable Concentrate D requires a 10 gallon/acre rate for the product when used alone. Therefore, it is rather unlikely that a tank mix would be satisfactory at a 5 gallon/acre rate.

#### Testing in Actual Spray Rigs

The final stage of testing BALAN Dry Flowable involved testing the product in a series of actual commercial spray equipment. The advantage of this type of evaluation is that it is the most realistic testing possible since this type of equipment will be used to apply the commercial product. The disadvantages are that substantial quantities of waste material are generated. Also, since each spray rig is a complete, separate system, there is little flexibility to test under different conditions. The variables included tank volume (from 30 to 1,000 gallons), types of pump (both roller and centrifugal), and type and level of agitation. Both BALAN Dry Flowable alone as well as potential tank mixes were evaluated. The results of this testing indicate that BALAN Dry Flowable will perform very well under a variety of conditions.

The spray rig testing resulted in the use directions which are now part of the BALAN Dry Flowable label: Fill the tank three-fourths full with clean water. Start agitation and increase pump speed to operating pressure. Add BALAN Dry Flowable, then add other dry flowables, wettable powders (WP), aqueous suspensions (AS), flowables (F), liquids (L), solutions (S), and emulsifiable or liquid concentrates (EC or LC) in this order to the water and agitate continuously until the product(s) are completely dispersed in the water.

Maintain agitation from filling through application. If spraying and agitation must be stopped before the tank is empty, the materials may settle to the bottom. In this case, it is important to suspend again all of the material in the bottom of the tank before continuing the spray application. Sometimes it is more difficult to resuspend settled material than it is to suspend it originally. A sparger agitator is particularly useful for this purpose.

### Summary

Three types of testing have been described:

1. Static Testing - This test is simple to run. The disadvantage is that since it is a static test, it avoids the dynamics of an actual spray rig. This test is very reproducible and is an excellent means of predicting incompatibilities.
2. Spray Rig Simulator - This test is rather simple to run. It does allow testing with different agitation systems. It simulates rather well the results obtained in actual spray rigs.
3. Actual Spray Rigs - This is the most realistic testing possible. It is not too flexible since each spray rig is a separate system. Testing of this sort will demonstrate most problems which a new formulation will have in field use.

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