Pesticidal Formulations Research

Physical and Colloidal Chemical Aspects

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

The formulation of organic pesticides is a young science, slightly more than two decades old. In any young science, the initial rapid advances come easily, by trial and error, as one finds combinations of ingredients that do the job. As a science matures, however, the "Edisonian approach" reaches the point of diminishing returns, and one must resort to more theoretical in-depth research. One must determine the physical variables that affect research results and determine the interrelationships among these variables.

According to Glasstone (*1*), "chemistry may be said to deal with matter and its transformations, whereas physics is concerned with energy and its transformations. It is clearly not possible to draw a sharp distinction between the two points of view for many problems in both physics and chemistry are concerned with interactions between energy and matter; it is these problems which constitute the fundamental basis of the subject of physical chemistry."

Weiser (*2*) states that "a colloidal system is a heterogeneous or dispersed system of at least two phases, one of which, a finely divided or dispersed phase, is more or less uniformly distributed in a continuous phase." Colloidal chemistry constitutes a study of the "colloidal system."

As the formulation chemist studies the "physical variables that affect the results of his research," he finds that the fundamental tools of colloidal and physical chemistry aid in the understanding and in the organization of his research.

The word "aspects" is intentionally used in the title of this book because of the broadness it allows in the subject matter. It allows a discussion of principles such as in Chapter 20. Here the principles have been established, and reference has been made to their possible utilization in determining the critical surface tension of an insect. Perhaps this paper will stimulate workers to do obvious research which could yield data explaining the specificity in control of various insects. The word aspects also allows a discussion of the direct use of these physicochemical principles to solve formulation problems such as the paper by Freed and Witt on the translocation of herbicides in plants. Thirdly, this symposium contains papers dealing with phenomena that clearly are physical and colloidal but which have not as yet been the subject of rigorous physical chemical studies. For example, in Lyon's paper the effect of varying crystal size is shown to be very important in controlling insects. Factors affecting these changes in crystal size are given. This paper could form an excellent base for a continued physicochemical study of the physical phenomena involved.

The purpose of this volume is to stimulate the further use of physical and colloidal chemical principles in this fledgling science called formulations research. It is hoped that the subject matter presented will open new approaches to pesticidal formulations research.

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St. Paul, Minn.
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J. W. VAN VALKENBURG

The Physical and Colloidal Chemical Aspects of Pesticidal Formulations Research: A Challenge

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The pesticidal formulations chemist combines inert ingredients with the active organic pesticide to make a composition that is easy to use, active, stable, and free of undesirable side effects. To accomplish this, the chemist studies the physical properties of the toxicant, reactivity of "inerts," performance of the formulation in application equipment, interaction of spray with the target, and final fate of the composition in the environment. Interaction of inert clays with pesticides may be studied by differential thermal analysis, acid strengths, and infrared analysis. Emulsifiable concentrates are best studied by investigating the physical properties of the emulsifier. Hydrophile–lipophile balance and micellization behavior are important. The penetration and translocation of herbicial sprays may be understood better by studying the passage of the active ingredient through semipermeable membranes.

To understand the physical and colloidal chemical aspects of pesticidal formulations research, one must first understand the objectives of the formulations chemist in his work. Simply speaking, the formulations chemist must take the pure organic chemical pesticide and put it in a usable form for field use. These forms include wettable powders, emulsifiable concentrates, dusts, granules, water-soluble concentrates, flowables, and an aerosol, to name a few types of concentrates. The formulations chemist desires to put together a formulation that (1) is easy and eco-

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nomical to use, (2) does the job that the label says it will do, (3) has adequate shelf life, and (4) has no undesirable side effects. In all of these objectives he keeps the consumer in mind.

The formulations chemist is concerned with the total system involving all that happens to the pesticide from the day it is synthesized to the day it does its ultimate job for the customer. Considering this total system, here are a few factors of concern.

When the chemist first receives a toxicant for formulation, a determination of the following physical properties will be of material aid to his studies: (a) melting point or boiling point, (b) rate of hydrolysis, (c) vapor pressure, (d) specific gravity, (e) solubility, (f) ultraviolet degradation, and (g) inherent biological activity.

Once these physical properties are determined, the chemist can then select the inert ingredients to be compounded with the toxicant. Once these ingredients are selected, the chemist is concerned with possible interactions which occur, including (a) compatibility of ingredients, (b) compatibility with container, and (c) physical properties of composition.

When the proper inert ingredients are selected and they are compatible with the system and have desirable physical properties, the chemist then considers the behavior of the composition in an actual spray situation. Here he is concerned with (a) homogeneity of spray solution, (b) foaming properties, (c) viscosity of spray solution, and, (d) particle size of spray droplets.

If the formulation performs satisfactorily in spray equipment, one is concerned with the way in which the spray interacts with the pest to be controlled, particularly with (a) percent retention on foliage, animals, and insects, including bouncing and wetting, (b) residual nature of sprays, (c) penetration and translocation, (d) crystal size of deposit, (e) control of the pest, and (f) site and mode of action.

Once a pesticide does its job, the toxicant doesn't immediately disappear but becomes a factor in the environment. Hence, the chemist must be concerned with the ultimate fate of this material in relation to drift, residual nature in soil, residue in run-off water, and effect on food chain.

To solve these problems the formulations chemist must have a good grasp of physical and colloid chemistry. He must use many of the theories and principles that are the foundation of physical and colloidal chemistry.

It is impossible here to point out all the areas where physical and colloidal chemistry have been used by the pesticidal formulations chemist. However, to illustrate this point, three problems will be discussed which are being resolved by using sound physical chemical principles. These include:

(1) The compatibility of clays with pesticides.
(2) The selection of emulsifiers for emulsifiable concentrates.
(3) The penetration and translocation of herbicidal solutions.

Compatibility of Clays with Pesticides

Examples of the use of physical and colloidal chemical principles are involved in studies on the compatibility of pesticides with clays. Many pesticides are catalytically decomposed by clays.

Walling (*11*) and Benesi (*1*) suggested a method of measuring the acid strength of a solid clay surface. They utilized a basic dye which adsorbed on the acid sites. By studying the color of several dyes of different basicity, they could ascertain the acid strength.

Malina *et al.* (*8*) used this principle in studying the stability of heptachlor, a chlorinated hydrocarbon, on several clays. Heptachlor was catalytically decomposed by acid clays with a pK_a of 1 or less and was stable on clays with a pK_a of approximately 3.3. When diethylene glycol was added to the clay at a concentration of 3-8 wt. %, the pK_a of acid clays was raised to 3.3. The resulting mixture did not break down heptachlor.

Yaffe (*12*) extended Malina's work to a study of stabilization of formulations of 2-(*p-tert*-butylphenoxy)-1-methylethyl-2-chloroethyl sulfite (Aramite). Moisture, pH, temperature, and type of diluent are factors that affect the rate of decomposition. Glycols with two or more free hydroxyl groups were effective stabilizers.

The shelf life of a thiophosphate—malathion—was studied by Yost (*13*). The most stable formulations were on nonabsorptive clays.

Fowkes *et al.* (*3*) brought more physical chemistry into this type of investigation. They measured acid strengths and reaction rates by differential thermal analysis. They found that the chlorinated hydrocarbons —dieldrin and endrin—when mixed with clays, decomposed at a fixed rate independent of concentration. Thus, a zero-order reaction is indicated.

They also studied decomposition rates at several different temperatures. These data were fitted into the Arrhenius equation with an excellent correlation (half-life in minutes was plotted against $1000/T$ in °K.). The slope of the lines is $E/2.303R$, where E is the activation energy. Stabilizers were shown to raise this activation energy. This is not surprising in that a stabilizer actually physically separates the toxicant from the catalytic site.

All these studies found that moisture affects the rate of decomposition of pesticides. Rosenfield (*9*) studied this more thoroughly by heat treating bentonite to various temperatures. Treatment at 300°C. drove off all the free water. The clay had great acid strength and severely decomposed ronnel, a thiophosphate. As the clay was heated to a higher temperature, bound water was released, and the clay structure began to collapse. Acid strength decreased as well as catalytic activity. Ronnel was very stable on bentonite and other clays previously heat treated at 950°C. The slight decomposition which did occur at room temperature on bentonite treated at 950°C. was entirely different. Ronnel underwent an acid catalyzed molecular rearrangement instead of a normal hydrolysis reaction.

Physical and colloidal chemical principles are being used to study catalytic breakdown of pesticides on clays. However, there is much more to be learned by applying these principles further.

Selection of Emulsifiers

An emulsifiable concentrate consists of a toxicant, a solvent or solvents, and a blend of emulsifiers. Physical chemistry is involved in the selection of these emulsifiers.

An emulsifier system must cause the concentrate to disperse spontaneously into small, stable droplets when mixed with water. To accomplish this, the surfactant system must have a most favorable solubility relationship: a proper balance between oil and water solubility or, in other words, a favorable hydrophile-lipophile balance in solubility. This balance in solubility is frequently referred to as HLB and was first described by Griffin (*6*). However, the HLB system is based on the structure of a surfactant molecule and, therefore, predicts the behavior of a single molecule. It does not take into account the fact that many surfactants form micelles in organic solutions. If a micelle is formed, its HLB may have no relationship to the HLB of the monomer unit. Therefore, to select an emulsifier well, we will need a better understanding of the behavior of surfactants in organic solvents.

Little and Singleterry (*7*) have published an interesting study on micellization of surfactants in a variety of solvents. Their data show that the better the solvent is for the surfactant, the less tendency there is for the surfactant to form aggregates or micelles. Yet to be determined is the effect of this micellization on emulsification properties.

Penetration and Translocation of Herbicidal Sprays

Government, university, and industrial research organizations are continually looking for ways and means to make herbicides more effective so that dosage rates can be reduced. Hence, considerable effort has been expended on the use of surfactants to optimize the activity of herbicides.

The word "optimize" is purposely used here. Herbicides have a certain level of innate activity. Adjuvants do not increase this activity but merely aid in the movement of an herbicide to an area or region of a plant where the herbicide will do the most good. It has clearly been established that surfactants do increase the apparent activity of herbicides (*2, 4, 5, 10*). The cause of this increase, however, is incompletely understood. Indeed, there may not be a simple explanation of the observed phenomenon. The answer may actually be a complex interaction of the various components.

The components in a simple penetration experiment consist of a surfactant, water-soluble herbicide, and water. Since the surfactant is at a concentration of 0.5 to 1%, it interacts with water and forms micelles. Since micelles are formed, these could solubilize some of the herbicide inside the micelle. Now we have five components, (1) water, (2) surfactant monomer, (3) surfactant micelle, (4) micelle with solubilized herbicide, and (5) an herbicide in anhydrous or hydrated form which all come in contact with the plant. Which one or more of these components has the greatest effect on the plant? Before a thorough understanding of this phenomenon can be achieved, the interaction of each of these components with a plant must be investigated separately, and perhaps the plant is too complex for initial study. Perhaps a homogeneous semipermeable membrane could be used instead.

An interesting study might be the effects of an aqueous solution of surfactant at various concentrations on osmotic pressure through a semipermeable membrane. Then, one could add a water-soluble herbicide and note how this osmotic pressure is varied. Perhaps changes of membrane porosity as affected by a surfactant could be measured with one of the new high resolution electron microscopes. Perhaps electrical resistance across semipermeable membranes could be measured. Perhaps a study of permeability affected by changes in micellar size as caused by salts and traces of polar organic solvents would be interesting.

The answers to the problems outlined here lie in the further utilization of sound physical and colloidal chemical principles. Therein lies the challenge.

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Rapid Estimation of the Critical Surface Tension of Fibers

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The theory of the flotation of a fiber-shaped solid by a liquid of lower density is presented in detail. Within the usual range of fiber diameters and densities, provided the cross section shows no protruding cusps, a very small positive contact angle is sufficient to float the fiber. If the contact angle is zero, the fiber will sink. The critical surface tension (CST) of a fiber surface can therefore be estimated by placing samples of the fiber on a series of liquids of progressively increasing surface tensions. The CST lies between the surface tensions of the liquid in which the fiber just sinks and the liquid in which it just floats. Agreement with the classical method is excellent.

Knowledge of the critical surface tension (CST) of a fiber is of great interest. This parameter is an index of the surface energy of the fiber and thus indicates the nature of the surface. Its numerical value is of practical concern in that it enables one to predict, on the basis of their surface tensions, which liquids or solutions are capable of spreading on an isolated fiber surface. The classical procedure for determining the CST of a solid surface (*5*) consists in measuring the contact angle (θ) of several liquids of different surface tension (γ), preferably from a homologous series, against the surface of interest. The extrapolation of the plot of γ *vs.* cos θ to cos $\theta = 1$ yields the CST—*i.e.*, the surface tension of the liquid which will just spread on the surface. Though such measurements have been made on fibers in this laboratory (*4*) and elsewhere (*2*), the procedure is time consuming, demands considerable skill, and is limited in its application. Very small liquid drops have to be used, placed carefully on the fiber, and observed under high power magnification. The

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microscopic drop size restricts the range of useful liquids to those of low volatility. Fiber surface roughness makes precise measurement of the contact angle difficult.

We now report a simple procedure for rapidly determining the CST of fibers with a relatively high degree of precision. This method can also be used to determine the CST of any material that can be uniformly coated onto a fiber substrate. It consists of placing small fiber snippets on a series of liquids graded with regard to surface tension, and observing whether the fibers sink or float. If the CST of the fiber is less than the surface tension of the test liquid, it will float owing to surface tension forces (just as an oily razor blade floats on the surface of water). If the CST of the fiber is greater than the surface tension of the liquid, it will be completely wetted by the liquid and will sink, provided the fiber is denser than the liquid. The test liquids, of course, must have densities less than that of the fiber.

It is important that individual fibers be used rather than yarns, batts, or fabrics. Such assemblages of fibers interact with liquids by wicking, a phenomenon which depends as much on geometrical factors as on the CST of the fiber surface. The present method is thus sharply distinguished from those utilizing fiber assemblages (*1*, *3*).

Experimental and Results

To establish the validity of this method for measuring CST, a series of fibers was prepared, and the CST of each was determined as described above. Snippets (*ca.* 1 cm. long) were carefully placed, by tweezers, one at a time, on the surface of the various test liquids contained in shallow glass dishes. Good replication was obtained among fiber samples of the same type. In no instance did any sample sink in a test liquid of higher surface tension than the test liquid which floated its duplicate. In a few instances some replicate fiber samples would sink and some would float in the same test liquid, indicating that the samples differed slightly in CST and that the surface tension of the test liquid was essentially equal to the average CST of the samples.

The fibers used in this study, and their properties, are listed in Table I. The fibers were all in the monofilament rather than the spinning fiber size range. Virgin hair from a caucasian human scalp was used. The HClO treatment was of interest because it provides a change in cuticle properties, and corresponds to a well-known shrinkproofing treatment of wool. It was applied as follows: 2 grams of hair were washed thoroughly in nonionic detergent and rinsed free of surfactant. They were placed in 50 ml. of phosphate buffer (pH 4); 0.06 gram active chlorine as commercial bleach was added dropwise. The hair was allowed to stand in the solution 15 minutes, removed, and placed in 30 ml. of 0.7% $NaHSO_3$ solution for 30 seconds, then thoroughly rinsed in water.

The polyethylene-coated glass fiber was made by taking a glass fiber of the indicated diameter, dipping it into a xylene solution of Marlex 6050, and drying at 80°C. It presents a polyethylene surface since the glass is completely and deeply covered. The two silicone-coated fibers—glass and viscose rayon—were prepared by dipping into a chloroform solution of DC 1107 (Dow-Corning), evaporating off the solvent, and curing at 80°C. for the rayon and 150°C. for the glass. The rayon was an unusually thick monofilament, which nevertheless had the round-crenulated cross section typical of viscose rayon. The cricket cercus samples were tested both before and after the relatively sparse hairlike projections had been removed mechanically. Both samples showed the same CST values. All fiber samples were cleaned sequentially in chloroform, ethyl alcohol, and water and were then air dried immediately before testing.

Table I. Fibers Used in CST Measurements

Fiber	*Density*	*Cross Section*	*Diameter, mils*
Hair (untreated)	1.35	elliptical	3.9 × 2.2
Hair (HClO treated)	1.35	elliptical	3.9 × 2.2
Dynel	1.3	kidney shaped	2.2 × 1.7
Saran	1.7	circular	8.0
Nylon 66	1.2	circular	4.3
Glass, polyethylene coated	2.5	circular	2.5
Glass, silicone coated	2.5	circular	2.5
Viscose rayon; silicone coated	1.5	crenulated circular	3.3
Cricket cercus	—	elliptical	5.8 × 4.2

No claim is made that the CST values reported are those of the hypothetically pristine polymer surfaces. They represent reproducible values of the polymer surfaces prepared and cleaned as described.

The test liquids, together with their surface tensions and densities, are listed in Table II. Surface tensions were measured by the duNuoy method at room temperature. Density values are from the literature. For intermediate values of surface tension the mixtures listed in Table II were used. The components of each mixture were chosen to be reasonably close to each other in surface tension, and wherever possible, to be of low volatility. In view of the small absolute distance between the two liquid fronts ($\overline{CC'}$ in Figure 1), it is necessary to avoid any Marangoni effect, which might bring the fronts together while the true equilibrium contact angle was still considerably greater than zero. Marangoni effect is minimized if the two components have about the same volatility or if both are of such low volatility that evaporation of either one at the front is negligible. Each of the five listed mixtures performed well. The dioxane–water mixture was particularly satisfactory for high CST values. In using mixtures the technique was to start by placing the fiber on the pure liquid of higher surface tension, on which the fiber floated. Mixtures were then prepared with increasing small amounts of the pure liquid of lower surface tension, testing each mixture with fresh fiber samples. Finally, the surface tensions of the "just sink" mixture and of the "just float" mixture were measured by the duNuoy method and recorded as the CST range (Table III).

Table II. Liquids[a] Used in CST Measurements

Pure Liquids	*Surface Tension, Dynes/cm.*	*B.P., °C.*	*Density*
Octamethylcyclotetrasiloxane	17.0	175	0.956
n-Nonane	23.0	150.6	0.718
n-Dodecane	25.4	216.3	0.749
Di-*n*-octyl ether	27.0	286.7	0.824
Di-*n*-decyl ether	28.4	310	0.818
Ethylbenzene	29.0	136	0.867
Bis(2-ethylhexyl)adipate	30.6	214(5 mm.)	0.922
1,4-Dioxane	36.0	101	1.034
Diethyl phthalate	38.0	296	1.233
Water	72	100	1.00

[a] Liquid mixtures: A = di-*n*-octyl ether, *o*-diethyl phthalate. B = bis(2-ethylhexyl)-adipate, *o*-diethyl phthalate. C = 1,4-dioxane, water. D = di-*n*-decyl ether, *o*-diethyl phthalate. E = octamethylcyclotetrasiloxane, di-*n*-octyl ether.

The contact angles of the "just sink" mixture and the "just float" mixture against samples of the fiber were determined, using the methods described by Minor *et al.* (*2*) and Schwartz and Rader (*4*). In every case the contact angles of the "just sink" liquids were zero. The contact angles of the "just float" liquids were noticeably greater than zero in every case but were in the very low range, where measurements made without some optical leverage system lack precision. The actual measurements were all between 3° and 6°. When liquids were used of surface tension 5 dynes/cm. higher than the "just float" liquids, easily measurable larger contact angles were observed.

As Table III shows, where previously published values of CST are available, they are substantially equal to the values found in this study. However, the literature value assigned to Saran is the composite value for poly(vinyl chloride) (*39*) and poly(vinylidene chloride) (*40*). The literature value for silicone is the CST of poly(dimethylsiloxane) sorbed onto glass rather than that of cured poly(methyl hydrogen siloxane) which is DC 1107. It would be expected, as found, that the CST values of these two substances would be similar.

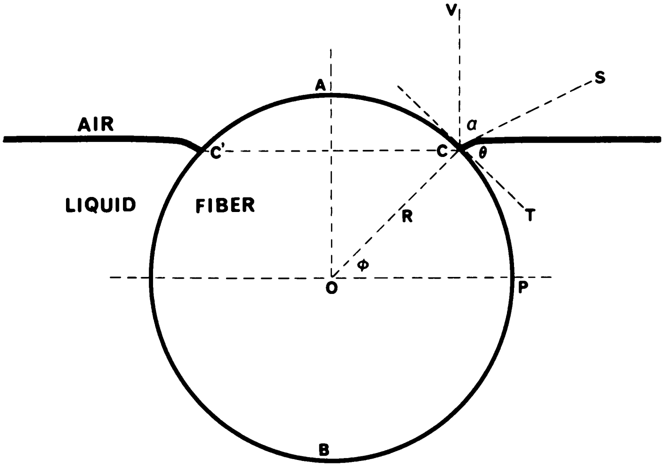

Figure 1. Flotation of an elongated cylinder (fiber) by surface forces. Density of fiber greater than density of liquid. Cross sectional view of fiber at equilibrium in the air–liquid interface

Table III. CST Range of Fibers

Fiber	*Surface Tension Range,[a] dynes/cm.* *Sink*	*Float*	*CST of Fiber Material from Ref. 5, dynes/cm.*
Hair (untreated)	27.0	27.8 (A)	—
Hair (HClO treated)	30.6	31.9 (B)	—
Dynel	27.8 (A)	28.4	—
Saran	38.4 (C)	39.5 (C)	39-40 (p. 20)
Nylon 66	40.3 (C)	42.3 (C)	42 (p. 305)
Polyethylene coated glass	28.7 (D)	32.1 (D)	31 (p. 20)
Silicone coated glass	20.6 (E)	23.7 (E)	23 (p. 351)
Silicone coated viscose rayon	21.1 (E)	23.9 (E)	23 (p. 351)
Cricket cercus	37.8 (C)	40.1 (C)	—

[a] Letters in parentheses after surface tension values indicate liquid mixtures (Table II) used.

Discussion

The theory of the flotation of an elongated solid cylindrical body by surface forces can be outlined with reference to Figure 1, which shows a cross-sectional view of a cylindrical fiber at equilibrium in the liquid–air interface. C and C′ are projections of the air–liquid–fiber boundary lines. T is the plane tangent to the cylinder surface at C. S is the plane tangent to the liquid–air interface at C. R is the radial plane from the cylinder axis, O, to C. OP and CC′ are horizontal planes; OA and VC are vertical planes, as shown. The fiber is assumed to have a density greater than that of the liquid, and the density of the air is considered negligible. The diameter of the fiber ($2\ \overline{OP}$) is assumed to be negligible compared with the fiber length. The angle TCS (θ) is the contact angle, a property of the system. The angle SCV (α) is the inclination of the liquid–air interface to the vertical plane at C. The angle POC (ϕ) is a convenient measure of the depth of the submerged portion of the fiber—*i.e.*, the portion below CC′. The value of ϕ is measured as positive counterclockwise from OP, and as negative clockwise from OP. The geometry of this system is such that

$$\alpha + \theta = 180^\circ - \phi \tag{1}$$

Since the fiber is heavier than the liquid, it would sink when placed on the liquid if it were not sustained by an upward force caused by the surface tension of the liquid. This force is exerted at the three-phase air–liquid–fiber boundary lines. If the contact angle θ and the surface tension γ are high enough, this upward force can become sufficient to balance the sinking force, and the fiber will come to rest when the two forces become equal, at an equilibrium depth corresponding to a definite value of ϕ. In this situation, as shown in Figure 1, the force exerted vertically upward on a unit length (1 cm.) of fiber, measured in dynes, will be:

$$F_u = 2\gamma \cos \alpha \tag{2}$$

where γ is the surface tension of the liquid measured in dynes/cm.

The sinking force, in dynes, will be:

$$F_s = g[d_F \cdot \text{Area AC'C} + (d_F - d_L) \cdot \text{Area BC'C}] \tag{3}$$

where g is 980, the indicated areas are measured in sq. cm., d_F is the density of the fiber, and d_L is the density of the liquid. It is evident that for any given fiber-liquid combination (having necessarily a constant value of θ) as the fiber diameter increases, the equilibrium value of ϕ will increase. As C and C′ approach A, α becomes smaller, and the sustaining force F_u increases until it reaches its maximum possible value just before the two liquid fronts C and C′ meet and coalesce at A, allowing the fiber to sink. Correspondingly, as C and C′ approach A, F_s decreases because the portion of the fiber which is not buoyed by the liquid decreases.

If $\theta = 0$ and $d_F > d_L$, the fiber cannot float. Let us examine, however, the magnitude of the forces involved in Equations 2 and 3 to see what order of value θ must have to sustain a typical fiber in a typical liquid medium. If an 8-mil monofilament (radius = 100 microns) 1 cm.

long and having density of 1.5 is laid on a liquid medium of density = 1 and sinks to a level where ϕ is nearly 90°, F_s is approximately 0.15 dynes. If $\gamma = 30$ dynes/cm., cos α need only be 0.0025 ($\alpha = 89.8°$) for the fiber to be sustained by surface tension.

Since ϕ must be less than 90°, θ in this case need only be greater than 0.2°. If θ is, for example, 5° (about as low a value as can be distinguished from zero by direct observation) ϕ becomes 85.2°, and the fiber floats with a 9.6° arc of dry cylindrical surface between C and C′.

A large proportion of the commonly encountered fibers have diameters much smaller than the 8 mils used in the illustration, and the densities of the test liquids can often be chosen so that d_F–d_L is less than the 0.5 value used above. In such cases the theoretical values of cos α necessary for flotation become extremely low. It should be noted, however, that even at the limit where $F_s = 0$ and $\alpha = 90°$, if θ is 5° (as in the example above), ϕ will still be 85°, and there will only be 10° of dry arc above the liquid.

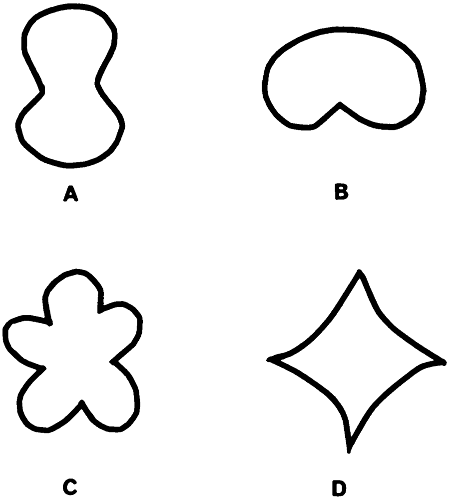

Figure 2. Satisfactory (A, B, C) and unsatisfactory (D) cross sections for determining CST

The only limitations of this method that are not also present in the classical method relate to the shape of the fiber. Although the above quantitative theory considers a cylindrical fiber, the method should work equally well (on a go–no go basis) for small diameter fibers of any cross section that do not have cusps pointed outward. Referring to Figure 2, irregular cross sections such as A, B, and C are satisfactory. A fiber of cross section D, however, must sink at contact angles much greater than zero. The fiber axis should preferably lie in a single plane, although slight coiling is not too harmful if the fiber diameter is small. Thus, the portions of the fiber in the liquid surface can support the coils that arch above the surface, even at low values of θ. The ratio of fiber length to diameter is of considerable importance. Along the flat vertical ends of a floating fiber the effect of any contact angle less than 90° is toward sinking. Thus, the test snippets should be long enough to make the end effects negligible. If the length-to-diameter ratio is less than about two orders of magnitude (*i.e.*, about 1 cm. long for a 100-micron fiber), maximum precision will not be attained.

The experimental work presented illustrates the precision of this method compared with that of the classical method.

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3

The Effect of Hydrophile–Lipophile Balance on Contact Angle of Solutions of Nonionic Surface-Active Agents

Relation to Adjuvant Effects

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Examination of the relevant theory indicates that the adjuvant effect of surface-active agents on herbicide action is maximized when the quantity $\Pi = \gamma_L \cdot \cos \theta$, or the film pressure at the liquid/solid interface, has a maximum value. Measurement of surface tension of 1.0% aqueous solutions and of contact angle on a number of substrates (Teflon, paraffin) and plant-leaf surfaces (soybean, corn) as a function of hydrophile-lipophile balance show at least one maximum, and these values are in good agreement with earlier experimental data on herbicidal activity.

In recent years, it has frequently been observed that the toxicity of herbicides can be affected markedly by the presence of various types of surface-active agents (*10, 11, 12, 13*). Jansen (*11, 12*) has paid particular attention to the effect of the structure of the surface-active agent on activity and thus implicitly, to that measure of the structure known as hydrophile-lipophile balance (HLB) (*1*). However, we do not believe that the explicit correlation has been shown to exist.

In a recent study (2), the problem of applying sprays was analyzed as follows:

(1) The spray droplet must get on the leaf.

(2) Once there, it must remain.

(3) Not only must it remain, it must penetrate into the leaf system. Eaton (*4*) has recently presented a similar point of view.

With respect to the first point, Hartley and Brunskill (*8*) have shown that unless the excess of adhesion energy over surface energy is greater than the kinetic energy of the droplet, the droplet will be reflected on impact with the leaf surface, using the following considerations.

Two quantities are defined. One is the surface energy of the free droplet, E_0, which is the product of the surface area and the surface tension—*i.e.*,

$$E_0 = 4\pi r^2 \gamma_L \qquad (1)$$

and the surface energy of the attached droplet over the drop/solid interface, which is found to be

$$E_S = \pi r^2 \gamma_L (4/3)^{2/3} [2(1 - \cos\theta) - \sin^2\theta \cos\theta] \times [1 - \cos\theta + 1/3(\cos^3\theta - 1)]^{-2/3} \qquad (2)$$

The quantity $(E_0 - E_S)/E_0$ then represents the minimum energy barrier between attached and free drops which must be exceeded by the kinetic energy of the drop for the drop to be reflected, all expressed as a fraction of the surface energy of the free drop. It may be more useful in the present context to say that the kinetic energy must be less than this energy barrier for the drop to be retained.

If the ratio $(E_0 - E_S)/E_0$ is plotted as a function of contact angle, the area above the curve corresponds to reflection and that below the curve to adhesion. It is immediately apparent that the droplet diameter is quite important since, of course, the kinetic energy of the drop is a function of size. For example, a drop of 100-μ diameter, falling at its terminal velocity (about 25 cm./sec.), will have a kinetic energy of approximately 1.5×10^{-4} erg, while its surface energy (if pure water) will be about 2.2×10^{-2}; hence, the ratio of surface to kinetic energy will be about 0.014.

The curve of the Hartley-Brunskill function shows that under these circumstances reflection of the drop will not occur unless the contact angle is very high—of the order of 179°. Since the contact angle of water on paraffin is only about 110°, 100-μ droplets will generally adhere.

However, for a 200-μ drop, the terminal velocity is about 75 cm./sec., and the kinetic energy is about 1.1×10^{-2} erg as compared with a surface energy of 8.8×10^{-2} erg. Even here, contact angles greater than about 105° are required for reflection.

At 400-μ diameter, the kinetic and surface energies are about equal; hence, a contact angle of zero—*i.e.*, complete spreading—is required for retention.

To consider a practical situation, a drop of water of about 250-μ radius (a reasonable average value for a spray), would have a ratio of kinetic to surface energy of the order of 0.2. Hence, contact angles greater than 90° would lead to reflection. Since the contact angle for water on paraffin is about 110°, reflection from a waxy leaf surface is quite probable. However, if the surface tension is lowered to about 35 dynes/cm. by adding a suitable surface-active agent, the energy barrier is raised to about 0.4. At this value, an angle of 65° will lead to reflection, but the surface-active agent may lower the contact angle to 60° or less (*cf.*, Table I), so that most of the droplets will adhere to the leaf.

Table I. Surface Tension, Contact Angle, and Film Pressure for Aqueous Solutions as a Function of HLB

HLB	*8*	*10*	*12*	*14*	*16*	*18*
γ_L	*32.8*	*33.5*	*40.3*	*40.4*	*40.0*	*43.7*
Substrate:						
Teflon						
θ	61	60	64	67	72	74
$\gamma_L \cos \theta$	15.9	16.8	17.7	15.8	12.4	12.1
Paraffin						
θ	54	53	63	71	68	67
$\gamma_L \cos \theta$	19.3	20.2	18.3	13.2	15.0	17.1
Corn						
θ	57	58	66	63	57	65
$\gamma_L \cos \theta$	17.9	17.8	16.4	18.3	21.8	18.5
Soybean						
θ	70	59	56	62	69	70
$\gamma_L \cos \theta$	11.2	17.3	22.5	18.9	14.3	14.9

Once the droplet is deposited on the leaf, the fact that the leaf is at some angle β to the ground surface must be taken into account. Now there is a gravitational force equal to $mg \sin \beta$ (where m is the mass of the drop, and g the acceleration of gravity) tending to make the drop run off the leaf. This is opposed again by the adhesive force acting between the droplet and the leaf, and at some particular angle, α, the gravitational effect will overpower the adhesive force, and the drop will run off. Thus, at the angle, α, at which runoff will just occur, according to Furmidge (*6, 7*):

$$mg \sin \alpha = \gamma_L w(\cos \theta_R - \cos \theta_A) \tag{3}$$

where w is the width of the drop, and θ_R and θ_A are the receding and advancing contact angles, respectively.

By a further analysis, Furmidge (*6, 7*) defines a retention factor, F, which is a measure of the number of drops which will be retained:

$$F = \theta_M[\gamma_L(\cos \theta_R - \cos \theta_A)/\rho]^{1/2} \tag{4}$$

where θ_M is the mean of the contact angles, ρ is the liquid density, and the other symbols have been defined. In measurements of runoff on beeswax and cellulose acetate model surfaces, good agreement with theory was found.

The actual area of the leaf which is covered by a given retained spray droplet will be a function of the spreading coefficient and ultimately the contact angle. Evans and Martin (5) have shown empirically that the area covered by the drop is given by:

$$A = k/[\gamma_L(1 - \cos\theta)]^{1/2} \qquad (5)$$

According to Moilliet, Collie, and Black (*14*), a first approximation shows that the empirical constant k must be equal to $(\rho g/2)^{1/2}V$ where ρ is again the density of the liquid, g the acceleration of gravity, and V the volume of the droplet. However, this value for k gives dimensionally incorrect results, and correct dimensionality is obtained by setting $k = (\rho g/2)^{1/2}V^{4/3}$.

However, the dimensionally-correct form gives unreasonably small values for the area covered, and even the values calculated from the dimensionally incorrect equation are at least an order of magnitude too small.

A more exact equation for the area can be obtained from the results of Hartley and Brunskill (8):

$$A = (4/3)^{2/3}\pi r^2[1 - \cos\theta + 1/3(\cos^3\theta - 1)]^{-2/3} \qquad (6)$$

[This relation does not explicitly contain the surface tension; implicitly the variation in contact angle reflects the change in surface tension, *cf. below*].

Taking again the case of a droplet 200-μ in diameter, for water ($\gamma_L = 70$, $\theta = 100°$), Equation 6 predicts that the droplet will cover an area of approximately 46,000 sq. μ. If surface-active agent is added so that $\gamma_L = 35$, $\theta = 60°$, the surface area covered is then 156,000 sq. μ or an increase of some 3½ times. Equation 5, under the same conditions predicts an increase in coverage by a factor of 2, so that irrespective of the accuracy of the relations, the predicted behavior is similar.

With the liquid more-or-less spread out on the leaf, we are finally concerned with the problem of penetration into the leaf. This requires a structural model for the leaf and some assumptions as to the route of penetration.

There are many models which may be adopted, of varying degrees of sophistication, depending, for example, on whether or not we wish to introduce a term for diffusion through the waxy cuticle. In a first approximation, such as this study, such sophistication is probably unnecessary, and we may proceed by considering the leaf to be represented by a bundle of capillaries, into which the liquid must penetrate.

The classical theory of capillarity shows that the penetration of a liquid into a capillary is brought about by a pressure difference across the curved meniscus. If the capillary is circular in cross section and fairly small, the pressure forcing the liquid into the capillary is given by

$$p = 2\gamma_L \cos \theta / R \qquad (7)$$

where R is the radius of the capillary. If the contact angle is greater than 90°, the cosine is negative, and instead of penetrating, the liquid would be forced out of the capillary.

In a real system, the contact angle inside the capillary may well be somewhat different than on the leaf surface, but this refinement need not concern us in the present approximation.

Having penetrated the leaf, the further progress of the liquid is the concern of the plant physiologist rather than the colloid chemist, and we will speculate no further at this time.

Also, since the present considerations do not include the interesting problem of emulsion sprays, the effect of the electrical properties of the leaf surface, cited by Haydon (9), need not be brought into the discussion.

If the various equations introduced above are taken into consideration, to a reasonable approximation the optimum conditions for herbicide activity will be realized when the quantity $\gamma_L \cdot \cos \theta$ is at a maximum. From the well-known relation of Dupré, it follows that

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \qquad (8)$$

where γ_S is the surface tension of the leaf surface, and γ_{SL} is the interfacial tension between the liquid and the solid surface (that fact that the two quantities on the right side of Equation 8 cannot be measured directly is of no importance).

It thus appears that $\gamma_L \cos \theta$ is the surface pressure at the liquid solid interface, and may conveniently be assigned that symbol, Π.

Although it is known that the surface tension increases with increasing HLB (all other things being equal), the dependence of contact angle on this quantity has not been studied previously. On the other hand, if one assumes that the linear relation between surface tension and contact angle found by Zisman and co-workers for both pure liquids and for solutions of surface-active agents (3) as a function of concentration holds for our herbicidal systems, it appears that the quantity, Π, will exhibit at least one maximum when plotted as a function of HLB.

In other words, we expect that maximum herbicidal activity will be found when Π is at a maximum value for the system. The purpose of the present investigation was to examine the variation of this function with the structure of the surface-active agent as measured by HLB and to determine whether a maximum in the surface pressure could be correlated with herbicidal activity.

Experimental

The solutions of surface-active materials were made up in distilled water to a concentration of 1.0 gram/dl. Mixtures of Span 80 and Tween 80 were used to obtain HLB-values of 8, 10, 12, and 14; a mixture of Tween 20 and Tween 80 for 16; and a commercial product with the composition polyoxyethylene (40) sorbitan monolaurate gave an HLB = 18.

Smooth surfaces were obtained on the Teflon samples by placing them between photographic ferrotype plates in a heated hydraulic press at about 300°F. and 2000 p.s.i.g. on a 4-inch ram. Blocks of microcrystalline paraffin wax (Enjay) were smoothed by passing a warm spatula over their surface.

Plant leaves were prepared by clamping freshly-picked leaves as smoothly as possible to a glass plate. Cementing the leaf to the plate with nitrocellulose lacquer gives a good surface for measurement but unfortunately changes the properties of the leaf. Contact angles were measured using a NRL contact-angle goniometer (Ramé-Hart Corp., Mountain Lakes, N. J.).

In the contact-angle measurements, 30-μliter droplets were slowly formed by delivery from a Hamilton syringe. The slow formation of the droplet insures equilibrium values. This measurement yields only an advancing angle. The retreating angle is also of interest (*10*), but the reproducibility of this quantity was found to be very poor. The advancing angles were reproducible to ±2-3° on Teflon and paraffin and to ±5° on the plant surfaces.

Measurements on plants were carried out on freshly cut leaves from greenhouse-grown Kent soybean and Agway hybrid (NE912) field corn.

Surface tension measurements were performed on the aqueous solutions by means of a Wilhelmy balance, using a sand-blasted platinum plate, and are equilibrium values. All measurements were carried out at room temperature (23° ± 2°C.).

Results and Discussion

The data for surface tension and contact angle, as well as the calculated values of the film pressure, Π, are given in Table I, and the dependence of the film pressure on HLB is shown in Figure 1.

The shapes of the curves are roughly similar, but there is a distinct dependence on the nature of the substrate, particularly with respect to the position of the maximum. Figure 2 shows the herbicidal activity of 2,4-D (containing 1.0% surface-active agent) on corn and soybean plants, from the data of Jansen (*11*). These data were not originally presented in terms of HLB, and the HLB-values have been calculated from the structures of the surface-active agents, as reported by Jansen, by the usual methods (*1*).

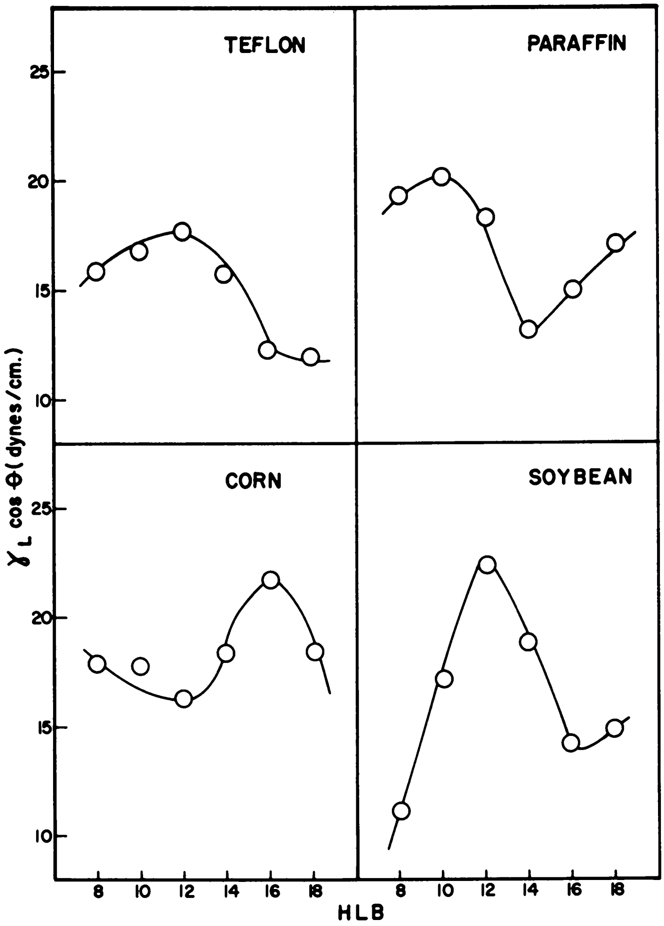

Figure 1. Relation between $\Pi = \gamma_L \cos\theta$ and HLB for Teflon, paraffin, and corn and soybean leaves

The shapes of these curves are markedly similar to those of Figure 1, although the maxima do not correspond exactly. This is not surprising since the herbicide itself must have some effect on the surface activity of the solution (if nothing more than an electrolyte effect), and the surface-active compounds used here were not identical in chemical type to those used by Jansen.

It thus appears that the adjuvant effect of surface-active agents on herbicidal activity can be explained in terms of the surface-chemical interactions between the droplet of herbicide solution and the plant-leaf surface. Although, as we have seen, capillary penetration is one aspect of

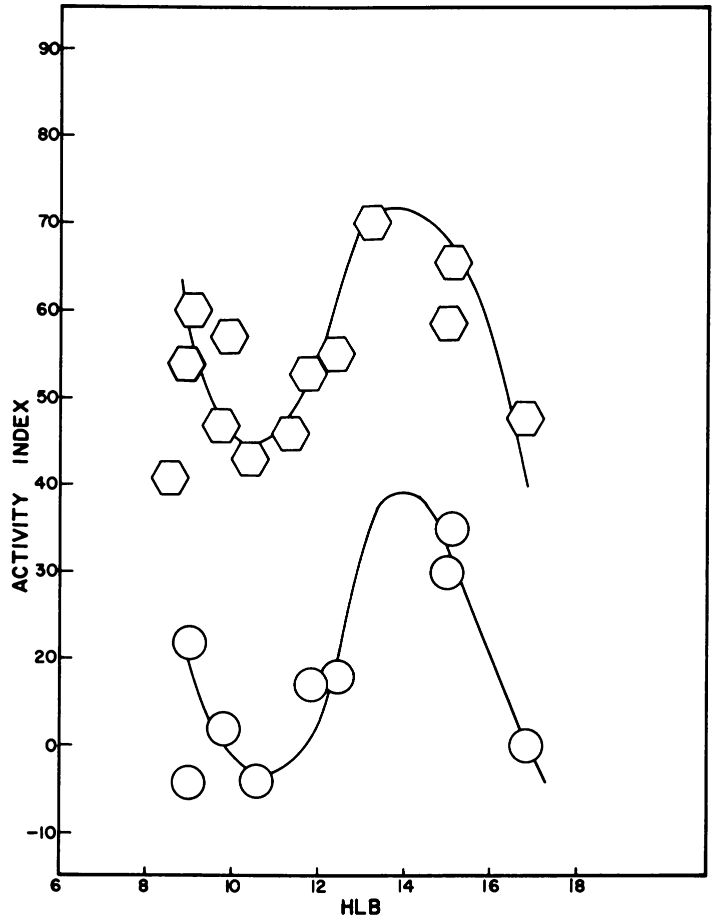

Figure 2. Herbicidal activity of 2,4-D on corn (O) and soybean (ring). Solutions containing 1.0% of surface-active agent applied at 40 gallons/acre, corresponding to 1/16 lb./acre of active herbicide. Recalculated from data of Jansen (11).

adjuvant activity, it is far from the only one and may well be less significant than such matters as reflection, runoff, and spreading.

Obviously, the considerations advanced here represent only a rather crude first approximation, but on the other hand, perhaps they can be extended to include other systems in which a liquid droplet is allowed to impinge on a solid substrate.

Acknowledgments

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Most of the measurements reported were carried out by David Z. Becher in connection with a project for the Science Seminar, an enrichment program of Brandywine High School, Wilmington, Del.

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4

Contribution of Micelles to the Transport of a Water-Insoluble Substance through a Membrane

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Some fundamentals of micelle formation and of the solubilization of water-insoluble substances by micelles are reviewed. The accelerating effect of micellization upon the rate of dissolution and of transport of solubilizate through bulk liquid is then considered. Membranes present an obstacle to transport. A larger fraction of the total driving force can be brought to bear upon this obstacle as other resistances are reduced by solubilization. Hence, transport across a membrane will, in general, be accelerated whether micelles are effective within the membrane or not. It is now possible to determine also this contribution of micelles to the transport within the membrane. In a specific case it was found to be negligible.

Solubilizing materials, especially micelles of association colloids, increase tremendously the solubility of many normally insoluble materials in water. Hence, they are often used to facilitate the interaction of water-insoluble substances—dyes, drugs, pesticides—with aqueous systems, especially biological ones. In these applications, membranes are often encountered as an obstacle to the desired distribution and interaction. This raises the questions: can solubilization help overcome this type of obstacle and, if so, what is the mechanism involved, and does it require that the solubilizing agent be effective within the membrane? It is of interest to know whether the micelles need to cross the membrane as such to facilitate passage of the insoluble component. The first question is easily answered: solubilizing agents are indeed most helpful, in practice, in transporting an insoluble material across a membrane. The last question about the role of micelles in the membrane is less readily answered. This paper describes a general method for studying this problem and shows by a specific example that even when micelles are unable to cross the membrane themselves, they may be very helpful because they bring the insoluble material up to the membrane and pick it up on the other side. To complete the picture, some general considerations about micellization and solubilization are included.

The experiments and the necessary theory were developed by Mohammad Abu-Hamdiyyah, Pasupati Mukerjee, and myself in connection with a related but different problem—an attempt to determine unambiguously the rate of transport of simple non-micellized detergent ions through a membrane (*1, 18*). We needed information about the ability of the micelles to cross the membrane, and the insoluble material was used mainly to indicate micelle behavior. The paper reporting that work (*1*) gives experimental details and further interpretation of the results. Since then I found that Dean and Vinograd (*4*) developed the qualitative aspects of this argument 25 years ago.

Solubilization

Although the word solubilization is sometimes used in a general sense to denote any large increase in solubility by adding a third component, it is generally restricted to the effect connected with the formation of micelles by association colloids, such as most surfactants and detergents. These are amphipathic molecules whose structure provides a hydrophilic part, the "head" and a hydrophobic one, the "tail." At sufficiently low concentrations these components dissolve as small ions or molecules giving normal solutions and then have no significant effect on the solubility of insoluble materials, although they greatly affect the surface tension of the solution. However, material present above a certain well-defined concentration, the critical micelle concentration (CMC), forms large aggregates or micelles which give the solution many special properties, among them the ability to dissolve some water-insoluble substances. Hartley (*8*) has discussed the fundamentals of micellization, and Mukerjee (*17*) has reviewed recent developments.

Figure 1 shows schematically the monomeric amphipathic particle, in this case an ionic one, with its polar head and its hydrophobic tail which is curled up in the aqueous medium. This is in equilibrium with a micelle formed by many monomers, all oriented with their heads outward toward the water and their tails randomly intertwined in the interior. A microdroplet of oil with an ionic hydrophilic surface is thus formed. The cooperative action of the many charged polar heads binds tightly a substantial fraction of the counterions thus effectively reducing the surface charge.

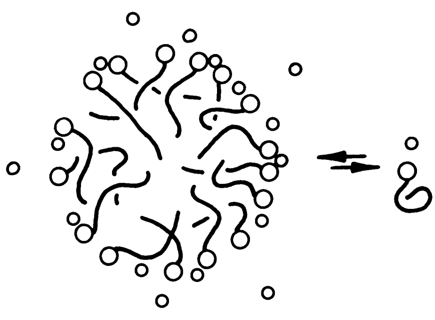

Figure 1. Equilibrium between a monomeric amphipatic ion and a micelle

The time in which micelles are formed from monomers and disintegrate into them is still uncertain, but it certainly is very short, less than 10^{-4} sec. (*15, 21*). This phenomenon is not easy to study, even by the newest techniques; part of the difficulty stems from the fact that in the dissociation two processes must be involved: one, the separation of counterions from the micelle and, the other, the disintegration of the micelle proper by separation of the amphipathic ions from each other.

Solubilization has been treated in detail in two monographs (*6, 13*). It involves the binding of molecules or ions of the insoluble material by the micelle, and this can occur in various ways as indicated in Figure 2. Thus, nonpolar oleophilic materials are likely to be incorporated into the hydrophobic core of the micelle. Polar materials are likely to be oriented with their hydrophilic part exposed to the outside and the hydrophobic one forming part of the core. Oppositely charged ions are likely to be taken into the tightly bound counterion sphere. If the salt of the association colloids with that ion is oil soluble, it may be dissolved in the core of micelle. These solubilizing processes continue until equilibrium is reached when solubilizate particles leave the micelle as rapidly as they are taken up. These are extremely rapid processes, a molecule being able to move in and out of the micelle more than 10^4 times per sec., at least in some cases (*21*). This exchange of the solubilized material between micelle and bulk liquid is likely to be superimposed upon the formation and disintegration of micelles and should proceed separately from these processes.

Solubilization of Orange OT

Figure 3 shows the effect of solubilization upon equilibrium in the particular system we used. The data were obtained many years ago by R. J. Williams (*24*) and agree excellently with recent results of H. Schott (*23*). The solubilized substance was a brilliant dye whose solubility in water is so slight that it cannot be detected with the naked eye, but according to spectrophotometric measurements, a saturated solution is approximately $10^{-7}M$ or about 3 millionths of 1% at room temperature. This dye, 1-*o*-tolylazo-2-naphthol, is called Orange OT according to a tradition dating back at least 25 years (*12*), yet a recent check showed that commercially this tradename designates a very different material, C.I. Pigment Orange 13, whereas our dye is the basis of C.I. Solvent Orange 2. The solubilizing agent was sodium dodecyl (lauryl) sulfate or NaLS whose CMC is about 0.236%. As seen from Figure 3, there is no perceptible increase in the solubility of Orange OT as the concentration of NaLS increases until above 0.2%. After a short transition region, the solubility increases sharply and linearly with the NaLS concentration. The transition region corresponds to the gradual buildup of the micellized fraction of any added surfactant according to the laws of chemical equilibrium. It is very narrow because of the cooperative nature of micellization, involving in this case about 60 monomers as determined by light scattering, by sedimentation equilibrium, and by sedimentation rate and diffusion measurements (*2, 9, 11*).

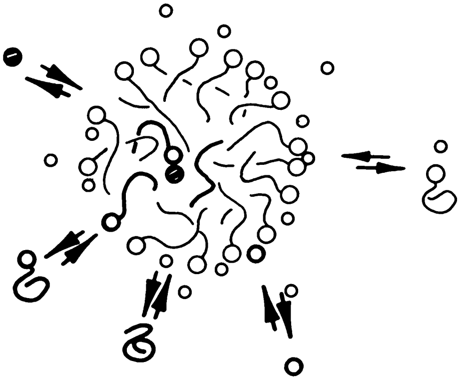

Figure 2. Schematic mechanisms of solubilization. Clockwise from 5 o'clock: ion exchange with the surface; solution in interior of micelle; oriented adsorption; formation of oil-soluble salt

The slope of the solubility line in Figure 3 corresponds to 1 gram of Orange OT dissolved per *ca.* 110 grams of micellized NaLS, or about 1 mole of the dye for 125 moles of micellized LS^- ions, or about 1 molecule of Orange OT per 2 micelles of NaLS. Thus, a 1% solution of NaLS can dissolve about 7 × 10^{-3}% of Orange OT, which is about 2000 times more than dissolves in pure water.

In other words, on the average, in a 1% NaLS solution the LS^- ion spends three-fourths of its time in micellized form and one-fourth as a monomer. The dissolved Orange OT molecule spends 99.95% of its time attached to a micelle and only 1/2000ths of its time simply dissolved in water. Furthermore, again on the average, when the solution is saturated with Orange OT, a given micelle contains a dye molecule less than 50% of the time and, if the distribution is completely random, two dye molecules less than 25% of the time, etc. If the solution is less than saturated with Orange OT, these last fractions decrease rapidly, especially for multiple occupancy of the micelle, whereas the distribution of Orange OT between water and micelles remains essentially unchanged.

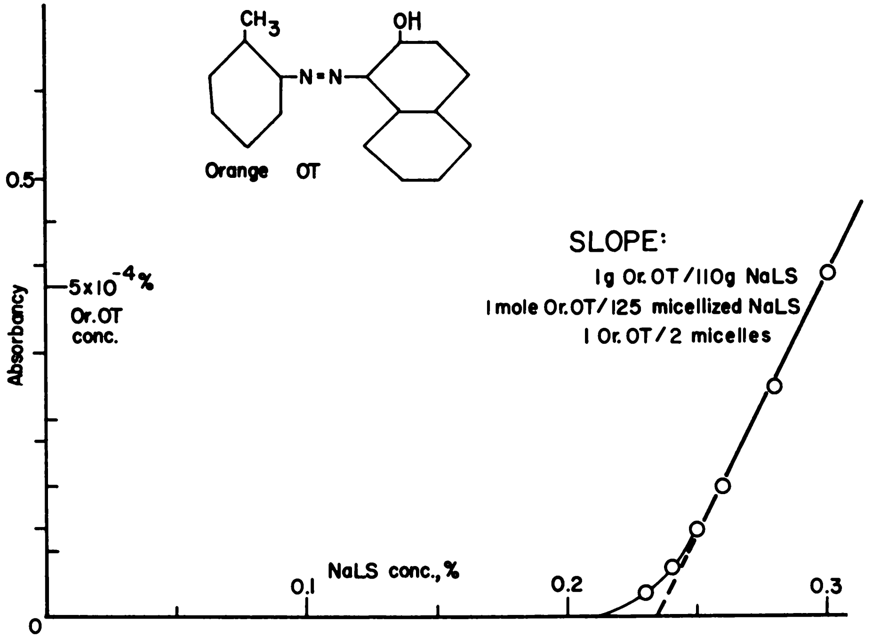

Figure 3. Orange OT and the effect of NaLS concentration upon its solubility in water

Other solubilized materials differ greatly from Orange OT and may be much more or much less soluble in the micelles; as far as I know there is always a limit to the solubility, and no case of continuous transition to a micelle consisting mostly of solubilized material—*i.e.*, to an emulsion droplet—is known. Solutes capable of dissolving extensively in micelles can and do, of course, affect significantly the properties of micelles—*e.g.*, lower the CMC (*7*, *22*). They may also affect the rate of micelle formation and disintegration, although there is little definite information on this subject. One of the advantages of Orange OT is that it is so slightly soluble in micelles that it has little effect on their properties (*19*, *24*), yet it is easily measured in micellar solutions because of its intense color.

The low concentration of Orange OT in the micelles, and especially in the water, keeps the competition between these two solvents unaffected by the dissolved dye. Hence, the distribution ratio between micelles and water is constant from zero to saturation, and at equilibrium the percent saturation is the same for both and for the whole system. This equilibrium is also presumably established extremely rapidly and is therefore maintained at each point during the relatively slow changes involved in the usual transport processes.

Solubilization in Transport Processes

The driving force for transporting the substance of interest through an aqueous system is always the difference of its chemical potential (or to a first approximation the difference of its relative saturation) between the starting point and its destination. The rate at which transport occurs depends, however, on both the magnitude of this total driving force and the resistances encountered along the way. In most cases, the principal steps involved will be: dissolution, if the material is initially a separate solid or liquid phase; diffusion through, or convection in, bulk liquid or a combination of both; and the step of most interest to us, the crossing of a membrane. The resistance encountered in each of these may be affected by solubilization.

Dissolution. Dissolution of a sparingly soluble substance, say a solid, is often slow. This slowness is generally caused by the slow transport of dissolved material away from the saturated boundary layers surrounding the solid itself and does not arise from the difficulty of passing from the solid to the dissolved state in these immediately adjacent layers. It is only this last step that involves the true rate of solution. Hence, the addition of a solubilizing agent is not likely to change the rate of solution proper, although it may affect the dissolution rate by affecting the transport away from the boundary layer (*14*). The dissolution rate can thus be greatly accelerated (3). Often the limit of solubility may also be increased to the point where the solid disappears, and dissolution is eliminated as a significant step in the total transport.

By eliminating the solid, solubilization actually may decrease the total driving force for the transport since an unsaturated solution necessarily has a lower activity than the undissolved material and the saturated boundary layer. In extreme cases, solubilization may thus slow down the rate of transport. This explains why so many germicides lose their effectiveness when incorporated into soap. They become so well solubilized in the high concentrations of soap used in abluting, that their tendency to diffuse to any site of action is greatly reduced (5).

Diffusion. The transport by diffusion in the bulk liquid obeys Fick's law which is conveniently expressed in terms of the flux J of the solute—*i.e.*, the amount of solute crossing a unit cross section in unit time as

$$J_D = D\frac{dc}{dx} \qquad (1)$$

where D is the diffusion coefficient of the solute, dc/dx its gradient of concentration, and the subscript identifies the flux J_D as being caused by diffusion. Addition of a solubilizing material will generally reduce the diffusion coefficient since, instead of a small molecule of solute diffusing alone, it will now move only attached to a bulky micelle. Since the diffusion coefficient is roughly inversely proportional to the radius of the diffusing particle, D is reduced generally by less than a factor of 10 which would correspond to a micelle having a volume 1000 times larger than that of the solubilizate. On the other hand, the presence of the solubilizing agent increases the concentration gradient in direct proportion to the increase of solubility. This is because Fick's law involves the absolute gradient of concentration which is necessarily small as long as the solubility is small, and not its relative value. If we denote the saturation value by S and express the gradient in relative values of %S, we can rewrite Fick's law as

$$J_D = D100S\frac{d(\%S)}{dx} \qquad (2)$$

which shows that for same gradients of relative saturation, the flux caused by diffusion is directly proportional to saturation. Hence, solubilization, since it can increase the saturation value by many orders of magnitude, will in general increase transport by diffusion even though it decreases the diffusion coefficient itself. This is assuming, of course, that the gradient of relative saturation is the same in both cases.

Convection. Transport by convection—*i.e.*, by mechanical movement of the solution as a whole—depends on the concentration of the solute and the velocity, v, of the moving liquid; hence, the flux caused by convection, J_C, is given by

$$J_C = vc \qquad (3)$$

Since solubilization can greatly increase the concentration, it can greatly increase convectional transport if the velocity is constant.

Membrane. In discussing transport across a membrane, we consider only the case where the pressures on both sides of the membrane are substantially the same so that no liquid is being pressed across it and there is no transport by convection. Diffusion is then the only mechanism by which the solute can cross the membrane and, in principle, Fick's equation applies again. By definition, however, a membrane is more than a stagnant layer of solution, and its presence will change both the diffusion coefficients and the solubilities of all components. The diffusion coefficients are generally decreased, and the solubilities can be either increased or decreased. Typically, the bulky and hydrophilic micelle will tend to have its solubility in the membrane greatly decreased, whereas the small and generally oleophilic solubilizate may be much less affected and for an oleophilic membrane, may even have its solubility increased.

Detailed considerations are unnecessary to show that solubilization will increase the flux through the membrane because this is already determined by what happens to the rest of the system and depends on the fact that a membrane is of interest in studying transport properties to the extent that it represents an obstacle, a significant resistance to the motion of matter.

The rate of transport by a number of successive steps through a system is determined by the total resistance and the driving force. Part of the total driving force is used to overcome the resistance of each step in proportion to its resistance. Solubilization clearly reduces the resistance of steps involving diffusion and convection in bulk liquid, and therefore it permits the application of a greater fraction of the total driving force to the membrane. In this way, solubilization accelerates the transport through the membrane even if the resistance of this step remains unchanged.

A hydrodynamic analogy may be useful. The upper part of Figure 4 shows a system in which a liquid flows from a reservoir on the left to one on the right through a series of pipes, whose cross sections indicate the resistances they may offer, the narrowest one corresponding to the membrane. On the right side, the same system is shown, but the wider pipes indicate lower resistance owing to solubilization. The lower part of Figure 4 shows the distribution of pressure in both cases, and obviously much of the pressure drop on the left is consumed in overcoming the resistance of the narrow pipes, so that only a small part of the total is applied to the constriction symbolizing the membrane. The wider pipes on the right side produce very little pressure drop, so that most of the driving force is applied to the constriction and will, of course, cause a more rapid flow whether the constriction remains the same or is widened also by solubilization.

The Role of Micelles in the Membrane

Thus, the simple fact that the flux of solubilizate is more rapid through a membrane in the presence of a solubilizing agent is not in itself proof that micelles mediate the transport within the membrane. A more detailed analysis is required.

To simplify the situation, let us consider a system in which the solvent is the same on both sides of the membrane—*i.e.*, the solubilizing agent is present in equal concentrations and the micelles are everywhere in equilibrium with monomers as shown schematically in Figure 5. The dye, however, is present in higher concentration on the left side, part of it being free in water and part solubilized in the micelles. The membrane has a certain permeability to the dye itself, a certain permeability to monomers, and perhaps a certain permeability to micelles and therefore to solubilized dye. These three are indicated as separate parallel channels through the membrane although in reality these would presumably be common. For our purposes, we can disregard the transport of monomers and concern ourselves with measuring the transport of dye.

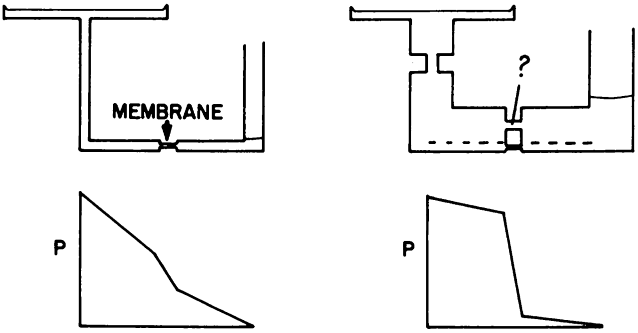

Figure 4. A hydrodynamic analogy to transport through bulk solution and a membrane. Left, without solubilization; right, with solubilization. Lower part shows distribution of pressure drop which is increased across membrane on the right by reduced resistance in rest of the system

Method Used. To learn about the contributions of micelles to the transport of dye through the membrane, we study this transport as a function of the concentration of micelles. If we do it under conditions where resistances other than that of the membrane are intrinsically small, even a small amount of solubilization will make them completely negligible, and the membrane resistance will be the only significant one. If micelles have a role in overcoming this resistance too, the flux across the membrane will depend on their concentration. If not, it will be independent thereof despite the fact that the concentration gradient dc/dx across the membrane will increase in absolute values as solubilization becomes more effective. On the other hand, Fick's law (Equation 1) indicates that a constant diffusion coefficient, D, gives an increasing flux, J, as the concentration gradient increases. Conversely, a constant flux, J,

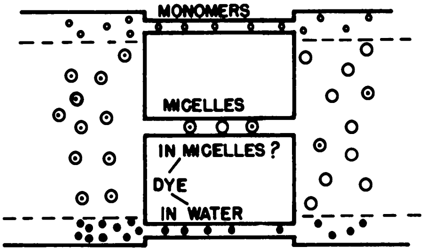

Figure 5. Transport through a membrane when solubilizing micelles are present on both sides. The dye may cross as if it were unsolubilized (bottom) and perhaps also solubilized in micelles (middle). Monomeric surfactant may also cross (top) but does not affect dye transport

under these conditions leads necessarily to a decreasing diffusion coefficient, D. Such a decrease shows that the mechanism of transport within the membrane changes as compared with that in solution. More quantitatively, this can be expressed as follows.

The total flux of the dye J_t is the sum of its flux in solubilized form J_s plus that dissolved in water J_w.

$$J_t = J_s + J_w \tag{4}$$

Each of these fluxes can be expressed according to Fick's law in terms of the corresponding concentrations and of a corresponding diffusion coefficient which takes into account also the truly available cross section and tortuosity of any passages through the membrane.

$$J_t = D_t \frac{dc_t}{dx} \tag{5}$$

We can therefore replace Equation 4 by

$$D_t \frac{dc_t}{dx} = D_s \frac{dc_s}{dx} + D_w \frac{dc_w}{dx} \tag{6}$$

Here, as in Equation 4, the left side represents the actually observed total transport of dye whereas the right side represents the two paths by which it occurs. In examining membrane behavior we no longer neglect implicitly J_w, the transport of unsolubilized dye, as was clearly justified in discussing bulk solution.

In accordance with Equation 2 we can express this equation in terms of saturation concentrations as follows:

$$100 D_t S_t \frac{d\%S_t}{dx} = 100 D_s S_s \frac{d\%S_s}{dx} + 100 D_w S_w \frac{d\%S_w}{dx} \tag{7}$$

Since the relative saturations are the same, owing to rapid equilibration between the various species, and hence the gradients are also equal, we can simplify and obtain

$$D_t S_t = D_s S_s + D_w S_w \qquad (8)$$

If the behavior in the membrane were the same as in water, the last term would be negligible and D_t would equal approximately D_s and be a constant. On the other hand, if the transport by micelles is negligible—*i.e.*, $D_s = 0$, the last term which does not depend on the behavior of micelles is constant; hence, the product $D_t S_t$ is also constant, and as the total solubility increases owing to solubilization, the measured diffusion coefficient, D_t, must decrease.

Another way of expressing these relations is to say that solubilization in our system greatly increases the amount of dye to be transported by increasing its solubility. It may also contribute to the transport, but unless this contribution is of the same magnitude, the approach to equilibrium will be slowed simply because there is so much more dye to be transported.

Experimental Determination. Experimentally, we measured the dialysis through a cellophane membrane, and Fick's equation was used in integrated form which involved not only the volumes V_i and V_o of the inside and outside compartments but also the somewhat uncertain area of the membrane, A, and its effective thickness, Δx, which is very difficult to evaluate.

$$\log \frac{c_{eq} - c}{c_{eq} - c_o} = \frac{A(V_i + V_o)}{2.3 \Delta x V_i V_o} Dt \qquad (9)$$

Here c_o is the initial concentration in the inner compartment, c the concentration of the outer compartment after time t, and c_{eq} is the equilibrium concentration reached after a sufficient time or calculated from a material balance. For simplicity, the experiments were all done with zero initial concentration in the outer compartment.

Strictly speaking, the D appearing in Equation 9 is an average taken over the membrane and its boundary layers and is assumed to be constant. The fractional expression on the right side of Equation 9 is a constant for a given apparatus and procedure, so that if one combines all the terms except t on the right side, one obtains:

$$\log (c_{eq} - c) = kt + \log (c_{eq} - c_o) \qquad (10)$$

This means that a semilogarithmic plot of $c_{eq} - c$ against time should give a straight line whose slope $k = DA(V_i + V_o)/2.3\Delta x V_i V_o$ is a rate constant of dialysis which is proportional to D for experiments performed under the same conditions.

Results. Figure 6 shows some experimental results for the dialysis of Orange OT between solutions of NaLS which had the same concentrations on both sides of the membrane in each experiment but differed from experiment to experiment. The slopes of the lines, corresponding to the rate constants, are well defined. These and additional dialysis rate constants, when plotted in Figure 7 as a function of concentration of NaLS present, decrease markedly, suggesting that micelles are not very effective within the membrane.

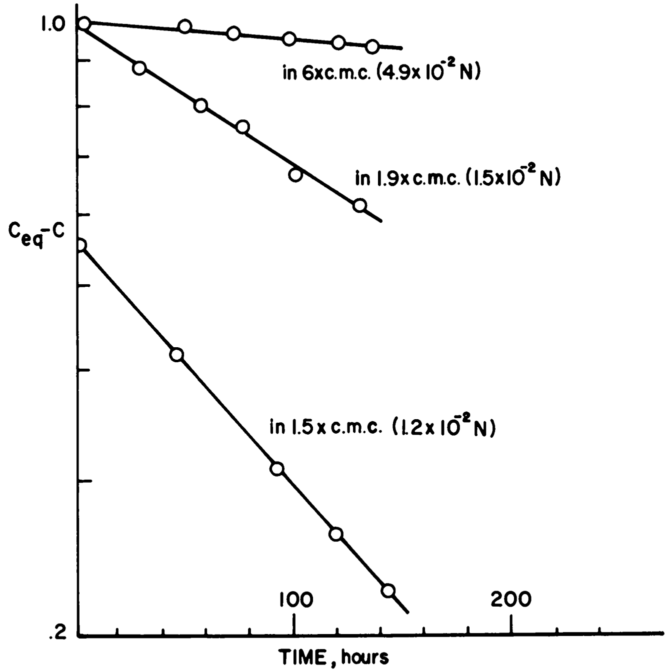

Figure 6. Effect of varying concentrations of NaLS upon the dialysis of Orange OT through cellophane under standard conditions. Dye concentrations are measured in optical absorbancy units. Data of Ref. 1

Quantitative Treatment. To obtain a more quantitative measure of the effectiveness, if any, of micelles within the membrane, we recall that for any given concentration of micelles the solubilizate distributes itself in a constant ratio between the micelles and the water. Further, as shown by the straight line of Figure 3, the amount dissolved per unit micellized material is also constant so that the ratio of the concentration of dye in water and in the micelles is a constant, r, that is

$$r = c_w/(c_s/c_M) \tag{11}$$

where c_M is the concentration of micelles—*i.e.*, the concentration of surfactant above the CMC. Since this ratio is very low for an efficient solubilizing agent, the concentration of the dye dissolved in water will be small compared with that solubilized and can often be neglected; thus,

$$c_t = c_s + c_w \simeq c_s \qquad (12)$$

The value of r is obtained from solubility measurements and for our system is found (*1*) to be 1.1×10^{-5} equivalents/liter and clearly justifies this approximation. We can now rewrite Equation 6

$$(D_t c_M/r)(dc_w/dx) = (D_s c_M/r)(dc_w/dx) + D_w(dc_w/dx) \qquad (13)$$

Thus, dc_w/dx can be eliminated, and since the rate of dialysis through a membrane, k_t, is directly proportional to the corresponding diffusion coefficient D_t under a given set of conditions, we can write

$$\frac{k_t c_M}{r} = \frac{k_s c_M}{r} + k_w \qquad (14)$$

or

$$k_t = k_s + \frac{k_w r}{c_M} \qquad (15)$$

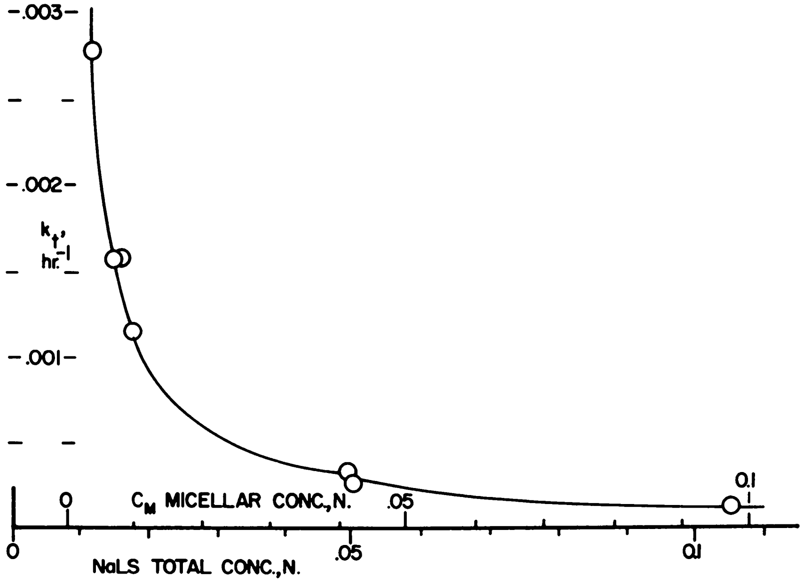

Figure 7. Variation of dialysis rate constants of Orange OT as a function of NaLS concentration. Abscissa shows also the concentration of micelles. Data of Ref. 1

This last equation shows that the observed total rate constant for dialysis is the sum of two terms, one representing the contribution of solubilized material and the other inversely proportional to the concentration of micelles and dependent on both the solubilization ratio r and the rate constant for the transport of dye in water k_w. Figure 8 shows the same results as Figure 7 but plotted as a function of $1/c_M$ in accordance with Equation 15. An excellent straight line is obtained. The intercept is found by a least-square calculation and gives for the rate of dialysis, k_s, of solubilized dye $3.6 \pm 3.3 \times 10^{-5}$ hr.$^{-1}$. This is very small, 1/10 as large as the value originally published (*1*) owing to an arithmetical error on my part. It is also within experimental error of zero and is quite negligible compared with the rate of dialysis of the unsolubilized dye, k_w, for which the slope gives the value of about 1.0 hr.$^{-1}$.

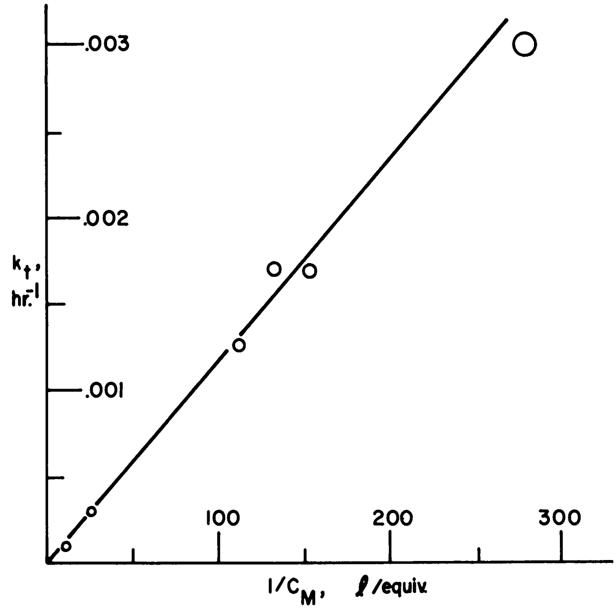

Figure 8. The data of Figure 7 plotted according to Equation 15. The intercept measures the contribution of micelles and is negligible. Data of Ref. 1

Clearly, micelles make no significant contribution to the transport of the dye through the membrane itself in this particular system, although they are extremely important in bringing the dye up to the membrane and in picking it up again on the other side. For other systems, the role played by micelles within a membrane may well be different, but the same experimental approach and analysis can be used to study it quantitatively.

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Vapor Pressure of Pesticides

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Vapor pressures at ambient temperatures of a number of pesticides can be determined by using a du Pont 900 differential thermal analyzer to measure boiling points for a series of pressures down to 10 mm., or by using an effusion method for compounds having vapor pressures from 10^{-3} to 10^{-7} mm. Less than 100 mg. of the sample are required in either case. Accuracy can be determined by comparison with direct measurements available in the literature. Vapor pressures for phenoxy herbicide esters are lower than values reported in the literature.

The measurement of vapor pressures of pesticides is an integral part of the continuing effort to understand the role of vaporization and vapor movement in their action and use. Accurate vapor pressure values are essential to this effort because vapor pressure represents gaseous concentration, and this must be known to understand both vapor movement by diffusion and the biological activity of vaporized pesticides. For example, the vapor pressure of a pesticide sprayed on the surface of a leaf determines the maximum vapor concentration at the leaf surface and, thus, the rate of diffusion away from the leaf. Since it appears that the rate of diffusion essentially controls the rate of evaporation, the residuality of a volatile pesticide may thus depend on vapor pressure. Furthermore, a chemical may reach and be absorbed by a pest as a vapor so that the biological effectiveness of the pesticide can also depend upon its vapor pressure. This can be particularly important for fumigants which act biologically in the gaseous state. Volatilization and vapor movement and, hence, vapor pressure are inextricably involved in the biological action of virtually any "volatile" pesticide.

The term "volatile" is ambiguous. Strictly speaking, every substance is volatile and would evaporate under proper conditions. In practice, of course, some materials have such low vapor pressures that no detectable volatilization is observed under normal use conditions. For pesticides the discovery of more highly active chemicals has pushed this limit steadily downward. Originally the fumigants like ethylene dibromide and carbon tetrachloride were considered volatile, with vapor pressures in the range of *ca.* 1 mm. or greater at room temperature. The discovery that the low molecular weight esters of 2,4-D could produce vapor damage to crops adjoining treated areas showed that an active pesticide with a vapor pressure of 10^{-3} mm. may be "volatile." Later developments such as the seed protectant, Panogen (cyano(methyl mercuri)guanidine), have shown that the term volatile can apply to vapor pressures of the order of 10^{-5} mm., and in the future, uses and chemicals may be found for which even lower vapor pressures would have to be considered volatile under certain conditions of use.

Therefore, any program for measuring vapor pressures must be able to handle a wide range of values—many mm. Hg to 10^{-5} mm. Hg and less. At present, no one method is capable of covering such a range, and several must be used. Published work in this area shows that virtually all available methods have been used at one time or another for measuring vapor pressures of pesticides. The reader is referred to standard works on this subject (*4, 10, 17*), but the following brief survey is offered for orientation.

The methods of measuring vapor pressure may be classified into two types: static and dynamic, depending on whether the system is at equilibrium (static) or whether a sample of saturated vapor is removed and the vapor concentration determined (dynamic). In most instances the static methods work for a higher range of values ($>$ 0.1 mm.) and the dynamic methods for a lower range ($<$ 0.1 mm.). Examples of static methods are (a) use of a gage to measure the pressure increase caused by the pesticide's being released in a closed system (*5*), and (b) measurement of the boiling point of the chemical under a reduced pressure. Examples of dynamic methods include (a) gas saturation (*12*), (b) the Knudsen effusion (*7*), and (c) the jet effusion method (*1*). In Method a, a measured volume of inert gas is saturated with the chemical vapor, and the vapor concentration is determined; in Methods b and c, the quantity measured is the loss of vapor through a small hole into a vacuum. In the Knudsen cell, this rate of loss is frequently measured by a weight loss of the container. In the case of jet effusion, the recoil from this jet of vapor is recorded as the twist generated in a long, fine fiber.

Besides the magnitude of the vapor pressure value, other considerations will influence the choice of method. For example, if the material is a solid at normal use temperatures, boiling point measurements are obviously out of the question. Of frequent importance to pesticide research is the size of sample needed and the influence of impurities. Often when an estimate of vapor pressure for an experimental chemical is needed, the material is available in such limited amounts that preparation of highly purified samples is not feasible. It is important, therefore, that a method be available which is as insensitive to impurities as possible and which requires a minimum of sample. In fact, it would be desirable at times to be able to measure the vapor pressure of a pesticide from a mixture such as a formulation of the pesticide. Sometimes highest accuracy may not be the most important consideration. The actual choice of method will depend on the relative weights assigned to the various considerations.

For pesticide vapor pressure measurements in our laboratory, we used two methods: one static and the other dynamic. For liquids with moderately high vapor pressures (approximately 1 mm. Hg or greater), the du Pont 900 differential thermal analyzer was used to measure boiling points at different pressures. The chief merits of this method are that extremely small amounts of sample are required (10 μliters) and the measurements are rapid. For lower vapor pressures (10^{-3} mm. and less) of both liquids and solids, the Knudsen effusion cell has been used. This use of the Knudsen cell differs from most published methods in that the effusing vapor is caught and determined directly rather than being estimated from the loss in weight of the cell. This has two advantages: (a) impurities can be "ignored" by appropriate choice of analytical method, and (b) the amount of sample required is small (50 to 200 mg.). A disadvantage is that for low vapor pressures long times may be required to collect sufficient material for analysis. Estimates of pressure in the intermediate range of 10^{-3} to 0.1 mm. have been obtained from measurements at lower or higher temperatures and well established temperature/vapor pressure relationships.

Experimental

A schematic of the du Pont 900 differential thermal analyzer is shown in Figure 1. In outline it is quite simple—namely, a heating block with two wells into which thermocouples are inserted, and associated instrumentation for sensitive determination of temperature difference between the two thermocouples. The bell jar over the block controls the pressure in the system. To determine a boiling point, thin-walled glass tubes, about 4 mm. in diameter, are loaded with 1 or 2 mm. of microglass beads, placed in the block, 0.01 to 0.02 ml. of liquid is injected into one capillary, and the thermocouples are inserted. After the pressure in the system is stabilized, the heating cycle is begun, and when the boiling point of the liquid is reached, vaporization prevents any further temperature rise in one capillary; hence, the difference in temperature which develops is recorded on the graph of the machine. The pressure in the bell jar which encloses the entire heating block can be and is quickly raised to quench the boiling, thus permitting several boiling point temperature measurements to be made on a single sample of pure material before loss of material terminates the run. For mixtures, however, the loss of volatile components during boiling changes the composition too rapidly to allow a valid measurement of boiling point. Figure 2 shows a graph or data sheet for a series of measurements from a run on ethylene dibromide. Each dip represents the boiling point at one pressure, so that seven or even more points were obtained from the single 0.01-ml. sample. The complete run of a number of points is made in a period of 10 to 20 minutes, depending on the rate of heating.

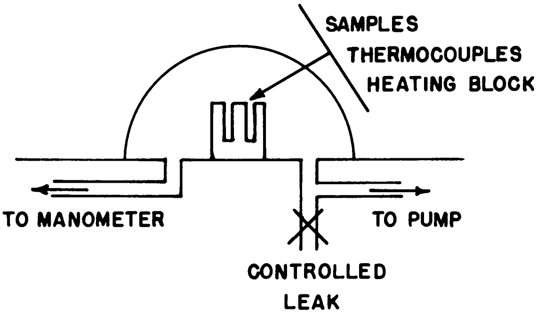

Figure 1. du Pont 900 differential thermal analyzer for determining boiling point–pressure curves

The apparatus used for many of the vapor pressure measurements by the Knudsen effusion cell was modeled closely after that described by Carson *et al.* (7). The vapor effusing into a vacuum from a small hole in a chamber is condensed on a surface cooled by dry ice–acetone or liquid nitrogen. Carson *et al.* used radioactive compounds and determined the radioactivity condensed as a measure of the quantity effused. We have found that organic chemicals can be removed satisfactorily by methanol, cyclohexane, and other solvents from a surface of glass or stainless steel disc (attached to the flat glass surface), so that this method can be extended to non-radioactive materials. Difficulties were experienced with the large taper joints used in the design of Carson *et al.*, particularly metal to glass. The liberal use of silicone lubricant was required to prevent breakage of the joint owing to differential expansion of the metal and glass; this produced a contamination problem when measuring low vapor pressures, especially below 10^{-5} or 10^{-6} mm. Hg. Therefore, the apparatus was redesigned to use O-ring seals as shown in Figure 3.

The sample disc is contained in a chamber formed from two nonmagnetic stainless steel parts, base and chamber cover. The vapor escapes from the chamber through a small hole (of accurately determined area and thickness) directly under and about 4 mm. from the collection surface. The collection surface, which is ground flat and polished, is the bottom surface of a well containing the coolant which is normally liquid nitrogen. This glass apparatus was fabricated from a section of standard borosilicate glass pipe, whose flange clamps to the metal units as indicated. Silicone O-rings are quite satisfactory if they are periodically soaked overnight in methanol or acetone to remove volatile contaminants.

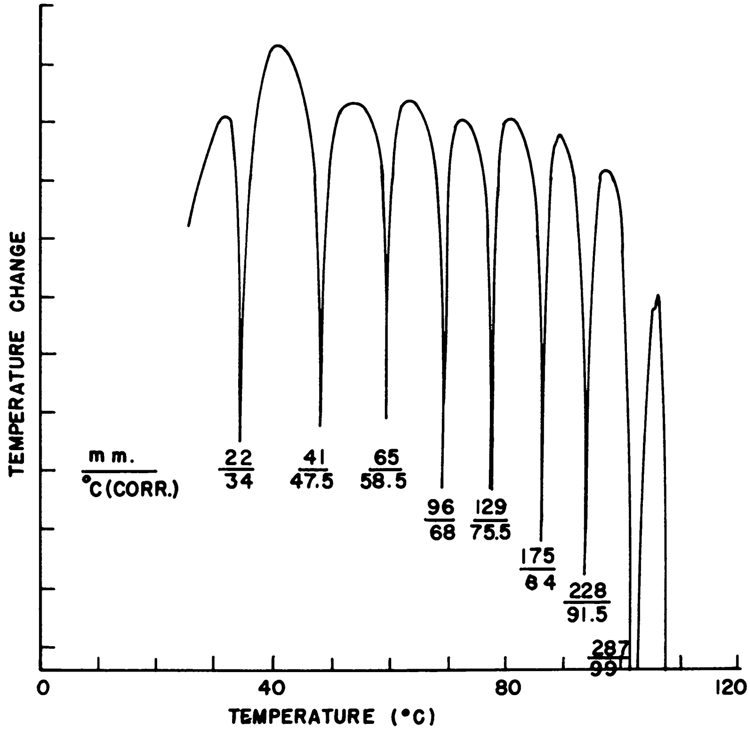

Figure 2. Boiling point vs. *pressure for ethylene dibromide as determined by the differential thermal analyzer. Heating rate = 15°C. per minute; vertical scale 0.1°C. per division*

There is also a small magnetic stainless steel disc which can be pulled on and off the effusion hole with a magnet and thus start and stop effusion runs. Hence, the rest of the apparatus must be nonmagnetic. A cover over the top of the chamber (not shown) provides a channel for movement of this disc and serves as a "heat shield" for the chamber. The opening in this cover is large enough so that there is no interference with the effusion "beam." The entire metal part of the apparatus is immersed in a water bath to control the temperature. Two accessories were found necessary for operating the apparatus. A U-tube type of trap (cooled with liquid nitrogen) was needed to protect the vacuum line from contamination and to check for efficient condensation of effusing vapors. When the apparatus is operating properly, washings from the trap and other portions of the glass equipment will show no trace of the chemical being trapped on the condensing surface. A large Dewar flask, which is attachable by a vacuum-jacketed glass joint, can be inserted in the cold finger to provide a reservoir of liquid nitrogen sufficient to allow an overnight run. Very low vapor pressures are, in theory at least, determinable in this way, but blanks, representing contaminants in the apparatus, including the O-rings, are a practical limitation. Normal cleaning precautions reduce the blanks to a level which does not interfere with vapor pressure measurements of approximately 10^{-5} mm. More heroic measures are needed for very low vapor pressures such as 10^{-7} or less. Fortunately, pesticides with such low vapor pressures are usually not volatile in any practical sense. The lower limit for vapor pressure will also depend upon the sensitivity of the analytical method available. In all this work, ultraviolet absorption has been used since the compounds of interest have been unsaturated ring compounds, but other methods could be used equally well.

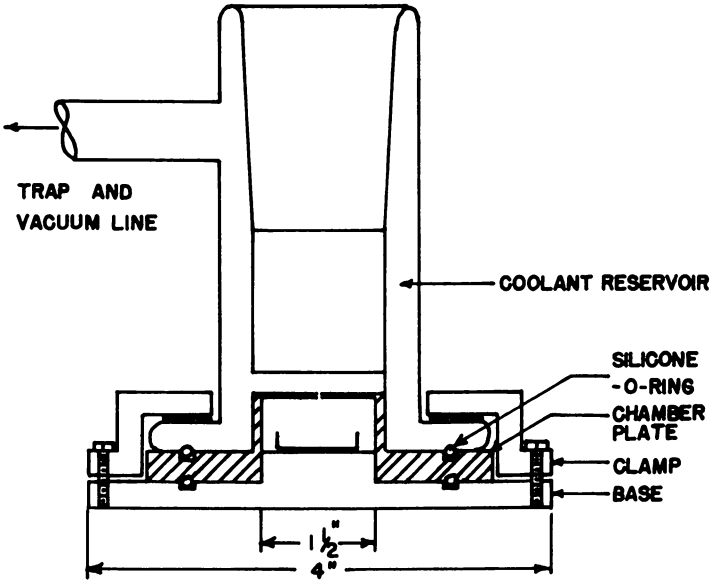

Figure 3. Improved effusion cell for vapor pressure measurement

Results

Some measurements with the differential thermal analyzer are summarized in Table I. The data are condensed into the two constants of the Clausius-Clapeyron equation:

$$\log P \text{ (mm.)} = A - B/T \text{ (°K.)}$$

From these constants, vapor pressure can be estimated for any desired temperature, and this is done for 25°C. or the melting point if that is higher. Since individual data points were lost in the curve fitting, some indication of variability is needed; this is provided as the standard deviation for the regression and the 95% confidence interval for the calculated value at 25°C. (or the melting point).

$$\text{Standard deviation} = \sqrt{\frac{(\log P\ (\text{calc.}) - \log P\ (\text{obs.}))^2}{(\text{No. of obs.} - 2)}}$$

$$95\%\ \text{Confidence interval} = t_{.05} \times \text{Std. Dev.} \sqrt{1/n + \frac{(\overline{X} - X)^2}{SSX}}$$

n = Number of data points.

$\overline{X}$ = Mean value for $1/(t(°\text{C.}) + 273.15)$ from data.

X = $1/(t(°\text{C.}) + 273.15)$ for temperature of calculated vapor pressure.

SSX = $\Sigma\left(\overline{X} - \frac{1}{t(°\text{C.}) + 273.15}\right)^2$ for all data points.

$t_{0.05}$ = Student's T for 0.05 level with $n - 2$ degrees of freedom.

(*See* any standard statistical reference such as Snedecor (*18*, pp. 43 and 125).)

The standard deviation is an indicator for the average deviation of the regression line from the experimental points. For example, with one of the ethylene dibromide runs the average for the absolute values of differences between calculated and observed values of log P was 0.0053, and the standard deviation was 0.0079.

It would appear from Table I that the available comparison data are just as variable as data obtained with the differential thermal analyzer. The second index of variability, the 95% confidence factor, is a measure of the expected precision for the estimated vapor pressure at 25°C. (or melting point). This includes not only the variation of the experimental points from the regression line but also the uncertainty in the slope of that line. This latter factor has a progressively greater effect as the line is extended—*i.e.*, the further the extrapolation is carried beyond the experimental data. For ethylene dibromide, for example, there is a 95% probability of the vapor pressure lying between 12.0 and 12.8 (12.4 ÷ 1.032 and 12.4 × 1.032).

It is obvious from Table I that this internal variability of the data does not account for differences between different observers. For bromobenzene and ethylene dibromide our values are higher than those in the literature. The value for water coincides closely. It seems reasonable to expect an accuracy of better than 10 or 20% for these types of compounds.

Vapor pressures obtained by the Knudsen effusion method are shown in Table II. The precision of the determinations is indicated by the 95% confidence interval computed either from an average of experimental determination or from the standard deviation of the regression equation.

Table I. Vapor Pressures Determined with the Squares Method to the

$\log_{10}$ P =

Compound	*Reference*	A	B
C_6H_5Br	Observed	7.7807	2105.4
	13	7.9336	2165.9
EDB (liquid)	Observed	7.8632	2018.1
	5	8.6615	2279.3
Water	Observed	8.8076	2215.8
	8		
Hydroquinone	Observed	9.9167	3509.3
(m.p., 170°C.)	*19*	9.4065	3629.2
Acetanilide	Observed	8.8854	3462.5
(m.p., 113°-114°C.)	*11*	9.5194	3767.1

[a] Unless temperature is otherwise indicated.
[c] *See* text under Results.

In most cases, the literature values lie within this range, indicating agreement within experimental variability. Again, it seems reasonable to expect an accuracy of better than 10 to 20%.

Data were also obtained by this method for the solid states for the methyl ester of 2,4-D, the *n*-propyl ester of 2,4,5-T, and the butyl ester (liquid) of 2,4-D. The results are shown in Table III. These data were fitted by the least squares method to the Clausius-Clapeyron equations given in footnotes to Table III. These equations were used to estimate the vapor pressures at several temperatures, including the melting point. In Table IV, these are compared with estimates from other sources. Jensen's unpublished data with the Knudsen method compare favorably with those reported in this work, but the published values obtained by other methods are larger.

The differences that are observed in Table IV reflect two factors: the melting point and extrapolation uncertainties. In the case of the estimates at 25°C. for methyl 2,4-D by Mullison and Hummer (*16*) and by Jensen and Schall (*14*), the fact was overlooked that the melting

Differential Thermal Analyzer Fitted by Least Clausius-Clapeyron Equation

$$A - \frac{B}{(t(°C.) + 273.15)}$$

Temp. Range, °C.	*Calc. V.P. 25°C.*[a]	*Std. Dev.*[b]	*95% Conf. Factor*[c]	*Comments*
49–131	5.23	.014	1.05	3 runs 29 points
30–190	4.67	.020	1.03	
47–109	12.4	.0079	1.03	3 runs 17 points
9.6–25.1	10.4	.021	1.07	15 points
34–91	23.7	.0096	1.04	1 run 10 points
	23.756			
181–254	17.7	.0079	1.04	1 run 8 points
174–268	17.5 (170°C.)	.00775	1.04	11 points
181–268	0.83	.017	1.24	1 run 7 points
150–251	0.58 (113°C.)	.019	1.19	11 points

[b] Sample standard deviation from regression of Snedecor (Ref. *18*, p. 125).

point of methyl 2,4-D is 39°C. with the result that their estimates could be expected to be high. The temperature coefficient for vapor pressure of the solid state is higher than that for the liquid state, to a degree determined by the heat of fusion for the substance. Jensen has kindly provided us with unpublished data from Knudsen cell measurements on methyl 2,4-D, one value for solid state (28°C.) and a range of values for the liquid state (60° to 100°C.). The agreement with our results, as shown in Table IV, is well within experimental variability.

The agreement in the case of the published data is not close. It is felt that this is contributed to by the process of extrapolation which is, at best, a hazardous occupation. In many cases such as this the measurements are made at elevated temperatures, and vapor pressures at room temperature are calculated from the Clausius-Clapeyron equation. There are two uncertainties in this extrapolation process: uncertainty in the slope of the line of best fit and inaccuracy in the equation itself.

The first factor, which arises because of the inevitable uncertainty present in any experimental data, can be estimated statistically as indi-

Table II. Comparison of Vapor Pressures by the Effusion Method with Literature Results

Compound	*Temperature, °C.*	*Average Pressure, mm. Hg*	*95% Confidence Interval*	*Literature Value*[a]	*% Diff., Obs.-Lit. / Obs.*
α-Chloro-*m*-nitroacetophenone	25	1.09×10^{-5}	$\pm .25 \times 10^{-5}$	8.7×10^{-6}	+20%
	35	3.37×10^{-5}	$\pm .30 \times 10^{-5}$	3.7×10^{-5}	− 9.8%
Thymol	0	5.79×10^{-4}	$\pm 1.1 \times 10^{-4}$	5.5×10^{-4}	+ 5.0%
	25	1.70×10^{-2}	$\pm .13 \times 10^{-2}$	1.6×10^{-2}	+ 5.9%
	35	7.90×10^{-2}	$\pm .19 \times 10^{-2}$	5.4×10^{-2}	−31%
4,6-Dinitro-*o*-cresol	35	3.6×10^{-4}	$\pm .22 \times 10^{-4}$	4.0×10^{-4}	−11%
2-Chloro-6-(trichloromethyl)-pyridine	23	2.71×10^{-3}	—	2.84×10^{-3} [b]	− 4.8%
Trifluralin[c]	29	2.19×10^{-4}	$\pm .14 \times 10^{-4}$	1.99×10^{-4}	+ 9.1%

[a] Data from Balson (*1*) except where otherwise indicated.

[b] Determined by the gas saturation method.

[c] Calculated from least squares fit of Clausius-Clapeyron equation:

$$\log_{10} P = 13.7126 - \frac{5249.2}{(t(°\text{C.}) + 273.15)}$$

Literature value from manufacturer's brochure.

cated in the discussion of the DTA data. For example, with Jensen and Schall's data for the vapor pressure of the methyl ester of 2,4-D, the experimental uncertainty at 225°C. for an estimate by the Clausius-Clapeyron equation can be expressed as a 95% confidence interval of 4.6% in the vapor pressure value. At 39°C., this figure has become 36%. For the data in Table IV, this extrapolation error is estimated to vary between 15 and 84%.

The second factor involves the particular mathematical function chosen to represent the data and is not easy to estimate. Some idea can be formed by considering data which are known to deviate from the Clausius-Clapeyron relation—*e.g.*, that of Balson and co-workers on lewisite and mustard gas. From careful measurements of vapor pressure over a wide range of temperature (120°C.), they showed that the plot of log *P* *vs.* 1/*T*(°K.) was not the straight line predicted from the Clausius-Clapeyron equation. However, the deviation was not large (< than twofold), and Balson concluded that for temperature ranges of 50°C. or less, the Clausius-Clapeyron equation fits within experimental error for even careful experimental work. It must be emphasized that he is speaking of both accurate and extensive data. In the case of mustard gas, Balson presents data for 20 well-spaced temperatures; in the case

Table III. Vapor Pressures of Esters of Phenoxyacetic Acid Herbicides by the Knudsen Effusion Method

Compound	*Temperature, °C.*	*Observed Vapor Pressure, mm.*	*Calculated*[a] *Vapor Pressure, mm.*
2,4-D methyl ester (m.p., 39°C.)	17.6	1.07×10^{-4}	1.16×10^{-4}
	17.8	1.23×10^{-4}	1.19×10^{-4}
	25.0	3.5×10^{-4} 3.29×10^{-4} 3.24×10^{-4}	3.25×10^{-4}
	34.6	1.28×10^{-3}	1.16×10^{-3}
	34.8	1.12×10^{-3} 1.17×10^{-3}	1.19×10^{-3}
	39	—	2.01×10^{-3}
2,4-D *n*-butyl ester (liquid at lowest temp.)	16.0	3.42×10^{-6}	3.33×10^{-6}
	16.5	3.01×10^{-6}	3.52×10^{-6}
	24.2	8.14×10^{-6} 1.33×10^{-5} 7.89×10^{-6}	8.14×10^{-6}
	24.8	8.43×10^{-6}	8.67×10^{-6}
	25.4	9.55×10^{-6}	9.24×10^{-6}
	25.5	8.28×10^{-6}	9.34×10^{-6}
	34.6	2.01×10^{-5} 2.05×10^{-5}	2.36×10^{-5}
	34.8	2.55×10^{-5}	2.41×10^{-5}
	44.0	5.84×10^{-5} 6.38×10^{-5}	5.82×10^{-5}
	25.0	—	8.68×10^{-6}
2,4,5-T *n*-propyl ester (m.p., 47°C.)	0	2.37×10^{-6}	2.83×10^{-6}
	25	7.46×10^{-5} 6.3×10^{-5}	4.70×10^{-5}
	25.5	4.57×10^{-5}	4.95×10^{-5}
	34	7.98×10^{-5}	1.15×10^{-4}
	35.5	1.24×10^{-4}	1.30×10^{-4}
	40	2.14×10^{-4} 1.81×10^{-4}	2.04×10^{-4}
	47	—	3.87×10^{-3}

[a] Values were calculated from the following equation which had been fitted by the least squares method to the data:

Methyl 2,4-D $$\text{Log}_{10} P\ (\text{mm.}) = 14.1598 - \frac{5261.6}{t\ (^\circ\text{C.}) + 273.15}$$

n-Butyl 2,4-D $$\text{Log}_{10} P\ (\text{mm.}) = 8.5912 - \frac{4067.9}{t\ (^\circ\text{C.}) + 273.15}$$

n-Propyl 2,4,5-T $$\text{Log}_{10} P\ (\text{mm.}) = 8.9984 - \frac{3973.4}{t\ (^\circ\text{C.}) + 273.15}$$

Table IV. Comparison of Vapor Pressure Values

Compound	*Temp., °C.*	*This Investigation*	*Literature Value*	*Estimate of Error: 95% Confidence Factor*
Methyl 2,4-D ester	25	3.25×10^{-4}mm.	1.55×10^{-3}	—
	25	3.25×10^{-4}mm.	2.3×10^{-3}	—
	28	6.86×10^{-4}mm.	7×10^{-4}	—
	39	2.01×10^{-3}mm.	2.04×10^{-3}	1.42
	(m.p.)			
	(m.p.)	2.01×10^{-3}mm.	6.78×10^{-3}	1.36
n-Butyl 2,4-D ester	25	8.86×10^{-6}mm.	3.97×10^{-4}	1.48
n-Propyl 2,4,5-T ester	47	3.86×10^{-4}mm.	1.37×10^{-3}	1.84

[a] The constants in this equation differ slightly from those in the reference because more data were used to obtain the latter. Vapor pressure estimates do not differ greatly, however; 7.39×10^{-3}mm. for 2,4-D methyl ester and 1.61×10^{-3} for *n*-propyl 2,4,5-T.

of lewisite, 37 points were used to establish the curve. Very little data in the literature of vapor pressure of pesticides are in this category.

The deviations observed between extrapolated estimates from GLC data, and direct measurements with the effusion measurements appear to be too large to be accounted for by extrapolation uncertainties. The best estimate can probably be obtained by fitting the combined data to the Clausius-Clapeyron equation (footnote *b* of Table IV). The obvious implication is that where possible, extrapolation of pesticide vapor pressures obtained at elevated temperatures be converted to interpolation by including a direct measurement at room temperature. In terms of the work described here, vapor pressure measurements requiring the DTA should be supplemented with Knudsen cell measurements. This would require a temperature at which the vapor pressure was 10^{-3} mm. or less.

Corrections in Knudsen Effusion Method. Two corrections must be applied in the Knudsen effusion method to prevent large errors: correction for (1) finite thickness of the orifice plate and (2) pressure drop owing to loss of vapor through the orifice. The first correction is necessary because the Knudsen effusion equation shown below is derived from an orifice with negligible thickness. Orifices whose thicknesses are an appreciable fraction of their diameter have collimating action that diminishes their effective area. A correction factor attributed originally to Clausing

for Esters of Phenoxyactic Acid Herbicides

Method	*Temp. Range, °C.*	*Reference and Regression Eqn.*[b]
B.p. *vs.* temperature	—	*16*
GLC	171-300	*14*
Knudsen Effusion cell	28	Jensen (private communication)
Knudsen Effusion cell	60–100	Jensen (private communication)
GLC	171-300	*14* $(\text{Log } P = 8.50747 - 3495.4/t(°\text{K.}))$[c]
GLC	171-300	*14* $(\text{Log } P = 9.01015 - 3700.3/t(°\text{K.}))$[c]
GLC	171-300	*14* $(\text{Log } P = 9.31670 - 3899.4/t(°\text{K.}))$[c]

[b] If the data of Jensen and Schall are combined with that of this investigation, the following equations represent best fit for the vapor pressure of the liquid state:

Methyl 2,4-D (39–300°C.) – $\text{Log } P = 9.70660 - 3909.3/[t(°\text{C.}) + 273.15]$

n-Butyl 2,4-D (16–300°C.) – $\text{Log } P = 11.41254 - 4917.9/[t(°\text{C.}) + 273.15]$

n-Propyl 2,4,5-T (47–300°C.) – $\text{Log } P = 44.95766 - 6399.7/[t(°\text{C.}) + 273.15] - 11.37000 \log [t(°\text{C.}) + 273.15]$

n-Propyl 2,4,5-T (47–300°C.) – $\text{Log } P = 10.1304 - 4311.0/[t(°\text{C.}) + 273.15]$

(9) (*see* Kenard (*15*)), when multiplying the actual area, produces an "effective" area which is valid in the Knudsen equation:

$$W = PA\left(\frac{M}{2\pi RT}\right)^{1/2} t$$

W = Weight loss by effusion
P = Vapor pressure in the chamber
A = Area of the orifice
M = Molecular weight of the vapor
R = Gas constant
T = Absolute temperature
t = Time

$$f = \frac{20 + 8\,(D/R)}{20 + 19\,(D/R) + 3\,(D/R)^2}$$

f = Clausing factor
D = Depth of the hole
R = Radius of the hole

Table V. Vapor Effusion of 2-Chloro-4-aminopyrimidine

Orifice Radius, cm.	*Area, sq. cm.*	*Average Effusion Rate, μgram/hr.*	*Flux $\frac{\mu gram/hr.}{sq. cm.}$*	*No. of Runs*
0.01060	3.530×10^{-4}	5.34	15,114	2
0.01809	1.028×10^{-3}	23.9	23,225	4
0.03886	4.744×10^{-3}	80.2	16,922	6
0.05332	8.932×10^{-3}	170.5	19,094	8
0.1793	0.1010	1,430	14,163	3

[a] From the least square regression equation: $\frac{\mu gram/hr.}{sq.\ cm.} = 10^4\ (1.9204 - .03378 \times \mu gram/hr.)$.

For the orifices in our apparatus, this factor varied from 0.5 to 0.7.

To determine the effect of orifice size on vapor pressure, five different orifices were used to measure the effusion rates at 25°C. of one compound, 2-chloro-4-aminopyrimidine. Carson, Cooper, and Stranks (*6*) have shown that the net rate of effusion is directly proportional to the flux (rate of effusion per unit area) if other factors are constant. That is, a graph of effusion rate (μgram/hr.) *vs.* flux $\left(\frac{\mu gram/hr.}{sq.\ cm.}\right)$ would be a straight line that can therefore be extrapolated to zero orifice. The results of this test, shown in Table V, were somewhat variable, but a best straight line was fitted by the least squares method. From this line the limiting flux was estimated.

The fact that Carson *et al.* found larger errors for comparable orifice sizes can probably be accounted for by their smaller chamber (approximately one-third in volume). Exact comparison is difficult because of uncertainty in the amount and nature of the sample surface. In any case, considering the experimental variability, the pressure-drop error apparently can be safely neglected (3%) if the orifice is 1 mm. or less in diameter, which was the case for all the work reported here.

In connection with the orifice test, the vapor pressure of the solid state of this pyrimidine was also determined over a range of temperature from 0° to 50°C. The Clausius-Clapeyron equation fitted by least squares to the 14 measurements made was:

$$\log P = 11.73591 - 4609.3/T\,(°K.)$$

and the calculated vapor pressures at 20° and 25°C. were 1.03×10^{-4} and 1.89×10^{-4} mm. This material is being developed in Japan as a nitrification inhibitor.

as a Function of Orifice Diameter

Std. Dev.	*Calc.*[a] *µgram/hr. / sq. cm.*	*% of Limiting Flux*[b]	*% Difference from Observed Value*
—	19,187	99.9	+21.2
286	19,121	99.6	−21.5
747	18,925	99.5	10.6
390	18,611	96.91	2.6
330	14,231	74.1	0.5

[b] Carson, Cooper, and Stranks (6) report the following for tetraphenyltin and tetraphenyllead:

orifice radius (cm.)—0.1, 0.05, 0.025

% of Limiting flux—50, 87, ~99

Conclusion

The two methods described for determining vapor pressures appear to give reliable vapor pressure data for "volatile" pesticides and fumigants. The precision is better than 10 to 20% in most cases. Care must be taken, particularly with the determination of low vapor pressures which can be difficult. Estimation of vapor pressures by Clausius-Clapeyron and other related functions is dependable for interpolation and limited extrapolation. Extensive extrapolation is, as always, dangerous, and a direct measurement should be made as closely as possible to the desired temperature. The literature contains a number of examples which violate this principle.

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The Role of Surfactants in Modifying the Activity of Herbicidal Sprays

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Surfactants, by virtue of their combined polar and apolar nature, often facilitate and accentuate the emulsifying, dispersing, spreading, wetting, solubilizing, and/or other surface modifying properties of herbicidal formulations. Reducing surface or interfacial tension and contact angle improves spreading and wetting, to a point, thus favoring penetration. However, subtler and more specific herbicide–surfactant–plant surface interactions must account for enhancement beyond that attributable to improved wetting. Both polar (hydrophilic) and apolar (lipophilic) absorption pathways through plant cuticle apparently exist. For certain chemical groups, definite structural configurations are apparently related to activity (or inactivation), translocation, and biodegradability. Radiotracer studies indicate that surfactants enhance primarily at the point of application and in immediately underlying tissues. Presently, there is no evidence for surfactant-facilitated herbicide translocation, per se.

Considerable information is known about the absorption, translocation, and gross physiological mode of action of several recommended herbicides (*1, 2, 10, 11, 12, 13, 14, 16, 25, 38, 52, 65*). Relatively little

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information is available, however, concerning the modifying effects of chemical additives on the uptake, distribution, and persistence of herbicides and the ultimate fate of the additives themselves in plants and soils.

Numerous herbicides are currently recommended and used for weed control in agricultural, industrial, and recreational areas. However, the method of formulation and application of such chemicals to plants or soils may markedly affect their biological efficacy and persistence. Chemical additives (primarily surfactants) in both oil and aqueous sprays are already used widely, and when properly understood, promise a virtual revolution in the use of agricultural chemicals. Conceivably, not only weed control performance and herbicidal selectivity can be altered but also distribution, metabolism, and accumulation of chemical residues. With the widespread introduction and increasing use of chemical additives in weed science and technology, we must therefore "learn to reflect on what before we knew" about the use of herbicides.

This article is a brief report on the state of knowledge in certain aspects of the field, selected literature citations, a resumé of some of our recently published articles (*22, 23, 24, 25, 26, 27, 28, 54, 55, 56, 57, 58, 59*), and summary statements relating to unpublished work by one or both of the authors at the University of California, at Ft. Detrick, Maryland, and at Virginia Polytechnic Institute.

Terminology

Surfactants are additive chemicals which possess surface modifying properties—*i.e.*, they possess the ability to reduce the surface energy of solvents at low concentrations. Many chemical substances qualify for inclusion under the name surfactant, and McCutcheon (*41*) lists over 3000 commercial materials. Many other chemicals not listed by McCutcheon also qualify as surfactants (surface-active agents).

Collectively termed additives, these chemically diverse substances are sometimes grouped according to type of action (*15*) as follows: surfactants (wetting agents, spreaders, penetrants), stabilizing agents (dispersants, emulsifiers), co-solvents (coupling agents), hygroscopic agents, deposit builders (stickers), activators, etc. These types of actions may sometimes be real, sometimes imaginary, but they are not necessarily mutually exclusive. Thus, in part because the role, function, and rate of such substances are poorly understood, even the terminology of herbicidal additives remains confused. The assumption that all of these commonly used terms are synonymous has only contributed to and perpetuated the confusion.

Nature of Surfactant Action

Surfactants are usually classified into three main groups—*i.e.*, anionic, cationic, and nonionic, depending on their ionic nature in solution. A fourth group is sometimes included, and these are called amphoteric surfactants, which show both anionic and cationic properties depending on pH.

The diversity of the chemical structures possible in these compounds is enormous, thus making it difficult to arrive at precise structure-activity relationships. In many instances commercial preparations are mixtures of surfactants with the mean length or weight of any side group or chain being distributed around a Poisson distribution curve. Thus, there is tremendous variation possible within individual surfactants and mixtures of surfactants, often making it difficult to interpret results.

In general, a surfactant molecule consists of two parts, a hydrophobic part and a hydrophilic portion. The combined polar and apolar nature of these molecules as well as their interactions with adjoining molecular groups appear to determine their emulsifying, dispersing, spreading, wetting, solubilizing, and other surface-active properties.

Increasing numbers of surface-active agents, detergents, and other chemical substances have found application in various phase of biological science in recent years (*15, 20, 41, 45, 49, 51, 53*). Several chemical compounds or mixed (formulated) products including the new biodegradable surfactants increase the effectiveness of herbicidal solutions, on occasion, presumably by promoting penetration (*7, 15, 16, 19, 22, 23, 24, 28, 29, 33, 34, 37, 42, 43, 44, 57, 58, 59, 60, 66*). The fact that certain surfactants may enhance the activity of herbicidal sprays has been known for the past 25 years (*66*), but precisely how and where do they exert their influence? Acceptance of various surfactants in agricultural practice has been based too much in the past on the results of empirical testing rather than fundamental scientific principles.

Although it is generally conceded that the nature of herbicidal enhancement is closely allied with penetration (*16*), surfactants could conceivably influence the activity of herbicidal sprays at several sites. These sites could include areas

(a) within the actual spray solution,
(b) on the cuticle surface,
(c) within the cuticle layers,
(d) within or on the surfaces of living cells underlying the cuticle, and/or
(e) within plant tissues removed from the treated area.

Generally, surfactants (surface-active agents) may facilitate and accentuate the emulsifying, dispersing, spreading, wetting, solubilizing, and/or surface modifying properties of herbicidal formulations to bring about enhancement of foliar penetration and herbicidal action (*12, 15, 19, 25, 37, 38, 60*). Surfactants presumably accomplish this by virtue of their combined polar and apolar properties in the same molecule, rendering compatible aqueous and lipoidal phases. Surfactants by their nature normally reduce surface tension of aqueous systems, improve wetting to a point, and may favor both stomatal and cuticular penetration (*12, 15, 16, 22, 23, 25, 28*).

Recently, herbicides which formerly showed little or no foliar activity (*e.g.*, atrazine and diuron) have been used effectively with surfactants and/or oils as post-emergence herbicides (*3, 17, 36, 39, 42, 43*). This approach offers promise in that lower rates may be required for equal weed control and at the same time residue hazards may be reduced.

Surfactants have also enhanced the uptake of herbicides by plant roots from nutrient solution, where neither stomata nor cuticle is involved (*15*). Altered herbicidal toxicity patterns have been observed in field studies using surfactants (*6*). Here, penetration rather than cuticle wetting is obviously of primary importance but still not understood. Also, as with foliar applications, influences on translocation, accumulation, and metabolism of herbicides may be involved. Exactly where do herbicides and surfactant applied in the same solution part company? Is it possible to enhance both absorption and translocation of herbicides by using suitable surfactants? The application of pesticide chemicals and additives to the soil may markedly affect the chemical, biological, and physical properties of both—another area of potentially great importance that is only now receiving meager attention (*54*). Water percolation and leaching of herbicides are apparently affected by the addition of surfactants to soil of irrigation water (*4*). It has been shown that surfactants can increase or decrease the leaching of diuron in the soil (Figure 1) and that structure–activity relationships exist between the structure of certain surfactants and the degree of adsorption of diuron by the soil (*54*).

The fact that certain surfactants alone may exhibit physiological, biochemical, and morphogenic effects, both stimulatory and inhibitory (*5, 8, 32, 38, 46, 48, 49, 61, 62, 63, 64*), has gone almost entirely unnoticed. Each of these aspects also requires study in relation to its influence on herbicide residues.

Comments on Herbicide–Surfactant–Plant Interactions

Numerous physical and chemical interactions among herbicides, surfactants, solvents (carrier), and plant surfaces are conceivable and probable, though inadequately studied as yet.

Surfactants do not always enhance, but may have no effect or even be detrimental to the action of a herbicide depending on many factors

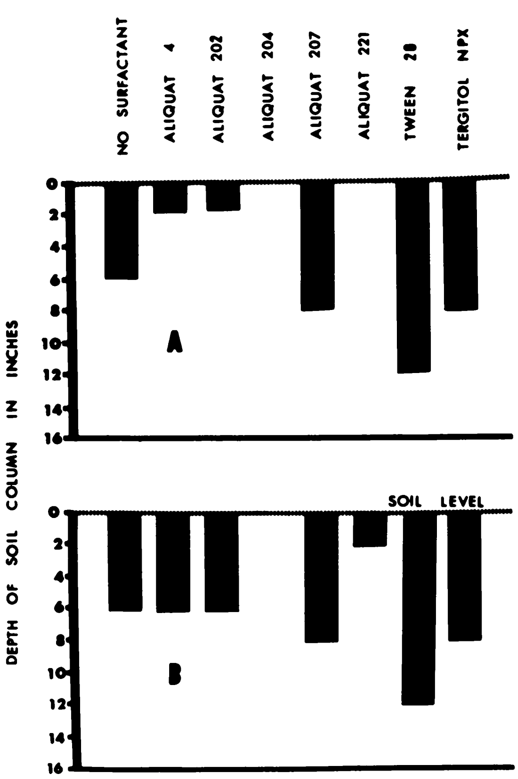


Figure 1. Influence of surfactants on leaching depth of diuron as determined by 50% kill of oats in 2-inch soil columns

(A) 10 grams/liter surfactant, 10 inches simulated rainfall

(B) 100 grams/liter surfactant, 10 inches simulated rainfall

From Soil Science (54), © *1966 by Williams & Wilkins Co., Baltimore.*

(*15, 33, 34, 37, 47*). The nature of total surfactant action in the uptake of herbicides is complex and poorly understood; however, influences of the chemical and physical environment must be important and appreciable. In some instances, specific interactions between herbicide and additive, ionic or otherwise, may occur at interfaces, altering both physicochemical properties and herbicidal performance (*18, 34, 35, 57*).

Interactions between surfactants and herbicides in spray solutions are known to occur (*57*), and those studied either have no effect or are detrimental to herbicide activity. No definite evidence exists that surfactant–herbicide interactions in solution cause enhanced activity of herbicides.

Table I. Initial Count Rate (c.p.m.) 5 Minutes after Mixing in c.p.m. 2 Hours Later Recorded at the Solution–Air

Surfactants, Ionogenic Class and Chemical Designation	*Commercial Designation*[b]	*Mol. wt.*[c] *(approx.)*
Nonionic surfactants		
Polyoxyethylene sorbitan monolaurate	Tween 20	1225
Dodecyl ether of polyoxyethylene glycol	Surfactant WK	438
Polyoxyethylene polyoxypropylene polyol	T-1947	1600
Polyoxyethylene glycol 400 monolaurate	Nonisol 100	626
Anionic surfactants		
Sodium lauroyl sarcosine	Sarkosyl NL	300-310
Sodium dioctyl sulfosuccinate	Vatsol OT	444
Alkylarylsulfonate	Ultrawet DS	350
Sodium dodecyl sulfate[e]	—	288
Cationic surfactants		
Alkyl imidazolinium chloride	Quaternary O	450
1-Hydroxyethyl-2-heptadecenyl glyoxalidine	Amine 220	350
No surfactant	—	—

[a] Surfactant concentration, 1.0 gram/liter. Trials were replicated twice each.

[b] Mention of commercial products and companies is for specific identification of the surfactants evaluated and does not imply endorsement by the University of California over others of similar nature not mentioned.

[c] Molecular weights as well as chemical identification of the surfactants studied were obtained mostly from company literature.

[d] Sources: (1) American Cyanamid Co., Princeton, N. J.; (2) Atlantic Refining Co.,

One type of interaction that can occur in solution is chemical in nature, as that between a positively charged molecule, such as the herbicide paraquat, and negatively charged molecule, such as the anionic surfactants. However, work at Davis (*57*) has shown that not all such interactions are detrimental to the effectiveness of the herbicide. It appears that even though the chemical interaction has occurred, it is not in itself sufficient to prevent the toxicity of paraquat. This seems to depend on the structural nature of the surfactant molecule and the concentrations of the surfactants and herbicides used. Table I shows that paraquat-^{14}C in solution with surfactants of the anionic type is adsorbed or oriented toward the surface layers of the mixture. Presumably this type of result indicates chemical ionic adsorption of paraquat-^{14}C into the multilayered or monolayered solution–air interface of anionic surfactant molecules.

Other molecular interactions in solution between herbicide molecules and surfactant micelles have been suggested (*58*), but no direct evidence exists for this assumption, although the cleaning action of detergents has been explained in this way (*20*).

Paraquat-^{14}C with 10 Surfactants, Together with the Increase Interface of the Paraquat-^{14}C and Surfactant Mixtures (*57*)[a]

Source[d]	*Initial CPM*		*Increase in CPM*	
	Trial 1[e]	*Trial 2*[f]	*Trial 1*	*Trial 2*
(3)	1250	887	443	163
(4)	1282	976	852	261
(8)	1325	720	347	259
(5)	1227	961	386	273
(5)	1536	992	1450	760
(1)	2386	1480	2199	2171
(2)	2098	1413	2683	1688
(6)	—	1048	—	174
(5)	1356	787	247	36
(7)	1319	802	121	−29
—	1294	819	253	9

Philadelphia, Pa.; (3) Atlas Chemical Industries, Inc., Wilmington, Del.; (4) E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.; (5) Geigy Industrial Chemicals, New York, N. Y.; (6) Matheson Scientific, Inc., Oakland, Calif.; (7) Union Carbide Corp., New York, N. Y.; (8) Wyandotte Chemical Corp., Wyandotte, Mich.

[e] 1/2 μCi paraquat-^{14}C (2 ml. containing 64.25 μgrams = 32,125 p.p.m.).

[f] 1/4 μCi paraquat-^{14}C (2 ml. containing 32.12 μgrams = 16,062 p.p.m.).

[g] Reagent grade.

Once a spray droplet lands on a plant surface, more interactions can occur between the surfactant, the herbicide, and the plant cuticle. Thus, the possible effects or roles of the surfactant are increased many fold. Currier and Dybing (*16*) list some nine causes in addition to surface tension lowering which may contribute to increased herbicidal effectiveness when surfactants are included in spray solutions. All of these possible factors involve interactions among the surfactant, herbicide, and plant, or at least between two of the three components: (a) improving coverage, (b) removing air films between spray and leaf surface, (c) reducing interfacial tension between relatively polar and apolar submicroscopic regions of the cuticle, (d) inducing stomatal entry, (e) increasing the permeability of the plasma membrane through stimulation or incipient toxicity, (f) facilitating cell wall movement in the region of the wall–cytoplasm interface, (g) acting as co-solvents, (h) interacting directly with the herbicide in some manner, (i) acting as humectants secondarily.

The inclusion of a surfactant in a solution of a dye or herbicide has conclusively been shown to increase the amount of solution penetrating through open stomata (*21*) and thus into the substomatal chambers.

However, even here penetration through a much reduced cuticle layer is often necessary before final penetration into the underlying tissues.

Penetration of herbicide solutions through cuticle in the absence of stomata is also common, and under field conditions it may be the dominant portion of the penetration of herbicides. The existence of both polar (hydrophilic) and apolar (lipophilic) absorption pathways through plant cuticle seems certain from several laboratory and greenhouse studies (*10*).

No physical removal of cuticle has been observed with microscopic and chemical studies when the cuticle is treated with a surfactant, although solubilization of waxes has been suggested. It is likely that orientation of surfactant molecules occurs towards the cuticle surface causing wetting and spreading of the spray droplets over the leaf surface. This would enhance the penetration of the herbicide solution into stomata, insect punctures, cracks, and other imperfections in the leaf surface.

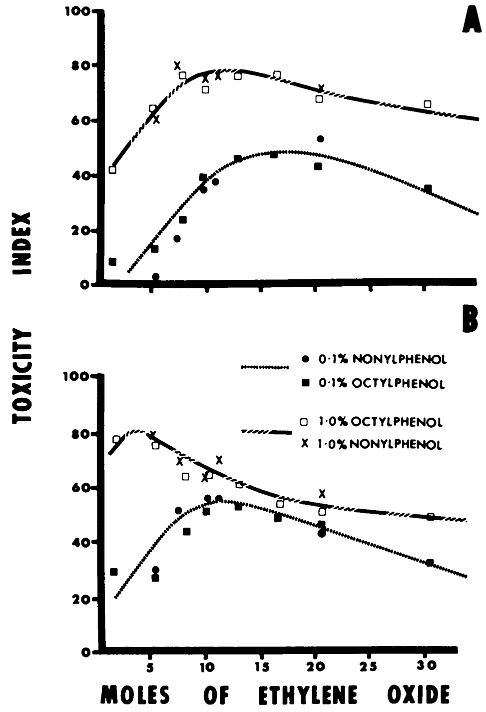
Much work has been carried out on the penetration process and the role of the surfactant. Sites both on and within the cuticle are involved. Factors such as pH, humidity, light, and temperature have been shown to influence this process (*50*). The main role or effect of the surfactant is thought by many to be involved somewhere in the penetration process through cuticle.

Herbicide–surfactant–plant surface interactions subtler and more specific than mere surface tension lowering and increasing wetting undoubtedly occur (*16, 28, 29, 33, 34, 35, 37, 49, 55, 57, 58*). For example, in one study (*28*) using several concentrations of anionic, nonionic, and cationic surfactants with dalapon, minimum surface tensions and contact angles occurred at 0.1–0.5% concentration for all surfactants. However, maximum herbicidal activity was observed at 10 times these levels or greater. Thus, above 0.1–0.5% surfactant concentration herbicidal enhancement was not correlated with surface tension lowering, contact angle, observed wettability, or initial toxicity of the surfactants. Precisely where and how does enhancement of herbicides by addition of a surfactant occur? Are mobility and accumulation as well as absorption of herbicides altered by solution additives?

Definite structural requirements relating to activity (*33, 34, 35, 55, 57, 58*), translocation (*56*), and biodegradability (*41*) appear to exist for certain chemical groups of surfactants. Whether these also influence herbicide persistence in plants and roots requires further study.

Structure–activity relationships between several nonionic surfactants and three water-soluble herbicides have been studied (*58*). In general it has been shown that the herbicide, the surfactant concentration, the hydrophilic constitution (ethylene oxide content), and the hydrophobic portion of the molecule all markedly influence toxicity.

Generally a peak of maximum enhancement is reached as the ethylene oxide content is raised and the molecule becomes more hydrophilic, but after a certain content (depending on concentration) the enhancement drops away again. This is illustrated for two herbicides and two surfactant concentrations in Figure 2.



Weed Research

Figure 2. Relationship between the number of moles of ethylene oxide in octyl- or nonyl-phenol polyoxyethylene glycol ether surfactant molecules and the toxicity index of these surfactants in mixtures with (a) paraquat and (b) dalapon on corn plants. Herbicides applied at 1/64 and 10 lb./acre, respectively; surfactant concentrations were 1.0 and 10.0 grams/liter. Toxicity index as defined in the text (58)

●, *0.1% nonylphenol*
■, *0.1% octylphenol*
□, *1.0% octylphenol*
×, *1.0% nonylphenol*

Extrapolation of these results with specific herbicides, surfactants, plant species, and environmental conditions to general conclusions about the behavior of another class of surfactants under other conditions would perhaps be hazardous at this point. However, the results of work thus far would tend to support the following as a possible mode of action of certain nonionic surfactants in herbicide solutions.

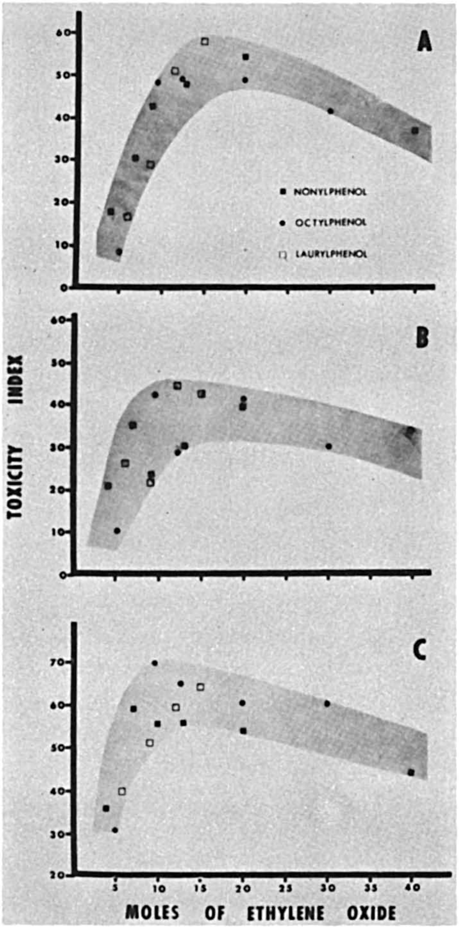
Studies on structure–activity relationships between herbicides and homologous series of surfactants indicate that definite relationships exist between the herbicide and surfactant structure for maximum herbicide penetration. The length of the molecular chains (either hydrophilic or lipophilic) of a surfactant molecule appears to have considerable influence on herbicide penetration, and the surfactant concentration also influences this process markedly.

It seems reasonable that molecules of a surfactant may diffuse from the spray droplet into the cuticle of leaves perhaps *via* imperfections and cracks and then align themselves in monolayers with their nonpolar ends oriented in the cutin and wax. The polar ends will thus also form a layer whose size depends on the length of the hydrophilic chain of the surfactant molecule. These layers or "hydrophilic channels" will presumably attract water, causing swelling of the cuticle, and thus channels or pores are formed along which herbicide molecules can diffuse according to their various chemical properties (solubility, residual chemical charge, polar properties, etc.).

One property of the surfactant molecule recently studied in detail has been the influence of the number of moles of ethylene oxide (EO) in the lipophilic side chain on herbicide penetration and activity. A surfactant with a small number of moles of EO—*i.e.*, 1–5—or a short hydrophilic chain appears to be too nonpolar, whereas one with a large number of moles of EO—*i.e.*, 40—is too large to form layers as efficiently as those with an intermediate number of moles—*i.e.*, 10–20. The relationship between the number of moles of EO in three alkylarylpolyoxyethylene glycol ether surfactants and the toxicity of three different herbicide solutions is illustrated in Figure 3.

The influence of surfactant concentration may possibly lie in the micellar structure of the solution and the adsorption of herbicide molecules into these micelles, or it could be caused by the increased diffusion rate of the surfactant into the cuticle with increasing concentration, thus satisfying all the binding or adsorption sites within the cuticle.

Studies on certain other physicochemical aspects of surfactant action have been reported or reviewed (*9, 24, 30, 31, 40, 47*). Entry of oils, some organic solvents, and aqueous sprays, with lowered surface tensions, into stomata is apparently a mass movement; entry through cuticle is by diffusion, at least initially (*12, 16, 25*). Cuticular diffusion is conditioned by particle size, pH and buffers, molecular structures (of penetrant, solvent, additive, and plant surface), prevalence of water and other factors (reviewed in Refs. *12* and *47*; *cf.* other references cited). The final influ-



Weed Research

Figure 3. Relationship between the number of moles of ethylene oxide in octylphenol (●), nonylphenol (■), or laurylphenol (□) polyoxyethylene glycol ether surfactant molecules and the toxicity index of these surfactants in mixtures with (a) paraquat, (b) dalapon, and (c) amitrole on corn plants. Herbicides applied at 1/64, 10, and 5 lb./acre, respectively; surfactant concentration was 0.005M in all cases. Toxicity index calculated by expressing fresh weight for each treatment as percentage of untreated control and subtracting this value from 100 (58)

ence of a surfactant, then, will be determined by the nature of the surfactant (charge or ionogenic class, hydrophilic–lipophilic balance (HLB), chemical structure, and concentration), the herbicide, the solvent, the plant surface, and the physical environment. Interactions must also be expected between plant surface and applied chemicals as follows: mechanical (relation of penetrant particle to pore size), physicochemical (competition for adsorption sites), and chemical or electrical reactions. Such interactions, recognized as possible but poorly understood in any given situation, undoubtedly contribute to the erratic results reported in the literature and to unpredictability in the field.

Work with labeled surfactants at Davis, Fort Detrick, and VPI by both authors has shown that with nonionic surfactants such as Tween 20 and Tween 80 very few of the tagged atoms are translocated away from the site of application (Figure 4). For Tween 20 less than 2–3% were found outside the treated leaf after 7 days (Table II). Even in cases where translocation of label had occurred such as with ^{35}S-labeled sodium lauryl sulfate the label in remote parts of the plant was not in the form of the original surfactant molecule but was in other metabolites.

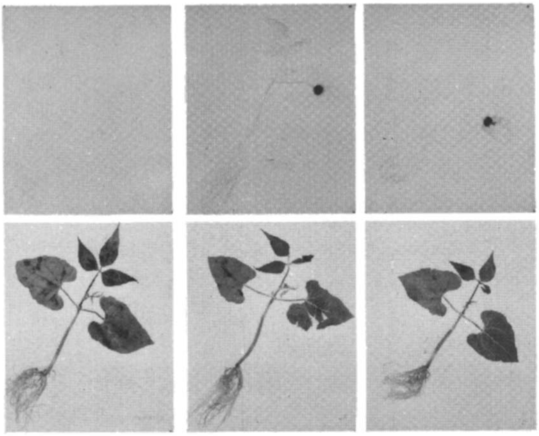


Figure 4. Autoradiographs of red kidney bean 4 days after applications of Tween 20-^{14}C. Left, untreated; middle, fatty acid labeled; right, oxyethylene labeled. Both these fractions were from the main peak of the Sephadex column elutions

Thus, all evidence to date indicates that surfactants do not facilitate herbicide transport *per se* but that their main site of enhancing action is primarily at the point of application and in the immediately underlying tissues.

Table II. Total Activity (c.p.m.)[a] Found in Various Parts of the Bean Plant 4 Days after Foliar Treatment with Tween 20-^{14}C (56)

Plant Part	*Tween 20* *Fatty Acid Labeled*	 *Oxyethylene Labeled*	*Untreated*
Washings	21,290	37,025	—
Treated spot	48,920	31,118	14
Treated leaf (distal portion)	122	1,729	24
Petiole and treated leaf (basal portion)	150	220	42
Roots and stem below treated leaf	208	102	16
Opposite primary leaf and trifoliate leaf	474	148	11
Total	71,164	70,342	107
Total counts applied (average of four)	70,942	70,378	—

[a] Average of two replications.

The main role of the surfactant seems to be concerned with the penetration process, but the exact nature of this role requires a more satisfactory explanation.

Through the further combined use of radiolabeled herbicides and additives in tracer and metabolic studies, it may be possible to develop new concepts regarding formulation of herbicides for differential absorption, translocation, and selective action, while at the same time minimizing chemical residues.

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7

Physicochemical Principles in Formulating Pesticides Relating to Biological Activity

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Pesticides are formulated not only for convenient dispersal but to offer them to the target organism in a way that maximizes biological activity. Examination of the phenomena of interaction of the chemical with the environment, transfer and absorption of the chemical into the target organism, and prevention of loss from the treated area reveal certain physicochemical principles whose application can maximize its biological efficiency. They can assist in selecting systems of solvents and additives to increase deposition and penetration into the target organism by overcoming absorption barriers and promoting conservation of the chemical. Additionally, application of well known laws can guide formulation to avoid losses through volatility and leaching and can be invaluable in selecting appropriate derivatives for specific uses.

Economic pressures for more perfect pest control and ecologic pressures for minimal dispersal of pesticidal agents have created a situation where efforts to improve the performance of pesticides by improving the formulation are being intensified.

The biological activity of a pesticide must eventually be a function of the concentration at the site of action which in turn depends upon the steady state attained between a system of compartments along the critical path of the pesticide. The transfer of pesticide from its formulated phase to the active site is a process which should follow sets of well-defined physical laws. If the investigator can discover what laws are operable on the system with which he is dealing, the optimum efficiency of formulation can be achieved more rapidly. This paper suggests some concepts and approaches which may be useful in quantifying the process of herbicidal penetration on plant surfaces.

Present-day organic chemicals used as herbicides present numerous formulation problems both from the standpoint of field use and more basic studies. Some problems encountered include: (a) selection of the proper derivative, (b) selection of the proper form of presentation to achieve maximum activity, and (c) use of surface-active agents and additives. Considerable work is needed to elicit the essential information to permit a systematic approach to the problem of formulation.

Frequently the type of formulation needed will be determined by the derivative of the parent compound used. Of course, there are many instances where, because of extreme modification of activity, there is no possibility of selecting different derivatives (*7*, *14*). There are many instances, however, where the herbicides have functional groups that may be modified to give a new derivative possessing only a slightly different biological activity. 2,4-D is an excellent example of this type of material, although others such as the nitrophenols might be cited. In general, it appears that where the functional group is strongly polar, such as a phenolic hydroxyl or a carboxyl group, such modifications may be made within reason.

Selection of a Derivative

The question arises as to what derivative to select where a multiple choice exists. The considerations leading to this selection are predicated on ease of formulation, solubility, biological activity, etc. The simplest derivative of strongly polar substances is a water-soluble salt. This is a purely practical consideration stemming from the ease of using such substances. However, it is necessary to consider whether the compound is active in an ionized or an unionized state. For the most part, the acidic polar compounds appear to be absorbed and to become effective in the unionized form as evidenced by the nitroalkylphenols and dichlorophenoxyacetic acid (*16*). In the highly ionized state this type of compound tends to be less active biologically than the unionized form.

A second and important consideration in selecting the derivative is to choose the one with the highest chemical potential or affinity of reaction for the particular system. The Le Chatelier principle postulates that a system under the influence of unbalanced forces will shift its equilibrium in such a direction as to minimize the unbalanced forces. This is the case with a spray solution on a plant surface. If the solution is considered as Phase 1 and the cuticular membrane of the plant as Phase 2, at equilibrium

$$\mu_\gamma{}^1 = \mu_\gamma{}^2 \tag{1}$$

where:

$$\mu_\gamma = \frac{\delta G}{\delta n_i} = \mu_\gamma{}^0 \cdot + RT \ln nf$$

μ = chemical potential
G = Gibbsian free energy
R = gas constant
T = absolute temperature
n = mole fraction
f = activity

From this fundamental relationship we deduce that the larger the potential in Phase 1, the greater the tendency toward the attainment of a "steady state." Obviously this will be facilitated further if the herbicide has a favorable distribution coefficient between the two phases. To attain equilibrium rapidly, one selects a derivative that passes readily through the type of membrane encountered, such as a cuticle in the case of the plant top or through a lyophilic membrane in the roots.

Where dealing with chemicals that are active soil herbicides, the length of residual effect is usually very important. Here it is generally desirable to extend the residual effect as long as possible to maintain weed-free conditions. In the soil, however, the chemicals are rapidly destroyed (*11, 13*). Destruction of these organic compounds in the soil is preceded by an outlay of energy which may be designated by the symbol, ΔH. The rate at which a chemical is destroyed in the soil is a function of this quantity. This energy or enthalpy of activation is the heat that must be absorbed by a molecule before it will react. The rate at which the chemical will react or be destroyed is determined by ΔH. The following equation (Arrhenius), from physical chemistry, illustrates how ΔH is related to the rate of reaction at different temperatures

$$\log \frac{k_2}{k_1} = \frac{\Delta H (T_2 - T_1)}{2.3\, R\, (T_2 \cdot T_1)} \tag{2}$$

where k_1 and k_2 are the specific rate constants at temperatures T_1 and T_2. To extend the residual life of a compound in the soil, it is necessary that ΔH be large. Thus, the surroundings must supply energy equivalent to ΔH to cause destruction of the chemical. The relationship between the heat or energy of activation and residual life of two herbicides is shown in Table I, which gives ΔH values for a short residual herbicide, IPC, and a longer lived herbicide, chloro-IPC (CIPC). By calculating the ΔH required for decomposition rather than the half-life, we have quantified a fundamental attribute of the molecule which enables predictions of behavior in a greater variety of situations.

Table I. Relationship Between Energy of Activation, Structure, and Residual Life of Herbicides

Compound	*Temp., °C.*	$k(day^{-1}) \cdot 10^{-2}$	ΔH
IPC	15	4.67	
	29	8.79	7,768
CIPC	15	0.425	
	29	2.39	21,237

To take advantage of this, one considers the organic linkage that will most probably be attacked. In most instances it is reasonable to assume that this will be the one of the bonds in the polar functional group, as in ester hydrolysis. By considering the energy of the bond between the parent moiety and the substituent used to form the derivative, the derivative of highest bond energy will have the greatest stability. This would call for the greatest expenditure of energy by the surroundings to cause destruction of the compound and hence a longer residual life. This is exclusive of other alterations in the molecule that might result in a loss of activity.

Another property of the derivative that has received considerable attention lately is volatility (*1, 2, 17*). This is important both as it relates to the length of residual effect and possible danger to nearby susceptible plants. Energy is required to bring about vaporization.

The energy which is absorbed in the form of heat contributes to the motion of the molecule. Therefore, there will be a point where the kinetic energy of the molecule equals or slightly exceeds the attractive forces, and the molecule will pass from one state to another. If the chemical is a liquid, when the kinetic energy of the molecule slightly exceeds that of the attractive forces, the molecule escapes as a gas or vaporizes.

A certain amount of energy will be required to raise the molecules to a level of kinetic energy where they will escape. In the special case of a liquid passing to the vapor state, the energy put into the system to cause volatilization is the latent heat of vaporization. The property is characteristic for a given chemical and may vary with temperature. The temperature relationship of the latent heat of vaporization may be calculated by the Clausius-Clapyeron equation.

$$\frac{d \ln P}{dT} = \frac{L}{RT^2} \tag{3}$$

Experimentally, however, the latent heat of vaporization is determined simply by evaluating the change in vapor pressure of the compound with temperature; the log of the pressure is plotted against the reciprocal temperature, giving a straight line, whose slope can be used to calculate the heat of vaporization.

The important thing concerning volatility at various temperatures is the relative amount of material in the atmosphere at the different temperatures. If one knows the latent heat of vaporization, the tendency of the material to vaporize can be calculated from Equation 3. If we now consider preparations of derivatives whereby vapor loss can be reduced, it is immediately apparent that the latent heat of vaporization must be increased. This can be done with the phenoxyacetic acid compounds in preparing the so-called low volatile esters as represented by the butoxyethanol ester as illustrated in Table II. Determinations of the ratio of the latent heat of vaporization of the butoxyethanol ester to that of the isopropyl ester indicated a value of about 2.

Table II. Vapor Pressure and Latent Heat of Vaporization of Esters of Growth Regulator Herbicides

Compound	*Mol. Wt.*	*Vapor Pressure, mm. Hg × 10^{-3} at 25°C.*	*Heat of Vaporization cal./mole*
MCP-isopropyl	242.69	21.6	3510
MCP-butoxyethyl	300.67	4.8	7400
2,4-D-isopropyl	263.12	10.5	2390
2,4-D-butoxyethyl	321.20	1.7	8400
2,4-D-butyl	277.15	3.9	2050

These basic considerations of volatility may be used advantageously where we wish to extend the residual life of a material. When the vapor pressure of a mixture as compared with that of a pure solvent is considered, the pressure of the solvent or one of the constituents in the mixture is less than its pressure in the pure state. This depression in vapor pressure in an ideal system is directly proportional to the pressure of the substance present as shown by Equation 4.

$$P_1 = P_1^0 N_1 \tag{4}$$

In other words, the vapor pressure of Component 1 of the system is equal to the vapor pressure of pure Component 1 times the mole fraction of Component 1 in the system. To extend the residual life of a volatile component in the deposit, we may admix either an inert ingredient or an ingredient of low volatility to the desired mole fraction. Further, the material used to reduce the rate of loss of Component 1 should have as low a molecular weight as practicable so as to have a relatively large mole fraction in the mixture.

This principle may not always be consonant with attainment of equilibrium. Careful attention must be paid to the choice of solvent so as to approach an optimum relationship.

The efficacy of a nonvolatile additive in reducing the rate of loss is immediately apparent from Table III. Here the rate of evaporation of the isopropyl ester of 2,4-D alone and in combination with chlorinated biphenyl was determined at 40°C.

Table III. Evaporation of the Isopropyl Ester of 2,4-D at 40°C.

	% Loss	
	24 hours	*48 hours*
Isopropyl 2,4-D, alone	1.83	8.55
Isopropyl 2,4-D and chlorinated biphenyl	0.41	4.17

Formulation

The next problem encountered after selecting the derivative is the form in which the material is to be offered to the plant. The decision here is predicated on: (a) whether a compound is active through the roots or the leaves, and (b) the solubility of the compound in various solvents. There are numerous ramifications of both predications, some of which are difficult to control. One underlying consideration, however, is the distribution of the material. For several cogent reasons, water is the primary carrier for spray material, and therefore the formulated material must form a reasonable and tractable system with water. Where the chemical is soluble in organic solvents, the resulting solution must form a suitable solution or proper emulsion upon subsequent dilution with water and thus expedite entrance of the chemical into the plant.

It was previously suggested that the chemical–solvent combination having the highest chemical potential was the one to use. Consider now the details of this requirement. Living systems such as plants are not in equilibrium, but rather in a "steady state," in which a number of sequential and steady state reactions occur. Obviously if the system were in equilibrium, the plant would be dead. When a chemical is placed on the plant surface, the difference in potential, μ_Y, between the two sides of the surface causes the material to be absorbed through the epidermal surface. This process is purely physical if the surface is nonliving. However, when the chemical comes in contact with the living cell, there is a shift in the steady-state equilibrium, which by the Le Chatlier principle results in shifts throughout the entire system to minimize the effects of this outside force. This shift takes the nature of either immobilizing the chemical by precipitation or, in the case of many of the compounds, translocating it from the point of highest concentration to a point of lower concentration. According to the affinity theory, at equilibrium quantity, affinity × velocity = zero. If we consider that the chemical potential of the applied substance creates a change in affinity or variation of affinity by ΔA, we have the situation shown by Equation 5.

$$(A + \Delta A) \cdot (V + \Delta V) = 0 \qquad (5)$$

This equation suggests that since the potential of Component 1 in Phase 1 is not permitted to attain equilibrium with Component 1 in Phase 1 (or the living system), we can get a sufficient quantity of chemical into the plant to bring about the desired end. This conclusion suggests the nature of the solvent required to obtain maximum activity. Obviously, it is not possible to violate any of the solubility laws determined by organic chemistry, but Equation 5 can help the experimenter choose the proper solvent. Hence, the solvent of choice will be the one best facilitating the entry of the compound into the plant and at the same time permitting the highest practical concentration. To make this choice we can use Equation 6.

$$N_1\, d_{\mu_1} + N_2\, d_{\mu_2} = 0 \qquad (6)$$

Since the sum of products of the mole fraction (N) times the change in potential (d_μ) equals zero, the change in chemical potential of one or the other of the components must be negative if the number of the moles or the mole fraction remains constant. On the other hand, as the number of moles of one constituent decreases, the chemical potential must increase. Hence, the most effective combination of solvent or solvents will be that which results in a large mole fraction of solute with a small change in chemical potential over a wide range of concentrations. This will give both a concentrated solution and a high potential to facilitate entry into the plant.

Another type of partition important in biological activity is that of the pesticide between the lipophilic phase and the aqueous phase within the cells of an animal or a plant biosystem. A principle, which seems to have been largely overlooked, was developed by Ferguson (*6*), which states that the relationship between the biological activity of a compound and concentration can be expressed as a thermodynamic activity which is a function of the relative saturation of the aqueous phase in equilibrium with the active site; hence, we can show a more meaningful relationship between structure and biological activity than when concentration is expressed in absolute terms. This relative activity is a function of both the partition coefficient and the absolute water solubility of the compound. Although Ferguson initially developed this concept for application to chemicals which might be involved in "indifferent narcosis," the partition and adsorptive forces involved at the site of action of many types of biological activity may be fundamentally similar. Since it can be adduced from his hypothesis that the lower the water solubility of a compound, the lower will be the absolute concentration needed to achieve an effective concentration, let us compare the rates of use and the absolute water solubility of some herbicides (Figure 1). Figure 1 shows that there is a reasonably good linear relationship, even though many complex environmental factors intervene between application and biological effect.

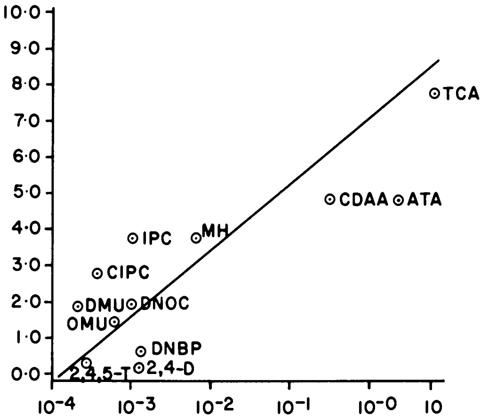

Figure 1. Relationship between dosages used in field application on solubility in water of a series of herbicides

In applying pesticides in control situations, one must consider the role of surface-active agents, particularly for those substances to be applied as an aqueous spray. Wetting agents lower the surface tension of water, thus decreasing the contact angle that a drop of water makes with the surface and increasing the interfacial area between the drop and the surface. Ennis presents some interesting data on spray retention of various types of leaves of aqueous and aqueous–surfactant combinations (5).

To visualize what occurs during a spraying operation, consider a leaf receiving the spray having an angle ϕ with respect to the plant axis and an angle θ with a coordinate in space of the X plane. A spherical drop of radius r impinging on the surface of the leaf exerts a vertical force downward, $F = 4/3\ r\ \rho g$, where ρ is the density and g is the acceleration caused by gravity. The force, F', tends to cause the drop to roll off the leaf. This force is equal to:

$$F' = 4/3\ v^3 \rho\ g \sin \theta$$

The drop does not immediately fall off the leaf owing to the fact that there are residual forces or force fields around all atoms and molecules. At surfaces, there are unbalanced forces which tend to become balanced by binding the droplet molecules to the leaf. These forces vary in intensity inversely as the cube of the distance between the molecules. Obviously, similarly shaped molecules will approach a more ideal juxtaposition than unlike molecules; therefore, it is not surprising that similar substances adhere better than unlike substances. This is why oil wets the leaf better than does water.

The attractive force between the spray droplets and the leaf surface has a given value per unit area of leaf. When the contact angle of the drop and the leaf surface is sufficiently small—*i.e.*, when the interfacial area is sufficiently large—the force tending to cause the droplet to bounce off the leaf is matched by or equal to the attractive forces, and hence the droplet adheres to the leaf surface.

This immediately indicates the necessity of using spray mixtures of sufficiently low surface tension so that the displacement of the droplet owing to impingment can result in a sizeable interfacial area and proximal contact so that these short range intramolecular forces can come into play in spray retention.

Although it is well established that surfactant chemicals usually increase the biological activity of herbicides on most plants up to an optimum point, it is also clear that this increased activity cannot be totally accounted for by increased retention, increased area of contact, and humectant action, nor is it correlated with surface tension. However, increased absorption does result from using surfactants. If one conceives of the process of absorption as a rate process, and applies classical physicochemical principles to the problem, it is immediately seen that, as in other reaction or equilibrium processes, there must be an "energy barrier" to the transfer of the herbicide from the external phase to the internal phase. If this is assumed to be an energy barrier similar to that encountered in reaction kinetics, it can be considered the energy of activation as illustrated in Figure 2, where A is the external phase and B is the internal phase. The pathway or complex between the two phases must be altered by the presence of the surfactant so that the energy barrier is lowered (Figure 2).

This can be expressed by the Arhenius equation showing the change in a reaction rate constant with temperature:

$$\frac{d \ln k}{dt} = \frac{\Delta E^*}{RT^2}$$

$$\log_{10} \frac{k_2}{k_1} = \frac{\Delta E}{2.3R} \frac{(T_2 - T_1)}{(T_1 \cdot T_2)}$$

$$E_a = \frac{(T_1 \cdot T_2)}{(T_2 - T_1)} \; 2.3R \log \frac{k_2}{k_1}$$

Thus, if the rate constants for the penetration process are determined at two different temperatures, the activation energy for the system can be calculated. If the activation energies for two systems, with and without surfactant, are compared and are different, the role of the surfactant can be inferred from the direction of the energy change.

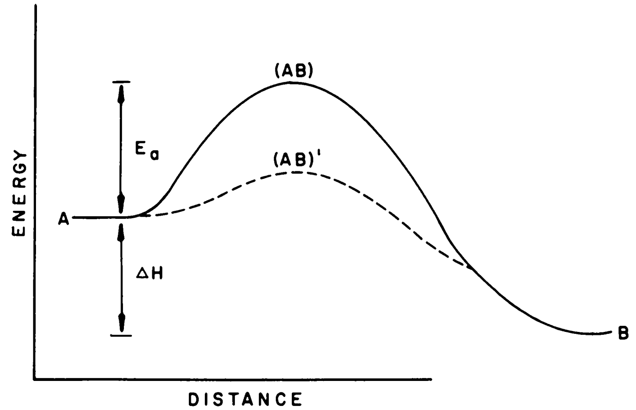

Figure 2. Transfer energy relationship for a herbicide moving from the external phase (A) to the internal phase (B)

Without surfactant: $A \rightarrow (AB) \rightarrow B$

With surfactant: $A \rightarrow (AB)' \rightarrow B$

Such a series of experiments was conducted to determine the Arrhenius absorption energies using an acidic series of water-soluble herbicides—2,4-D, dicamba, and picloram. A constant total volume (25 μliters) of a 2000 p.p.m. solution (pH 7.0) of each herbicide was dispersed on the primary leaves of bean seedlings. The surfactant Tween 20 (ethylene oxide condensate with sorbitan monolaurate) was incorporated in the herbicide solution in the appropriate tests at a 0.1% concentration. The initial rate of uptake was assumed to be a first-order rate process. This is probably not a simple first-order process because of the complex action of transport, degradation, evaporation, re-issue, etc., but logic suggests that in the initial stages it may be a workable assumption. The rate constants were determined from the slopes of the plots of log $(a)/(a - x)$ *vs.* time, and the absorption energy was calculated from the rate constants at 13° and 24°C. The results are shown in Table IV.

Table IV. Effect of Surfactant on Absorption Energy

		E_a *(kcal./mole)*	
Herbicide	*pK*	*Without Surfactant*	*With Surfactant*
Picloram	1.94	18.9	
Dicamba	2.94	12.0	10.4
2,4-D	3.31	6.5	3.0

The baseline values for the energy barrier to absorption are quite different for different herbicides, and the surfactant tends to lower the energy barrier. While there is an uncertainty in these values because of scatter from experimental limitations, basic physicochemical laws can be used to understand the processes affected by formulation.

Fundamental relationships can be used to solve present and future problems of herbicide formulation. Careful consideration of some of these relationships will point the way to new experiments to obtain information that will permit solution of even more general relationships.

Acknowledgments

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The Decomposition of Guthion in *N*-Methyl-2-pyrrolidone and Butyrolactone

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The chemical stability of Guthion phosphorodithioate was investigated in two solvent systems: N*-methyl-2-pyrrolidone and butyrolactone. Epichlorohydrin was found to alter the rate of decomposition of the two systems. Kinetic treatment of the data revealed a second-order rate process. Rate constants and activation energies were calculated for each system.*

In developing any new pesticide formulation many factors must be considered: physical form, method of application, pests to be controlled, compatibility with other toxicants, and many more that are too numerous to mention. For a formulation to be useful, however, it must meet certain minimum chemical and physical stability requirements. Guthion (*O,O*-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl] phosphorothioate), which has been used for a number of years to control many insects, was the toxicant used in this investigation.

Initial stability studies carried out at temperatures higher than normal storage conditions, are essential in helping to determine whether or not a given formulation will possess the necessary chemical stability required to make it a commercially satisfactory product. Accelerated decomposition data of this type lend themselves well to a quantitative interpretation of over-all rate processes, thereby allowing for an accurate prediction of product shelf life. Despite the many studies conducted on agricultural pesticide formulations there is a conspicuous absence in the literature of kinetic interpretations of toxicant decomposition data. Predictions of real storage conditions have been made largely on the basis of extrapolated accelerated-storage data without regard to the order of reaction. Knowledge of the over-all rate constants associated with the toxicant decomposition should allow a more accurate calculation of the percent toxicant remaining under normal warehouse storage conditions.

Ideally, one hopes that the impurities found in a technical toxicant are of such a chemical nature that they do not affect in any way the rate or mechanism of decomposition in the finished formulation. Unfortunately, this utopian situation is seldom realized. In a case where several minor impurities affect the course of chemical decomposition it is highly desirable to investigate each of these impurity parameters to predict which should be controlled so as to obtain a formulation of superior stability.

Because of the recent interest in the ultralow volume spraying technique, high boiling solvent systems for Guthion were sought. Owing to their low volatility and high solubility for Guthion, *N*-methyl-2-pyrrolidone and butyrolactone were chosen for study. The chemical stability of the toxicant in these solvents was investigated at a number of temperatures. Since no surfactants were added to the systems, they were simpler than most liquid pesticide formulations.

The Guthion solutions were analyzed by measuring absorbances in the infrared region at 645 cm.$^{-1}$ and by the copper chelate method (*1*, *3*). The latter method is the more specific and depends on basic hydrolysis of Guthion followed by formation of a colored Cu^{2+} chelate with the dimethyl dithiophosphoric acid formed. In instances where the Guthion concentrations were quite low, thin layer chromatographic techniques were employed.

Experimental

The *N*-methyl-2-pyrrolidone and butyrolactone used in this investigation were supplied by the General Film and Aniline Corp. and were of technical grade. Guthion toxicant was also technical grade. The solutions also contained epichlorohydrin which was of 98% purity and supplied by Dow Chemical Co.

The solutions were prepared by dissolving Guthion in *N*-methyl-2-pyrrolidone or butyrolactone, filtering, and storing in clear glass bottles at the desired temperature. A small sample of each solution was stored in a freezer to serve as a standard assuming no decomposition at low temperature (−5°C.). The initial Guthion solution concentrations were prepared to contain 44% by weight of technical material. Initial analyses showed these concentrations to range from 45.3 to 45.8%. In addition to technical Guthion and solvent, epichlorohydrin (*2*, *5*) was added, to the extent of 1, 2, and 4%, to observe what effect, if any, an acid scavenger would have on the stability of the system. Kinetic evaluations were conducted on each of the resutling solutions.

These solutions were stored at −5°, 0°, 25°, 40°, and 50°C. Toxicant analyses were conducted at weekly intervals to determine the extent of decomposition. For the 50°C. solution, sample decomposition was so rapid in the methylpyrrolidone solvent that daily analyses were carried out.

Results

Kinetic analysis of the data revealed that the decomposition obeyed a second-order rate law in both solvent systems. A simple kinetic approach was used where

$$-\frac{dc}{C^n} = kdt \qquad \text{where } n = \text{the order.}$$

For $n = 2$, integration yields $\frac{1}{c} - \frac{1}{c_0} = kt$; therefore, a plot of $\frac{1}{c}$ *vs.* t should be linear, with a positive slope equal to k. Figures 1 and 2 are typical data plots showing second-order behavior at constant temperature as a function of epichlorohydrin concentration for both the *N*-methyl-2-pyrrolidone and butyrolactone formulations. The points for $t = 0$ in Figure 2 were not included owing to the fact that the samples were destroyed during analysis. In addition to a rate dependence on epichlorohydrin there was also, of course, a temperature dependence. The rate constants are shown in Table I, tabulated according to temperature and epichlorohydrin concentration. At constant temperature the addition of epichlorohydrin accelerates toxicant decomposition in the *N*-methyl-2-pyrrolidone solvent, while in butyrolactone the reverse is observed. Arrhenius plots were constructed using the rate constants obtained graphically. These are shown in Figures 1, 2, 3, and 4. The activation energies obtained from these slopes agree with observed epichlorohydrin dependence in their respective solvents. The activation energies (E_a) obtained in the absence of epichlorohydrin are shown graphically in Figure 5. The difference in energies is not as great as expected; however, there is still a slight solvent effect difference indicated. A greater energy difference was expected, largely based on the appearance of the solutions. The *N*-methyl-2-pyrrolidone system darkened more quickly and appeared to contain a light floccular residue. It was assumed (apparently incorrectly) that this darker solution was the result of greater toxicant decomposition.

Although time did not permit more extensive investigation of the behavior in a typical aromatic type solvent, some limited data were available that enabled a rate constant to be calculated at 40°C. in the absence of epichlorohydrin and compared with *N*-methyl-2-pyrrolidone and butyrolactone. Aromatic solvent systems have demonstrated good solvency for Guthion and have yielded formulations exhibiting good chemical stability. A comparison of the three solvent systems would, therefore, be informative. In this limited set of data a solvent effect is more clearly indicated (Table II).

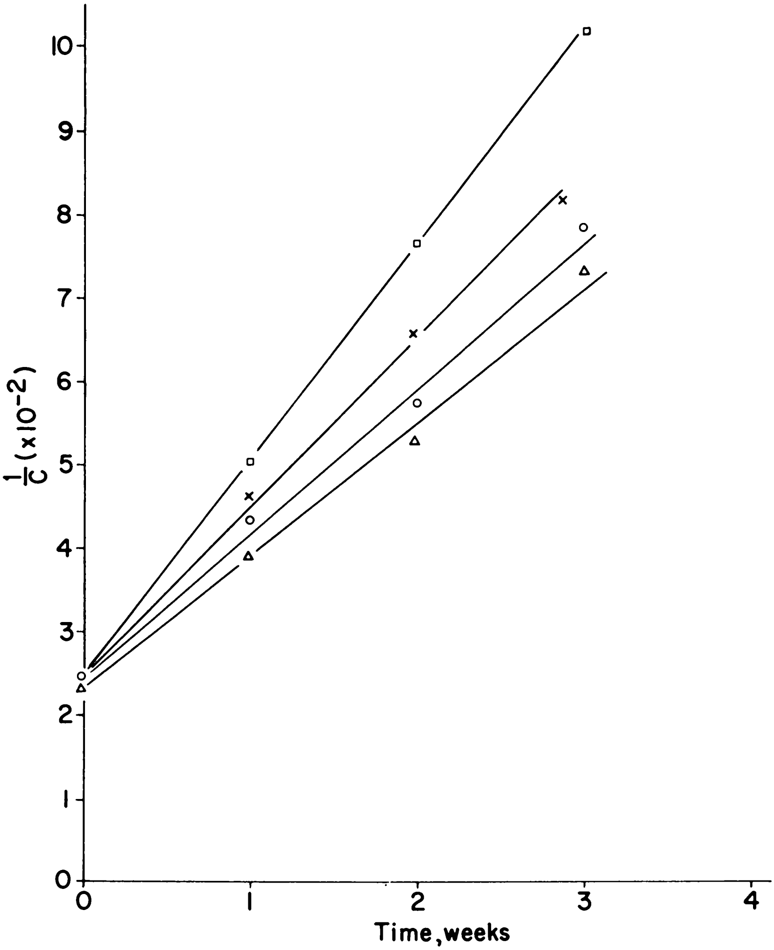

Figure 1. Typical plot of Guthion in N*-methyl-2-pyrrolidone at 40°C. Epichlorohydrin:*

□, *4%*
×, *2%*
○, *1%*
△, *0%*

The tabulated activation energies are shown in Table II. The half-life was calculated for the *N*-methyl-2-pyrrolidone system containing no epi-

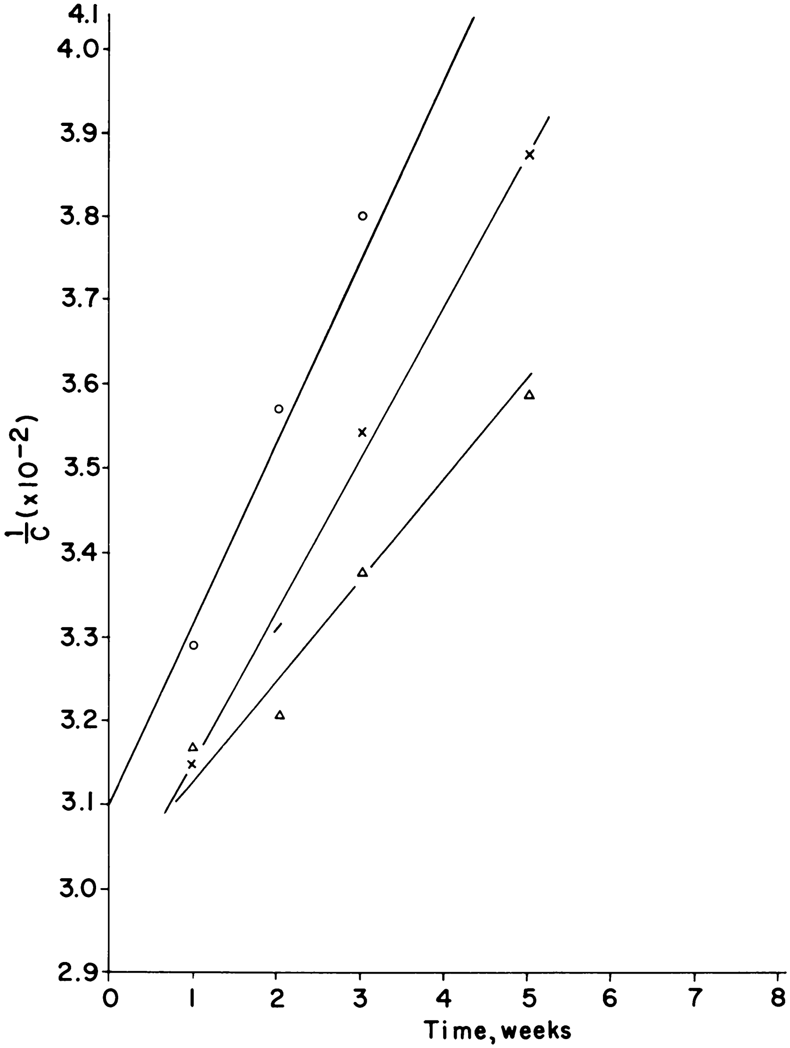

Figure 2. Typical kinetic plot of Guthion in butyrolactone at 40°C. Data obtained by infrared analyses.

Epichlorohydrin:

○, *0%;* k = *2.1* × 10^{-3}
×, *1%;* k = *1.6* × 10^{-3}
△, *2%;* k = *1.2* × 10^{-3}

chlorohydrin and found to be 1.7 weeks at 40°C., while the half life of Guthion in butyrolactone was 16.5 weeks at 40°C. in the absence of epichlorohydrin.

Table I. Rate Constants for Degradation of Methyl Guthion in *N*-Methyl-2-pyrrolidone and Butyrolactone

Temperature, °C.	*Epicholoro-hydrin, %*	k^a N-*methyl-2-pyrrolidone*	*Butyrolactone*
25	0	2.5×10^{-4}	5.0×10^{-4}
40	0	1.5×10^{-2}	2.1×10^{-3}
50	0	7.7×10^{-2}	4.7×10^{-3}
25	1	2.5×10^{-3}	2.0×10^{-4}
40	1	1.7×10^{-2}	1.6×10^{-3}
50	1	—	3.3×10^{-3}
25	2	3.1×10^{-3}	2.0×10^{-4}
40	2	2.1×10^{-2}	1.2×10^{-3}
50	2	1.1×10^{-2} (calc.)	2.9×10^{-3}
25	4	1.2×10^{-2}	1.6×10^{-5}
40	4	2.5×10^{-2}	1.0×10^{-3}
50	4	—	2.8×10^{-3}

[a] Values obtained by visual fitting.

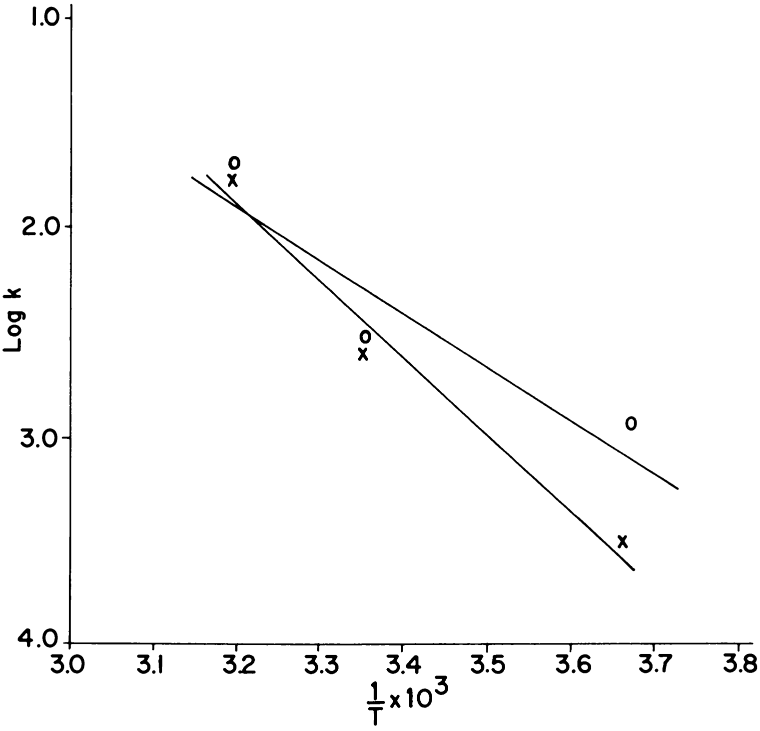

Figure 3. Arrhenius plot of N-*methyl-2-pyrrolidone and methyl Guthion*

Epichlorohydrin:

×, *1%;* $E_a = +18.1$ *kcal.*
O, *2%;* $E_a = +13.9$ *kcal.*

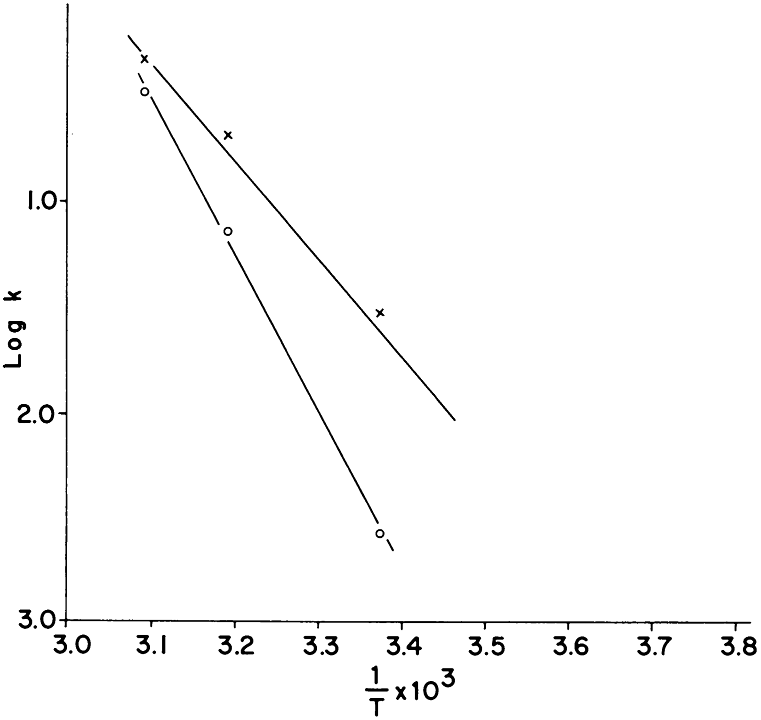

Figure 4. Arrhenius plot of methyl Guthion in butyrolactone Epichlorohydrin:
×, *0%;* E_a = *+19.8 kcal.*
○, *4%;* E_a = *+34.2 kcal.*

Discussion

Clearly the addition of epichlorohydrin to these formulations played a substantial role in enhancing stability and accelerating decomposition, depending on which solvent system is chosen.

The chemistry of the decomposition of Guthion in the solid state has been studied rather thoroughly (*4*). On the other hand, decomposition in solution has received little attention, at least to the extent that mechanisms are well understood. The mode by which epichlorohydrin enters into this reaction is at present even less understood. The rationale for this study, of course, was to investigate useful and economic pesticidal formulations. Many of the questions that remain unanswered are of academic interest and will be pursued as time permits. An understanding of the decomposition mechanisms of a toxicant and those parameters that effect the decomposition is essential for the production of superior pesticidal formulations.

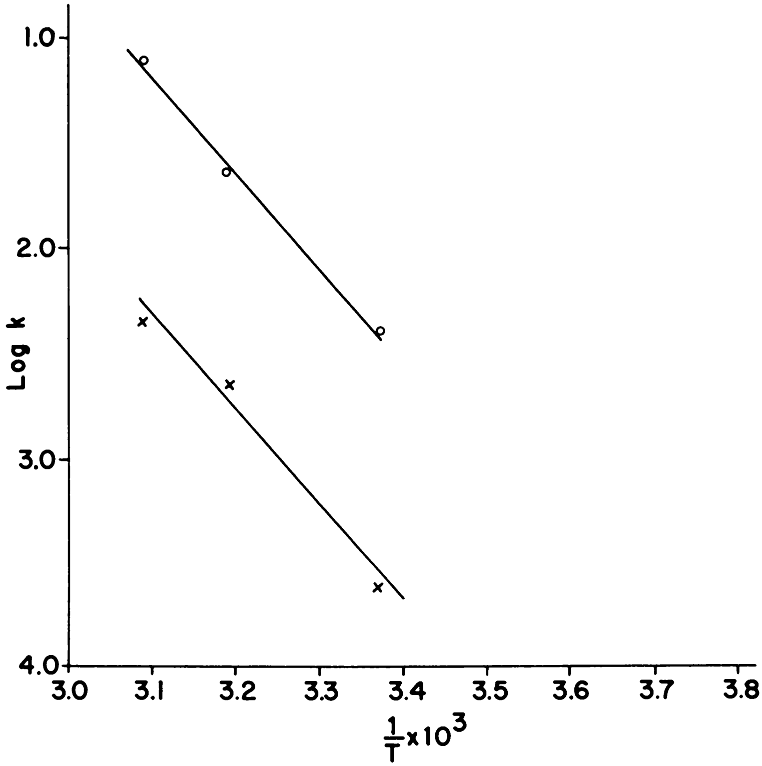

Figure 5. Arrhenius plot of methyl Guthion in butyrolactone and N-methyl-2-pyrrolidone with no epichlorohydrin present

O, *N-methyl-2-pyrrolidone;* $E_a = +22.8$ *kcal.*
×, *Butyrolactone;* $E_a = +20.6$ *kcal.*

Table II. Rate Constants at 40°C. in Three Different Solvents

Solvent	k
Heavy aromatic solvent	1.6×10^{-3}
Butyrolactone	2.1×10^{-3}
N-methyl-2-pyrrolidone	1.5×10^{-2}

Table III. Activation Energy as Obtained from Arrhenius Plot Data

Solvent	*Epichlorohydrin, %*	E_a, *kcal.*
N-Methyl-2-pyrrolidone	0	21 (infrared)
	0	23 (copper chelate)
	1	18 (copper chelate)
	2	14 (copper chelate)
Butyrolactone	0	20 (copper chelate)
	4	34 (copper chelate)

In addition to the effect of additives, such as epichlorohydrin, there is strong evidence of solvent influence itself. This may be seen by examining the rate constants in Table II. As an additional check on the utility and validity of the kinetic results several rate constants were calculated and compared with those obtained graphically. These constants were calculated in the following way: k_1 was calculated from the Arrhenius equation in which k_2 at 25°C., obtained graphically, was assumed to be correct as well as the activation energy, which was obtained from all graphically calculated rate constants. The results of these calculations can be seen in Tables IV and V.

Table IV. Methyl Guthion in *N*-Methyl-2-pyrrolidone Containing No Epichlorohydrin

$E_a = 2.1 \times 10^4$ cal./mole

Temp., °C.	k *(Graphic)*	k *(Calc.)*
25	3.7×10^{-3}	—
40	2.2×10^{-2}	1.9×10^{-2}
50	7.7×10^{-2}	5.1×10^{-2}

Table V. Methyl Guthion in Butyrolactone Containing No Epichlorohydrin

$E_a = 1.98 \times 10^4$ cal./mole

Temp., °C.	k *(Graphic)*	k *(Calc.)*
25	3.0×10^{-4}	—
40	2.1×10^{-3}	1.5×10^{-3}
50	4.7×10^{-3}	4.1×10^{-3}

The relatively good agreement shows that the experimental data from which the activation energies were obtained is quite reliable and that half-lives and rate constants can be calculated with reasonable accuracy at a variety of times and temperatures.

This study has yielded valuable information that can be used to great advantage in choosing solvents and decomposition inhibitors. The contaminants in Guthion, which is generally 90% pure, may number as many as 15–20. The concentration of each is rather low. Studies of the effect of these contaminants on the decomposition of pure Guthion in aromatic type solvents has been both encouraging and confusing. Each contaminant studied has had no effect on the acceleration of decomposition, which of course, is not beneficial from the formulation point of view. On the other hand, it has complicated and confused the issue from the pure chemistry point of view.

We hope that in the near future additional studies will clarify many unanswered questions and result in better products for the consumer and contribute to the basic chemistry of organophosphorus pesticides. Although the solvents chosen for this particular formulation were inadequate, useful information was obtained, and newer and better systems are currently being investigated.

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9

Correlation of Carrier Properties with Malathion Stability

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The stability of toxicant-carrier combinations used in pesticide wettable powder formulations cannot be easily predicted by evaluating various properties of the carrier. Several types of synthetic calcium silicates and their modifications were evaluated for malathion stability and other properties. The carriers were evaluated for pH (slurry), pK_a *(surface acidity), moisture content, absorptive capacity, and/or ion exchange capacity. These properties were correlated with actual malathion stabilities as measured at 40°C. storage for 1, 2, 3, and 7 months. The carrier properties evaluated did not offer a simple means of predicting compatibility in the variety of carriers tested.*

One aspect of the development of pesticide formulations is the selection of suitable carriers for wettable powders and for similar dry formulations. With some sensitive toxicants, it is often difficult to find a carrier that can be used for high percent formulations without some loss in activity. To select a suitable carrier, the pesticide formulator would like to utilize his knowledge of carrier properties rather than proceed by trial and error modified by prior experience. During a program to develop an improved, inert, absorptive carrier for malathion, we had an opportunity to attempt to correlate actual stability results with various carrier property measurements.

We worked with a variety of synthetic silicates and their modifications by various physical or chemical treatments or by various chemical additives. We particularly evaluated many synthetic hydrated calcium silicates, with and without additional treatments. These treatments included various organic and inorganic acid compounds, organic surface-active agents, and inorganic salts. We also studied samples dried to remove free moisture and/or some water of hydration. The modifications were selected to effect favorably the properties of the carriers.

Table I. Data Obtained

pH	*Water Absorption, %*	pK_a	*Ion Exchange meq./gram*	*Moisture, %*
8.80	588	+3.3/1.5	0.200	5.0
8.50	590	+3.3/1.5		0.5
8.50	590	+3.3/1.5		0.5
8.45	400	+1.5/−3.0		5.6
6.25	200	−3.0		9.7
8.10				3.7
7.80	185	−3.0		3.4
7.75	300	+4.0		3.0
11.60	394	<−3.0		3.6
8.45				
10.25	290			0.5
	520			
	520			
	490			
	490			
	490			
	490			
	490			
8.15		+3.3		3.6
9.20	200	+4.0		4.0
9.05	200	+3.3/1.5		4.7
9.55	210	+3.3/1.5	0.224	5.2
8.30		+3.3		
8.55		+3.3		
8.95		+3.3		5.1
8.15		+3.3		3.6
7.50				
		+4.0		
7.05	467	+4.0/3.3		4.9
8.35	363	+3.3		
9.05	500	+3.3	0.196	5.0
8.40	452	+3.3		
8.25	448	+3.3		
8.25	420	+3.3		
8.35	450	+3.3		
8.35	528	+4.0	0.192	6.0
9.20	364	+4.0		
8.35	215	+3.3		
8.25	528	+3.3		
8.20	495	+3.3		
9.30	400	+4.0/3.3		
9.25	356	+4.0/3.3		
9.40	423	+4.0		
7.90	378	+3.3		
9.05	567	+3.3		
8.90	510			

for Carrier Properties

Starting Malathion, %	*Loss after 40°C. Storage, %*			
	1 mo.	*2 mos.*	*3 mos.*	*7 mos.*
51.6	23.2	31.8	37.2	
48.4	17.3	22.3	25.6	
48.0	0.0	5.8	15.4	
50.4	17.4	19.8	25.4	
49.6	0.8	3.2	5.6	8.9
51.2	21.1	24.2	29.7	
49.2	2.4	4.1	4.9	13.0
40.0	3.0	7.0	10.0	17.0
49.2	49.6	73.3	92.0	
56.8	4.9	4.9	6.3	11.2
49.2	2.4	4.1	8.2	38.2
51.2	35.2	40.0	41.5	
51.2	36.0	41.5	43.0	
51.6	17.0	21.7	24.8	
50.4	26.2	29.4	34.2	
50.4	29.3	34.9	37.3	
50.4	27.0	32.6	36.5	
51.2	29.6	35.2	37.5	
50.4	2.4	2.4	2.4	4.0
50.4	7.1	11.1	11.9	22.2
50.4	4.0	4.0	4.0	11.9
50.0	25.6	53.6	72.0	
53.2	0.7	9.0	9.8	16.5
53.2	15.0	19.5	20.3	27.1
52.0	23.1	29.2	36.2	
53.2	0.0	0.0	0.0	2.2
52.8	12.9	25.8	35.6	
52.8	8.3	14.4	17.4	25.5
48.0	23.3	35.8	45.0	
51.6	10.8	13.9	17.0	25.5
49.6	16.9	25.0	29.0	64.0
49.2	11.4	15.4	16.2	33.4
49.2	11.4	16.2	16.2	33.4
49.6	9.7	14.5	16.1	31.4
48.4	8.3	12.8	15.3	30.2
48.4	37.2	54.9	66.5	
49.6	19.3	33.1	39.6	
46.0	9.6	10.4	13.0	21.7
52.8	8.3	11.4	15.1	29.5
51.2	10.1	13.3	11.7	35.2
49.2	30.9	42.4	50.5	
47.2	31.3	44.0	48.3	
48.0	38.3	58.3	70.0	
49.6	8.9	13.7	14.5	29.0
41.2	25.2	31.1	36.9	
41.6	25.9	34.6	43.2	

Table I.

pH	*Water Absorption, %*	*pK_a*	*Ion Exchange meq./gram*	*Moisture, %*
8.45	526		0.140	5.0
8.45	505		0.138	6.0
7.45	552			
8.25	389			
8.25	389			
8.60	566			
8.30	505			
8.35	474			
8.50	538			0.1
		+3.3		
	517			0.6
		+3.3		
8.50	408			0.7
	420	+3.3		
	500			
	500			
	444			
	450			
	435			
	500			
	380			
	200			
3.0	111			
	464			
	477			
	372			
	341	+4.0		
	439			
	495			
	495			
	380			
	575			
	494	+3.3		
8.20	168	+3.3		2.7
8.30	287	+3.3		3.8
	500			
8.50	204	+3.3		2.6
8.50	266	+3.3		2.6
8.50	250	+3.3		4.0
8.50	436	+3.3		2.4
8.40	384	+3.3		2.0
8.40	470	+3.3		3.0
8.15	344	+3.3		1.8
	380			
7.70	214	+3.3		0.7
		+3.3/1.5		

Continued

Starting Malathion, %	*Loss after 40°C. Storage, %*			
	1 mo.	*2 mos.*	*3 mos.*	*7 mos.*
42.8	16.8	28.1	40.2	
41.6	21.1	31.7	43.2	
38.4	3.1	19.8	26.1	36.5
40.0	0.0	23.0	27.0	21.0
39.2	10.2	31.6	38.8	
46.0	18.3	29.6	33.1	
42.4	24.6	35.0	52.0	
40.4	24.8	28.7	38.6	
40.4	14.8	32.6	51.5	
40.4	7.9	20.8	34.7	
42.4	9.4	16.0	27.4	41.6
40.4	12.9	19.8	29.7	42.6
40.4	11.9	23.8	34.6	
38.4	8.3	15.6	28.2	37.5
39.2	21.4	30.6	45.8	
39.2	17.3	32.6	47.9	
39.2	13.3	25.5	36.7	
40.4	15.8	23.8	38.6	
40.4	18.0	25.0	38.0	
38.8	38.2	62.8	87.6	
41.6	34.6	54.8	85.6	
38.8	7.2	14.4	28.8	47.5
32.0	8.8	10.0	27.5	33.8
41.2	12.6	22.3	31.1	
41.2	12.6	26.2	37.0	
42.4	27.4	42.5	60.5	
43.6	38.5	54.2	71.6	
39.2	19.4	34.7	50.0	
42.4	8.5	24.5	32.1	
41.6	9.6	21.1	34.6	
32.8	53.6	64.1	83.5	
38.4	21.8	37.5	51.0	
39.2	9.2	9.2	22.4	29.6
39.2	0.0	0.0	0.0	5.1
43.6	1.8	1.8	1.8	15.6
41.6	5.8	10.6	15.4	21.1
39.2	0.0	1.0	1.0	4.1
36.8	0.0	0.0	0.0	10.9
41.6	1.0	5.8	6.7	9.6
48.0	0.0	0.0	1.6	5.0
48.4	0.0	0.0	0.0	0.8
52.0	5.4	9.3	13.1	14.6
49.6	0.8	0.8	2.4	5.7
45.2	29.2	42.1	54.8	
41.2	0.0	1.9	1.9	6.8
49.2	0.0	0.0	1.6	5.7

Table I.

pH	*Water Absorption, %*	pK_a	*Ion Exchange meq./gram*	*Moisture, %*
7.20	140	<-3.0	0.005	0.5
10.20	240			16.4
8.15	370	$+3.3$	0.250	3.8
8.30	120	$+3.3$		1.6
5.60	45	-3.0	0.336	2.7

Table II. Regression Results *vs.* 3 Months' Malathion Loss

Independent Variable	*No. of Data Points*	*% Variation Explained*	*Correlation Coefficient*
pOH	64	5	−0.25
Water absorption	85	7	+0.28
pK_a	54	0	+0.14
Ion exchange	7	39	+0.70
Moisture	39	6	+0.28
Starting concentration	97	9	+0.14
Water absorption × starting concentration	85	7	+0.14
Moisture/pOH	28	29	+0.56

Unfortunately, we found only a weak correlation of the properties we measured and the actual malathion stability results. Therefore, this paper shows that the carrier properties we measured do not offer a means of predicting carrier-malathion compatibility. We did not find a significant correlation with actual stability results and some of the properties suggested in the following references.

Malina, Goldman, Trademan, and Polen (*4*) discussed the rate and extent of heptachlor decomposition as a function of carrier catalytic activity, as measured by the surface acidity pK_a values of Walling (*7*). They also said that the rate of change of concentration with time was equal for different concentrations. Eaton and McKane (*2*) discussed the formulation of aldrin, dieldrin, and endrin and felt that although pK_a was important, it gave only a partial correlation with stability. Mulryan (*5*) indicated that he found a correlation between carrier ion exchange capacity and the stability of methyl parathion formulations. He felt that pK_a and ion exchange involved the same active sites. Yost and Frederick

Continued

Starting Malathion, %	Loss after 40°C. Storage, %			
	1 mo.	2 mos.	3 mos.	7 mos.
32.8	0.0	0.0	0.0	2.4
62.0	16.1	39.4	50.0	
6.2	32.9	65.8	80.0	
5.6	4.3	7.9	11.0	18.0
5.6	12.9	33.8	50.0	

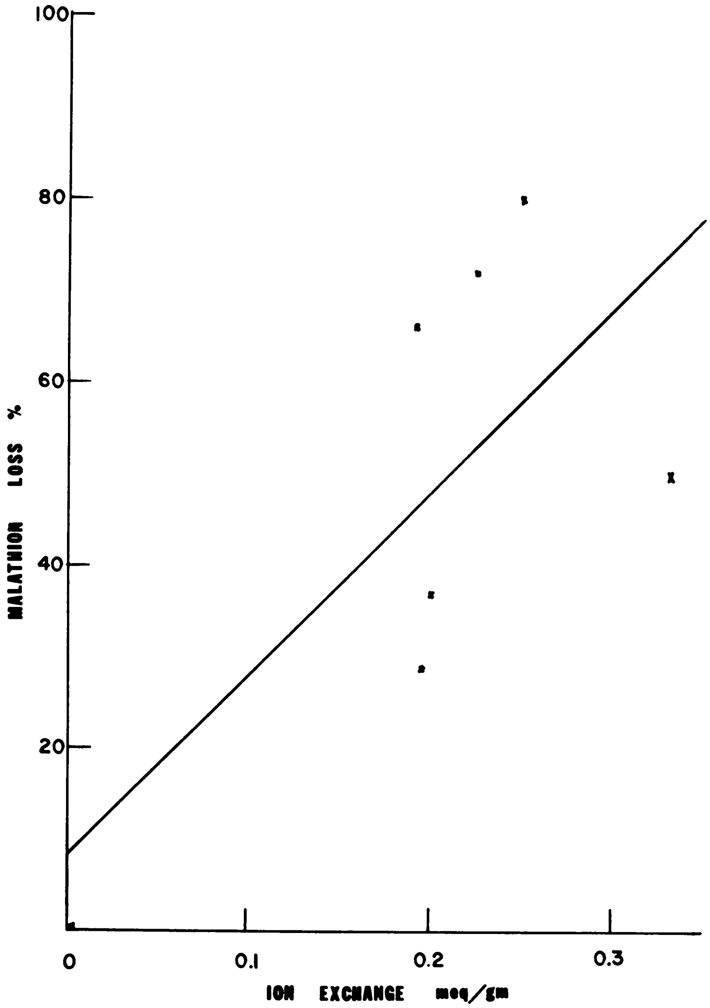

Figure 1. Correlation of stability vs. *carrier ion exchange capacity*

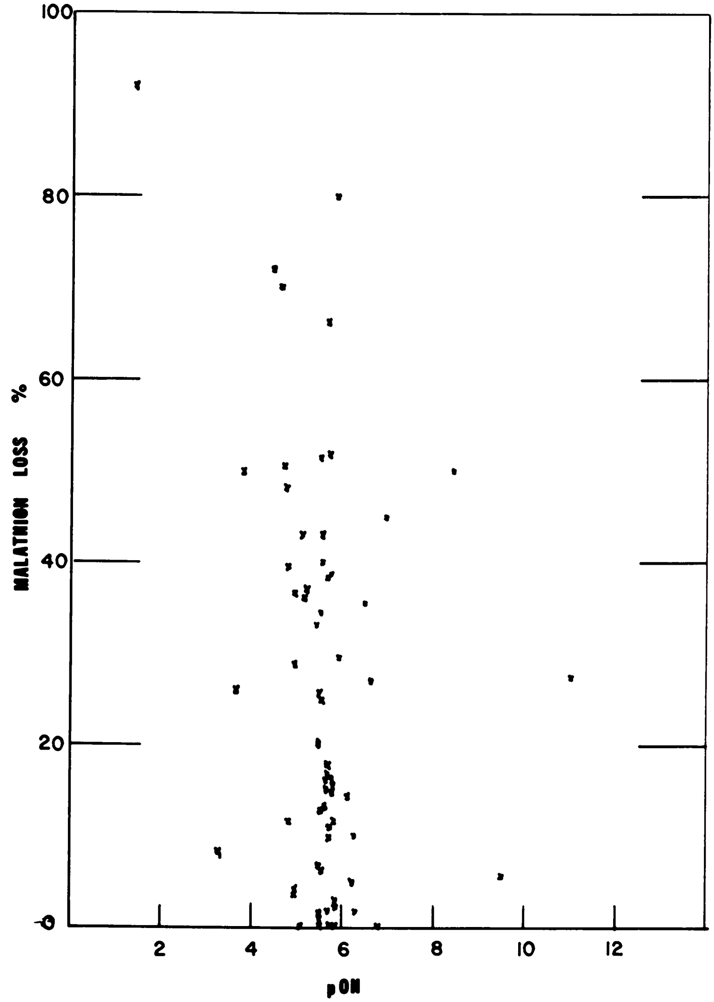

Figure 2. Correlation of stability vs. *carrier pOH*

(8) found that malathion is relatively stable in neutral or moderately acidic formulations, and in the absence of moisture a low degree of alkalinity could be tolerated. They indicated that the presence of moisture and pH above 7 could cause rapid hydrolysis. Further, stability would be better if the carrier were essentially saturated. Fowkes *et al.* (3) related pK_a to the stability of endrin and dieldrin formulations. They also mentioned the relationship of acid sites and exchange capacity. Polon and Sawyer (6) reported work with malathion and referred to moisture, pH, pK_a, and surface areas as causes of degradation.

Experimental

As a result of the above comments, we believed that the following carrier properties should show a correlation with malathion stability and should serve as easy methods of screening new carriers as they were developed. Therefore, we measured:

(1) pH: after 30 minutes' shaking of a 10% slurry;

(2) Moisture: weight loss after 1 hour at 105°C.;

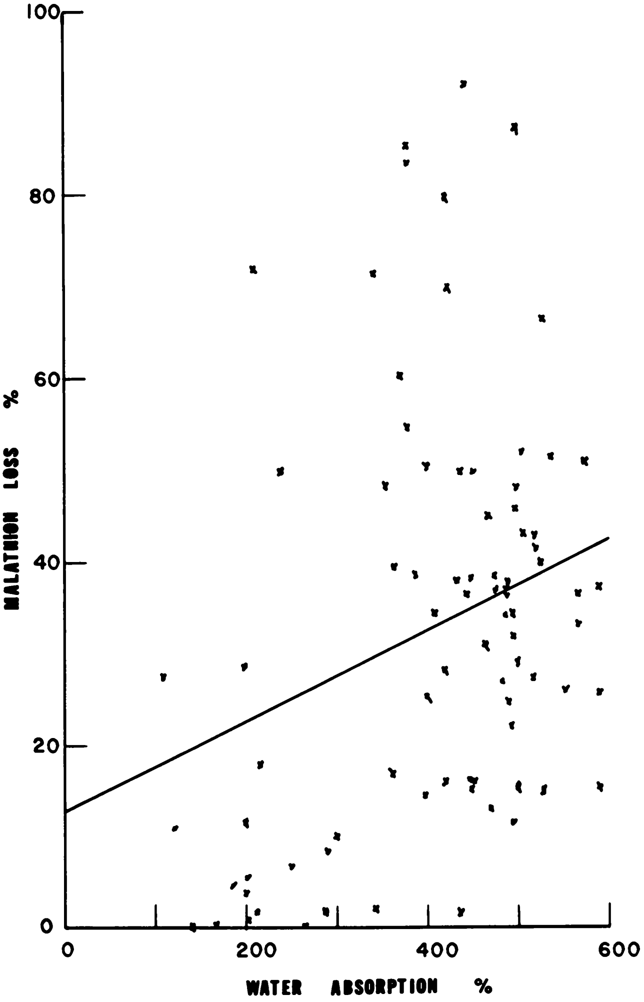

Figure 3. Correlation of stability vs. *carrier water absorption*

(3) Water absorption: by a modified Gardner-Coleman method, ASTM D1483-60, to a drop end point, with water addition rate at 3 drops per second;

(4) pK_a: by the method of Walling (7) using isooctane;

(5) Ion exchange: calculated from the difference in Versenate calcium titration between a sample contacted with 0.1N NaCl and one contacted with distilled water.

The data reported here were developed by evaluating these properties on the various synthetic silicates and their modifications that we

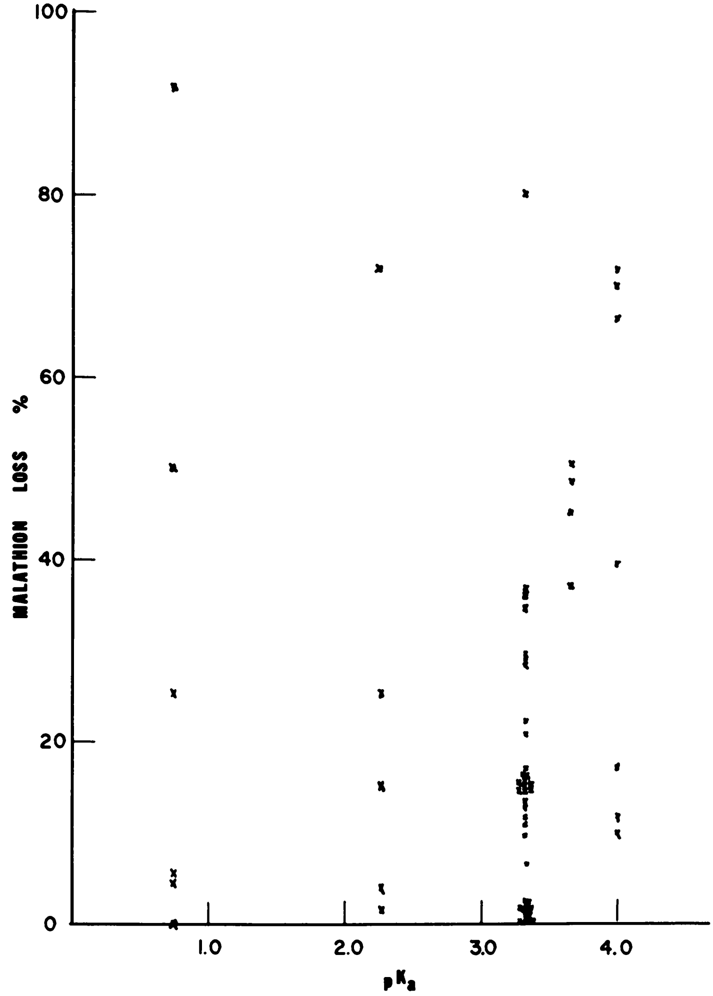

Figure 4. Correlation of stability vs. *carrier surface acidity coefficient*

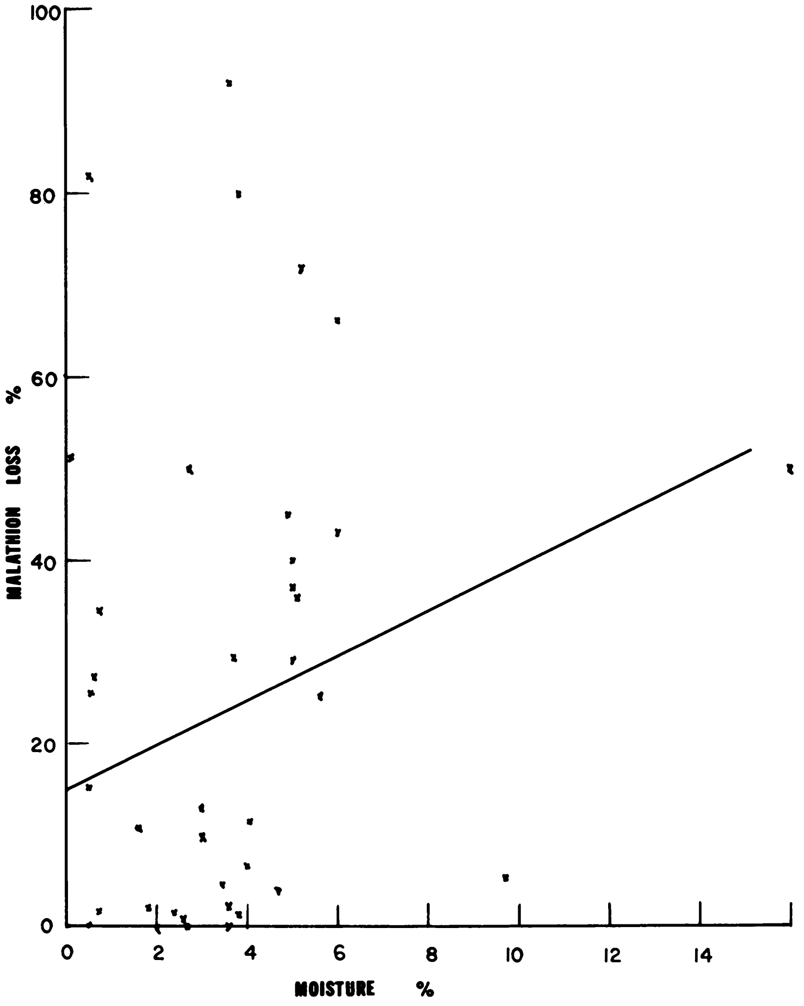

Figure 5. Correlation of stability vs. *carrier moisture content*

prepared. We also ran actual malathion stabilities by an accelerated oven storage test.

Procedure. Malathion-carrier concentrates were prepared by spray impregnating commercial malathion onto the carriers in a blender with an air-atomizing nozzle. The blended samples were placed in closed 8-ounce bottles in an oven controlled at 40°C. Samples were removed from the reblended bottles and analyzed colorimetrically after intervals of 0, 1, 2, 3, and 7 months in the oven. The colorimetric method was developed by American Cyanamid Co. (*1*) and used 95% ethanol extrac-

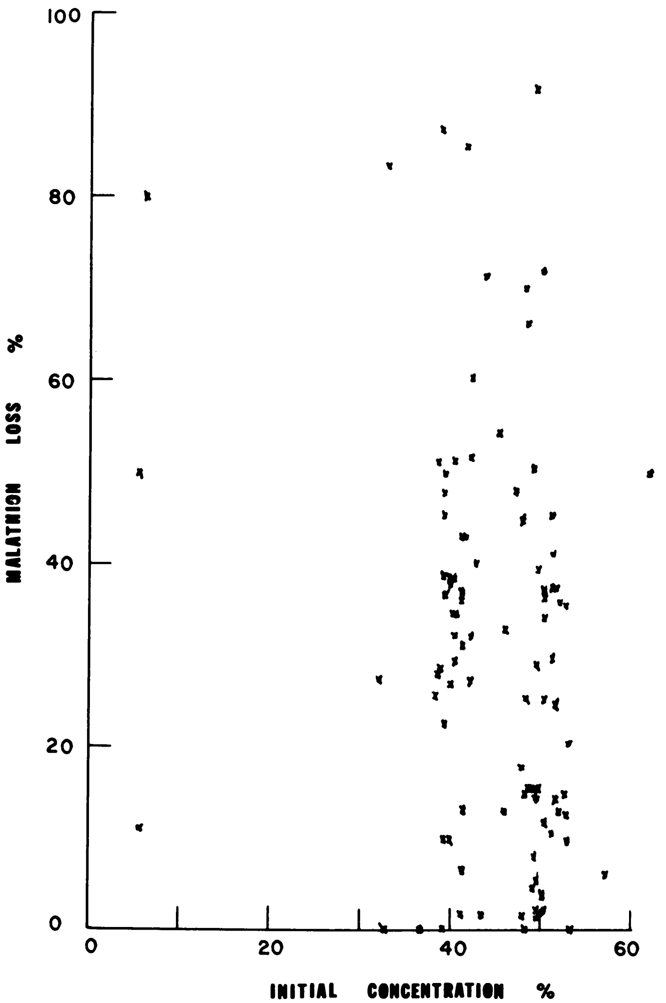

Figure 6. Correlation of stability vs. *initial sample malathion concentration*

tion and ferric oxidation to develop the color measured at 420 mμ in carbon tetrachloride. A Beckman DU spectrophotometer was used.

Analysis. During our project, we evaluated 97 variations of carriers (Table I). We did not measure all carrier properties on all samples, and unfortunately, we measured only a few samples for ion exchange capacity.

To evaluate the data carefully, we used a computer to run a linear regression analysis on the data. This type of analysis is based on several assumptions that are probably not rigorously true for these data. It must be assumed that there is no variation owing to data measurement, which of course is not exactly true. Also the pK_a data represent integer or point values rather than real, continuous values as required for linear regression.

To make maximum use of available data and yet to eliminate samples with missing properties, a number of separate computer runs were made, handling each property individually and handling various combinations of properties to evaluate interrelationships.

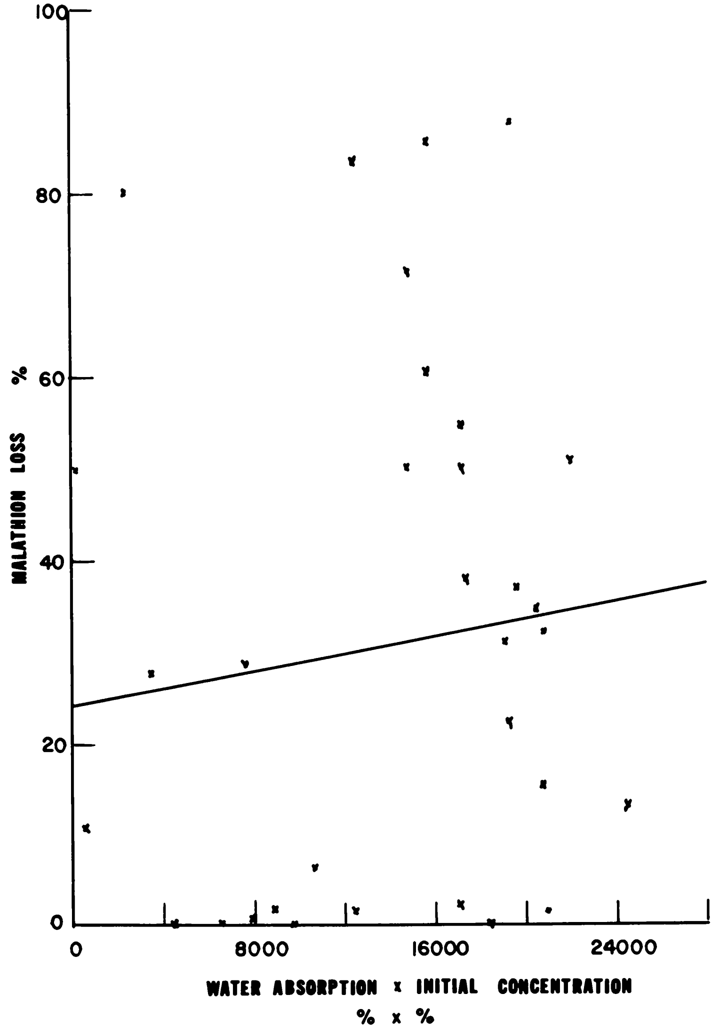

Figure 7. Correlation of stability vs. *function of degree of carrier saturation*

Results

The results of the computer evaluation indicate that at best there is only a weak correlation between the measured stability results and the measured properties of the carriers (*see* Table II). Taking the properties one at a time, we find insignificant correlation with the three months' malathion losses. The correlation coefficients, which should be close to 1.0 for good correlation, show that there is not much correlation with the individual properties. The only exception was ion exchange, and here there are so few data points that any conclusion is questionable. We also

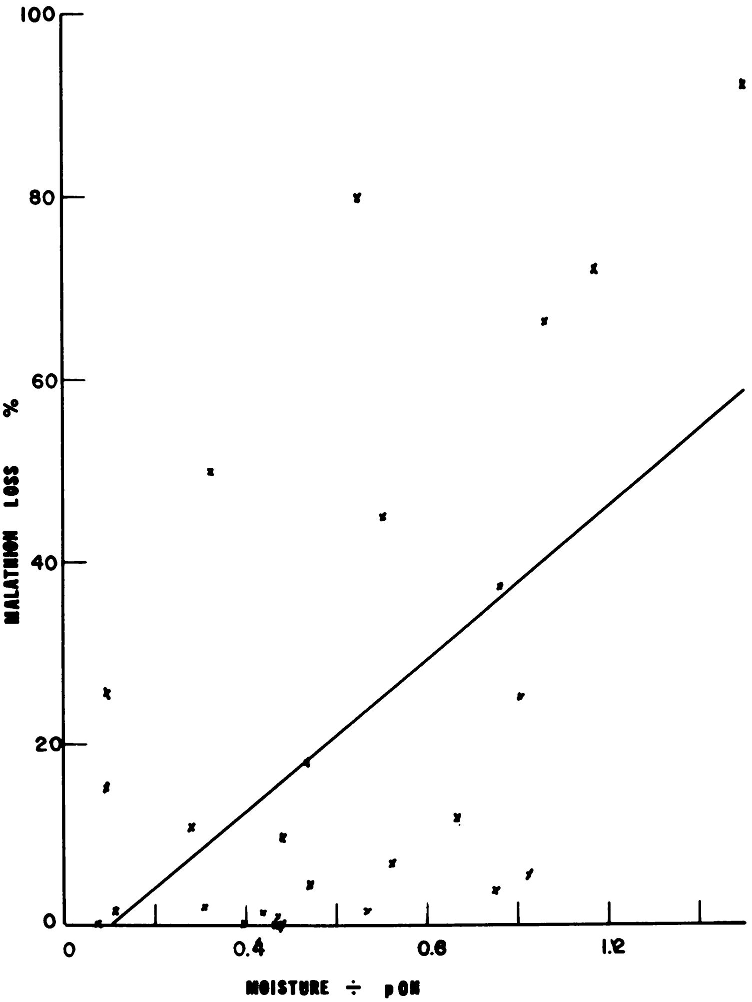

Figure 8. Correlation of stability vs. *function of carrier available alkalinity*

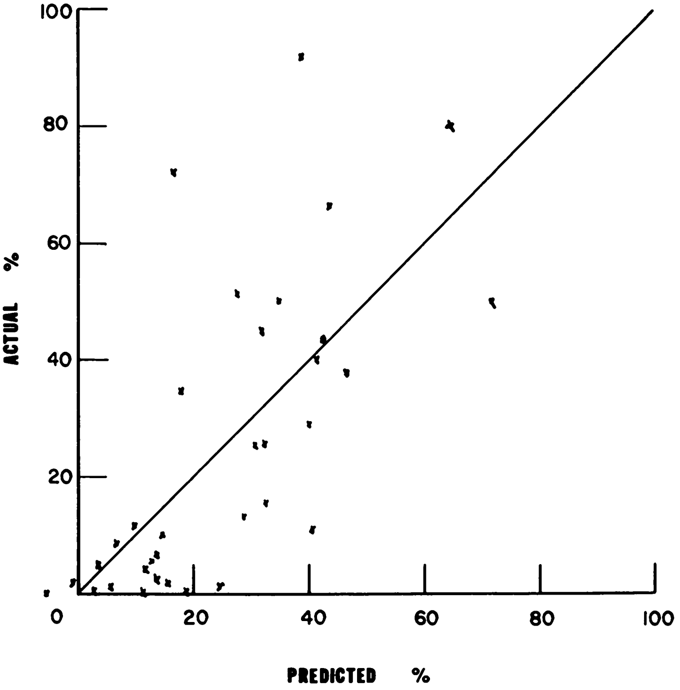

Figure 9. Correlation of actual stability vs. predicted stability calculated by Equation 1

tried to correlate the combined properties of water absorption times initial concentration, which should be a function of carrier saturation, and we combined moisture and reciprocal pOH to give some function of available alkalinity.

The poor correlation of these properties is shown by the essentially shotgun patterns seen in Figures 1–8. The straight line where shown is the computer-calculated regression line. In some cases, the computer could not calculate even a poor regression line, and it was omitted from the graph.

The best correlation resulted from regression of three variables that combined four of the measured carrier properties. The variables, moisture divided by pOH, water absorption, and reciprocal initial concentration, resulted in the following equation:

$$Y = -28.7 + 17.1\,(\mathrm{Mt/pOH}) + 301.8\,(1/\text{initial conc.}) + 0.09\,(\mathrm{WA}) \qquad (1)$$

This equation explains only 43% of the variation in results. This was further shown when the actual stability results were plotted *vs.* the predicted values in Figure 9. A large amount of scatter appeared around the theoretical line.

Conclusions

The properties that we evaluated predicted stability results only weakly. Perhaps under special conditions, such as specific carrier groups, such properties could give the desired correlations. However, for general carrier selection the correlations appear too weak, and therefore we should rely only on actual carrier stability tests. Reliance on correlations of these properties could lead to elimination of useful carriers or to selection of marginal ones.

Apparently the properties of moisture divided by pOH, reciprocal initial concentration, and water absorption as given in Equation 1 are only part of the story. Measurement of other properties, better able to indicate interactions between the surfaces of the toxicant and the carrier, might give significant correlations. These properties should probably include some function of available alkalinity and some function of the absorption capacity of the carrier and its degree of saturation. It is hoped that eventually someone will develop test methods for more useful properties of carriers that will correlate significantly with stability results.

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10

Parameters Affecting the Performance and Storage Stability of DDT 75% Water-Dispersible Powder

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DDT powder for use in malaria eradication programs must be highly suspendible to be used in hand spraying equipment and must withstand transport over long distances and storage for long periods in tropical climates. Several factors may affect the performance of DDT powders in the field after long term storage. Introduction of atmospheric moisture through small tears in the package did not affect the powder, but excessive amounts of clay diluent in the formulation are detrimental; a safe limit is about 3% clay. Compaction of DDT powders has an adverse effect upon their suspensibility when tested after accelerated storage treatment and after long term storage at ambient temperatures.

The most widely used insecticide in public health programs is DDT 75% water-dispersible powder. It is used in large quantities by the Agency for International Development (AID) World Malaria Eradication Program and by the domestic *Aedes aegypti* Eradication Program. In the malaria program, the powder must be shipped to remote areas of the world, where it is frequently stored for long times under tropical conditions. Therefore, high suspensibility after long term tropical storage becomes an important factor in producing a satisfactory formulation. Good suspension characteristics must be maintained for at least 1 year and preferably 2 years since it is often this long before the powder is used.

Miles *et al.* (*1*) conducted experiments showing the effect of moisture, pressure, and temperature on suspensibility. In each case, critical increases had an adverse effect. In the present work, three experiments were carried out to determine the effects of moisture, inert diluent composition, and compaction on the suspensibility. Suspensibility values were determined by the procedure outlined in the current AID Specification No. 2373-5 for DDT 75% water-dispersible powder. To conduct this test, sufficient powder is weighed and dispersed in a 100-ml. graduated cylinder to prepare a 2.5% suspension. The graduated cylinder is placed in a water bath and held at 30°C. for 30 minutes. After removal from the bath, a 25-ml. aliquot is taken at the 50-ml. mark of the graduate. The amount of DDT in the aliquot is determined, and from this the suspensibility is calculated. The AID specification requires that the above test be conducted on the powder in distilled water without pretreatment and in hard water after an accelerated storage treatment. The accelerated storage treatment was designed to indicate as nearly as possible the effect of 1 year of storage in tropical areas. In this treatment a test tube containing 5 grams of powder is heated for 2 hours in an oil bath maintained at 70°C. To meet the specification, the DDT in suspension in the aliquot taken from the center of the graduate must not be less than 1.75% for the sample before pretreatment or not less than 1.625% for the sample after pretreatment.

Moisture

The first experiment was designed to study the effect of ambient moisture under conditions simulating defective packaging. DDT water-dispersible powder is required to be packaged in hermetically sealed polyethylene bags enclosed in cardboard boxes for shipment. However, during the period from packaging to use, the bags may develop holes or tears, allowing the contents to be exposed to ambient moisture which could adversely affect the formulation.

To determine if ambient moisture has any effect on powders stored in damaged bags, eight 40-lb. boxes of fresh DDT 75% wettable powder were obtained from commercial sources. The boxes were numbered 1–8 and paired. They were then opened and sampled. The bags were examined for existing holes, and if any were found, they were sealed. Boxes 1, 2 were used as controls with no openings in the bags. A piece of glass tubing was secured in the open end of each of the other bags to expose the contents of the bag to the ambient conditions within the box. Tubing, 2 mm. in diameter, was used in Bags 3, 4, tubing 1/2-inch in diameter in Bags 5, 6, and tubing 2 inches in diameter in Bags 7, 8. The boxes were sealed and stored for sampling every 4 months. During the 12-months storage period the temperature ranged from 16° to 98°F. The average temperature was 65°F., and the average relative humidity was 75%. Results of suspensibility tests conducted in the aged samples are given in Table I. After 12 months in storage, there was no significant difference in suspensibility of the exposed samples compared with the control.

All samples for the following experiments were prepared in the laboratory. The formulation was typical of that used in commercial practice

Table I. Suspensibility of DDT Powder after Storage in Bags with Simulated Defects

		Suspensibility, %				
		Initial		*Ambient Storage, months*		
		BAS[a]	*AAS*[b]	*4*	*8*	*12*
Control	1	2.02	1.96	1.96	1.73	1.72
	2	1.96	1.90	1.93	1.82	1.72
2-mm. Tubing	3	2.02	1.86	1.91	1.73	1.74
	4	2.07	1.90	1.95	1.91	1.79
1/2-inch Tubing	5	2.01	1.89	1.92	1.86	1.76
	6	2.04	1.91	1.88	1.70	1.74
2-inch Tubing	7	2.02	1.85	1.96	1.79	1.72
	8	2.01	1.91	1.88	1.82	1.76

[a] Before accelerated storage.
[b] After accelerated storage.

and had the following composition: DDT, technical, 75%; Hi-Sil 233 (hydrated silica manufactured by Pittsburgh Plate Glass Co., Pittsburgh, Pa.), 18%; Attaclay (an attapulgus clay marketed by Minerals and Chemicals Corp., Menlo Park, N. J.), 3%; Marasperse N (a purified sodium lignosulfonate manufactured by the American Can Co., Marathon Products Division, New York, N. Y.), 2% and Igepon T-77 (a product containing 67% sodium *N*-methyl-*N*-oleoyl taurate manufactured by General Aniline and Film Corp., New York, N. Y.), 2%. Technical DDT was in powdered form and was aged for 12 months prior to formulation. The ingredients were mixed thoroughly and passed through a Wiley mill. The samples were then micronized in a 4-inch MicroMaster (Jet Pulverizer Co., Palmyra, N. J.) air mill. This reduced the average particle size to the range of 1.5 to 2.0 μ, as determined by the Fisher Sub-Sieve Sizer, which is somewhat finer than most commercial powders.

Percentage of Clay

The second experiment was carried out to test the effect of various percentages of clay on suspensibility. For economy, the industrial practice is to substitute diluent clay for Hi-Sil carrier. Up to this time the critical percentage of clay that can be added without adversely affecting the powder had not been well established. Combinations of diluent and carrier (*see* Table II and Figure 1 below) yielded results sufficient to establish this level.

Suspensibility was not affected in any of the formulations tested prior to accelerated storage treatment, but after this treatment there was a steady reduction in suspensibility as the percentage of clay was increased. Based on after-accelerated storage data, it appears that 3% clay is the safe maximum limit to ensure long shelf life.

Table II. Suspensibility of DDT Powders with Varying Clay Content

Clay, %	*Carrier, %*	*Suspensibility, %* *BAS*	*AAS*
0	21	2.36	2.16
3	18	2.48	1.88
6	15	2.43	1.62
8	13	2.40	1.20
11	10	2.40	0.78

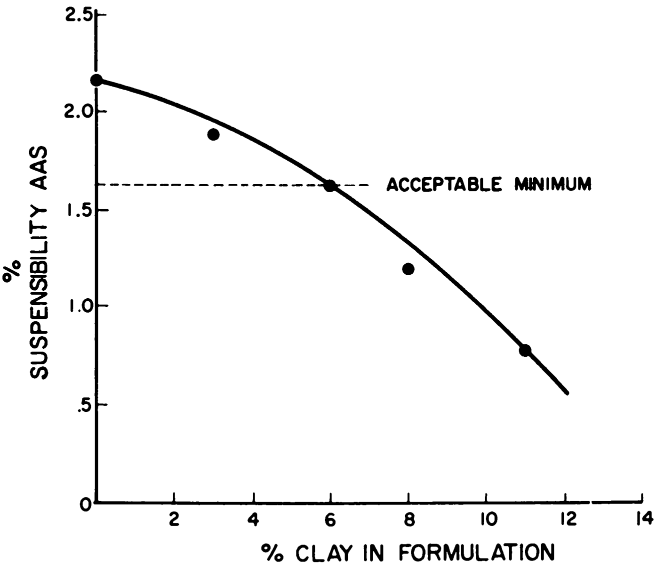

Figure 1. Change in suspensibility with clay concentration

Compaction

A third experiment was conducted to study the effect of compaction upon suspensibility. To reduce costs of ocean shipment, all industrial powders are compacted at the time of manufacture. Although the effects of compaction are unclear, the current practice is to compact immediately after air milling. Miles *et al.* (2) have shown that compaction decreases suspensibility when the formulation is subjected to conditions of tropical storage; however, their observations were made on aged formulations. This experiment, which is an extension of their work, used freshly ground powder to study the effect of the time interval between milling and compacting on suspensibility.

An instrument was designed to compact the powder on a laboratory scale. It consisted of a piston and cylinder arrangement (*see* Figure 2). By means of compressed air the piston was driven into the cylinder which was loaded with a weighed sample of the formulation. The piston and the bottom of the cylinder were perforated to allow air to escape. Filter paper retained the powder. The cylinder was calibrated for 100 ml. To duplicate the AID specification for packaging of 75 lb./18.24 gal., 49.27 grams of powder were added to the cylinder and compressed to 100 ml. After compaction, the pressure was released, allowing the piston to return to its original position. The powder was then removed from the compaction cylinder by a wooden ram.

A batch of powder was prepared according to the typical procedure given above and ground in the laboratory air mill. Samples were compacted by applying varying amounts of pressure in the laboratory compactor. One series was compacted when the powder was freshly ground, another series after storage for 2 days, and a third series after 7 days. The samples were tested for suspensibility without heat treatment as well as after accelerated storage treatment for 2 hours at 70°C. They were then stored at ambient temperatures and tested again 3 and 5 months later. Data from these tests are presented in Table III and Figures 3 and 4.

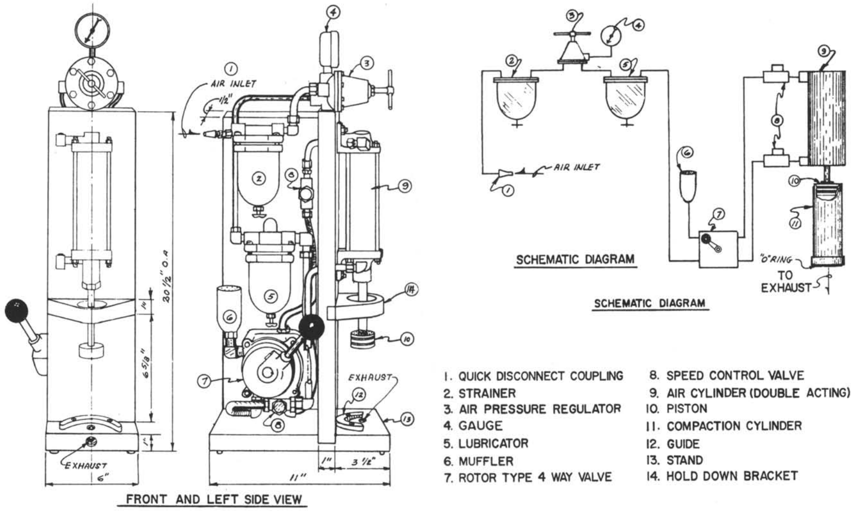

Figure 2. Shop drawing and schematic diagram of laboratory compactor

Compaction has little effect on the suspensibility of DDT powders when tested without accelerated-storage pretreatment; however, when tested after accelerated-storage pretreatment, the suspensibility decreased with increasing compaction. The aged powders, although tested without heat treatment, exhibited the same pattern of loss of suspensibility with increased compaction as did the fresh powders after the accelerated-storage treatment. This is a good indication of the validity of the accelerated-storage test. The data also show that aging of powders for up to one week after milling prior to compaction does not improve the suspensibility characteristics.

Table III. Suspensibility Values of DDT Powders Subjected to Varying Degrees of Compaction

Lb./18.24	*Lb./gal.*	*Age Before Compaction, days*						*Time in Storage, months*	
		0		*2*		*7*		*3*	*5*
		BAS	*AAS*	*BAS*	*AAS*	*BAS*	*AAS*		
40	2.19	2.42	2.28	2.46	2.40	2.43	2.28	2.42	2.33
50	2.74	2.43	2.27	2.44	2.27	2.46	2.28	2.44	2.34
60	3.29	2.43	2.17	2.47	2.27	2.47	2.25	2.42	2.28
70	3.84	2.42	1.97	2.43	2.03	2.46	2.03	2.40	2.00
75	4.11	2.41	1.80	2.46	1.79	2.46	1.92	2.19	1.93
85	4.66	2.41	1.24	2.44	1.22	2.44	1.21	1.16	1.48
95	5.22	2.41	1.03	2.44	0.82	2.38	0.79	0.68	1.24
105	5.76	2.29	0.86	2.39	0.69	2.27	0.75	0.54	0.75

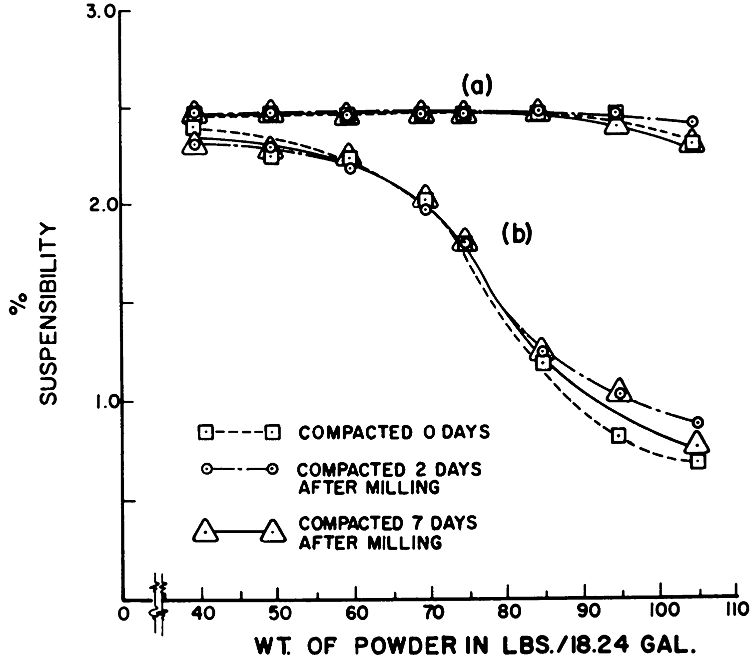

Figure 3. Effect of compaction on suspensibility of DDT powder tested before and after accelerated-storage treatment. Series a was tested before accelerated-storage treatment. Series b was tested after heating for 2 hours at 70°C.

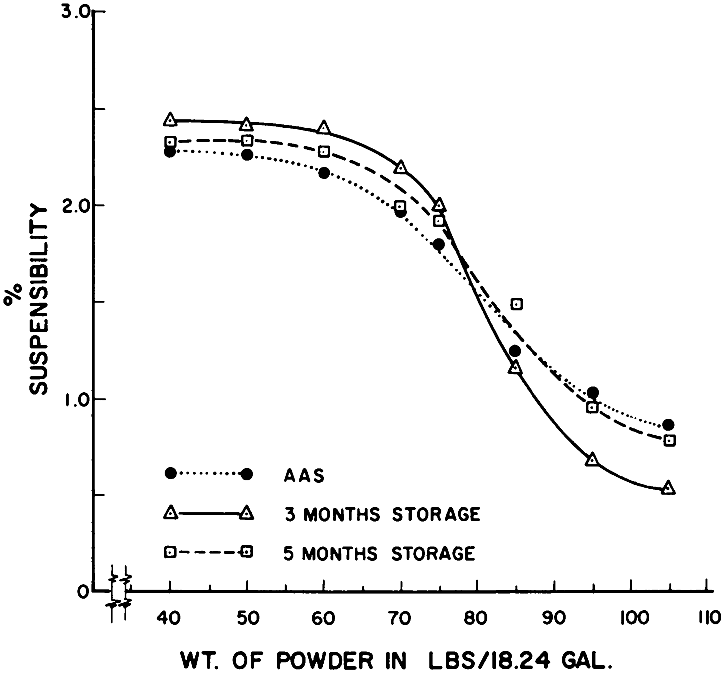

Figure 4. Effect of compaction on suspensibility of DDT powder held in long-term storage compared with short-term accelerated storage

Conclusions

From the data obtained on studying several variables in the production, packaging, and storage of high performance DDT water-dispersible powders, some practical conclusions can be drawn. The effect of small leaks and tears in the polyethylene bags has little or no effect on the quality of the powder in storage. The amount of clay diluent used in the formulation has a great influence on the quality of the powder. A safe limit for clay content appears to be about 3%. Although the data presented here were based on results obtained with Attaclay, similar values were observed when Barden clay and Hydrogloss clay were added as diluents.

Compaction of DDT powder has little effect on the suspensibility when the test is made on the fresh powder without a heat treatment; however, after accelerated-storage pretreatment at 70°C. for 2 hours, there is a consistent decrease in suspensibility with increasing compaction. Furthermore, compacted samples held in long-term storage exhibit the same pattern of loss of suspensibility as the samples subjected to accelerated-storage treatment. This is good evidence of the validity of the accelerated storage test as an indication of the probable long-term storage life of a given powder. These data also indicate that the present package volume is critical, and additional compaction would seriously affect the suspensibility after accelerated-storage treatment as well as after long-term storage. In fact, in the interest of good storage stability it would probably be prudent to increase the volume of the present container.

Aging of the DDT powder up to 1 week after air milling but before compaction does not affect its storage characteristics.

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Evaporation of Pesticides

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Pesticides are subject to considerable loss by evaporation when they are thinly spread over large areas of crop exposed to moving air. In this situation they are subject also to biochemical, photochemical, and solution losses which make it difficult to assess directly evaporation under field conditions. The rate of evaporation of water is easily determined and has been the subject of much experiment. The relationship of loss of pesticide to loss of water from the same surface can be verified by laboratory experiments. Crystallization and solution in leaf substances exert some effect also. When the pesticide is distributed in the soil, evaporation of water can accelerate that of the water-soluble pesticide; the mechanism lies in capillary flow of solution and not in the evaporation process itself.

The saturation vapor concentration (SVC) of any pure substance is related to its vapor pressure at any one temperature. It is closely analogous to solubility—*i.e.*, saturation concentration in a liquid—and might be called the solubility in a vacuum or in air. For our purpose the composition of the rest of the gas phase can be ignored because it is only at pressures much higher than atmospheric that this has any influence on the SVC. Solubility in liquids, however, depends strongly on the nature of the liquid because the molecules in a gas spend nearly all their time apart, suffering only brief mechanical collisions, whereas molecules in a liquid are always under the strong influence of the force fields of their neighbors.

In high vacuum processes, which are related to our subject only by electron microscope technique, the rate at which a substance evaporates has an ultimate limit depending on the number of molecules having momentarily enough energy to break away. Thereafter, they follow a straight line until they collide with an object. When a substance evaporates into air (unless it is in the form of an isolated particle less than about 1μ diameter), its rate of evaporation is determined solely by the SVC and the rate of diffusion through the air closely surrounding the substance.

In air at 20°C. the mean distance traveled by water molecules between successive collisions is about 5×10^{-6} cm. Even if the stagnant air layer around the object were only 0.1 mm. thick, each escaping water molecule would experience 2000 collisions if these did not alter its direction. In fact, as a result of these collisions the molecule would be just as often going backards as forwards, and the number of collisions would be much greater (and proportional to the square of the thickness). If the water could be maintained at 20°C. and the outer air were dry, the rate of escape by diffusion would be about 3×10^{-4} gram/sq. cm. sec., whereas the ultimate rate in a high vacuum has been calculated to be about 0.25 gram/sq. cm. sec., some 600 times greater (*1*).

Rate of Solution or Evaporation

The rate of solution of a substance in a liquid depends even more strongly on diffusion in the surrounding liquid because in this denser population of molecules, diffusion is much slower. However, there are cases where the rate of solution is determined by other factors—*e.g.*, the anomalously slow rate of solution of anhydrous lithium carbonate. Such cases are exceptional, involving a special mechanism, and I know of no evidence that any organic substances enter this class.

The less soluble a substance is in a liquid or in air, the slower its absolute rate of diffusion into previously pure liquid or air. The final content of a limited volume at saturation is proportionately less, so that the rate at which any chosen proportion of the saturation capacity is reached does not depend on solubility or SVC. It depends only on the diffusion coefficient, which does not depend strongly on the size of the diffusing molecule. An empty flask or one full of clean water can be 99% saturated with parathion just as quickly as it can with benzene or sodium chloride—in fact more quickly, for two reasons. First, benzene diffusing into air or sodium chloride diffusing into water builds up a large density gradient which stabilizes the fluid against convection owing to slight temperature variations, while a substance of low solubility or SVC leaves the fluid subject to chance stirring. Secondly, considerable heat exchange occurs during solution or evaporation, so that the vessel containing the volatile or soluble substance must be allowed time to settle to ambient temperature. These differences are, of course, reduced by rapid stirring, which is therefore more necessary with higher solubility or SVC.

This point is important because many experimenters intuitively believe the opposite. They assume that the less soluble or volatile a substance is, the more difficult it is to saturate a given volume of liquid or air. Consequently, they resort to excessively violent agitation, and, in the case of liquids, may build up stable fine dispersions of significant concentration, thus introducing more errors than they avoid. The idea is latent in that description cherished by 19th century German chemists—"schwer löslich" —slavishly translated as "difficultly" soluble, the only context in which this adverb is used. The phrase may mean that the substance has the rare property shown by lithium carbonate—*i.e.*, that the rate of solution is not determined by liquid-phase diffusion, but it more often simply disguises the presence of complicating impurities, or the author just cannot be bothered to find out the facts. The phrase should be eliminated by editors of reputable journals.

In one important respect it is true that the less soluble or volatile a substance is, the longer it takes to saturate its environment—*i.e.*, when adsorbing surfaces are present. At extremely low solubility or SVC even the glass walls of a simple vessel may be significant, but the porous walls of a room, the greater area of the foliage in a crop, or the even greater area of particles in the soil are much more important. The amount adsorbed is limited by area and is generally a much greater fraction of the content of the total volume the less the solubility or SVC. For soil, much more substance may be adsorbed on particles than is dissolved in soil water or present as vapor in the air space. This adsorption does not reduce the rate at which a particle dissolves or evaporates. In fact, it increases it, but since more must dissolve or evaporate down a limited concentration gradient, the rate of saturation of the environment is decreased.

Influence of Air Currents

Since the rate of evaporation is determined by diffusion of vapor in the surrounding air, it depends strongly on air movement and the geometry of the exposed surface. Close to this surface there will be relatively no movement of air. The substance will be transported from the surface only by molecular diffusion. Further away from the surface there is movement of air which can carry away the vapor more rapidly than molecular diffusion. This air movement operates in two ways. It continuously replaces the air around the evaporating surface, which is the only important factor for a small object like an isolated drop of water. This mere replacement, however, would be of little help to evaporation from a large area such as a lake because the replacement air has already been saturated upwind.

Here the second factor enters, arising from the fact that wind is never smoothly laminar in flow, except a very gentle wind under inversion conditions (when evaporation of water is not occurring). Normally a "drying" wind is turbulent, having a complicated structure of eddies of various sizes. This leads to a mixing of air composition which, over long enough time and distance, follows the mathematical laws of diffusion but with a diffusion coefficient hundreds of times greater than that of molecular diffusion. The process, of enormous importance for the entire atmospheric behavior, is called "eddy diffusion" (*20*).

At the simplest, therefore, the evaporation of water from a large area can be represented as diffusion into a horizontally shearing volume of air, the coefficient of vertical diffusion increasing from the molecular value of 0.24 sq. cm./sec. to several hundred times this value with increasing height. Most of the increase from slow molecular diffusion to rapid eddy diffusion occurs in the first few millimeters above the surface. From a few meters upward the atmosphere becomes more stable except for major wind changes which, if we are considering a large evaporating area like Lake Superior, are largely determined by the evaporation itself.

Obviously the theory of evaporation from large areas is quite complex, requiring computer evaluation even if all relevant data were available. There is, however, a vast amount of accumulated experimental data about water evaporation, and if we can establish the relationship between water and pesticide evaporation, we can use this material for prediction. The evaporation of water over a large area can always be viewed either as a small- or large-scale process. Thus, we can measure total evaporation from a lake in relation to wind conditions and the humidity and temperature of the air as it reaches the lake, or from small identical open vessels floated at various locations on the lake surface. The first would show an average rate roughly proportional to the 3/2 power of the lake diameter (if circular), to the 1/2 power of the wind velocity, and to the humidity deficit of the incoming air. The second would show a rate approximately proportional to the local humidity deficit but more nearly proportional to vessel area.

The local measurement would at first seem the best comparison for the evaporation of a pesticide deposit, allowing for the humidity of the local air into which the water is evaporating and assuming that the pesticide is evaporating into "clean" air—*i.e.*, there is no counterpart to the partial previous loading of the air with vapor. However, this assumption cannot be made without careful consideration. Is there a significant general loading of the whole air above a large field with evaporated pesticide, or is the rate of loss from any local deposit the same as if the rest of the crop had not been sprayed?

Heat Effects in Evaporation

Before attempting an answer, we must closely examine the factors governing a small-scale evaporation process. The simplest case is that of a small drop in free fall or suspended on a thin thread. If the drop is in the range of 10–200μ diameter, the peculiar mathematics of spherically divergent diffusion dictate that the rate of evaporation is proportional to radius, not area, and almost independent of any air flow of realistic magnitude.

The rate of evaporation of water from such an isolated drop, although governed entirely by diffusion, is not governed entirely by diffusion of water vapor. Latent heat must be supplied during evaporation. The drop cools until this heat is conducted in from the air at a rate equalling the outward diffusion of water vapor. There is no other significant heat source since even if the drop were black, the direct radiation contribution of full sunlight would not be important for drops of this size.

The balance between conduction and diffusion still operates for a much larger isolated wet object, provided radiation is excluded. This is the basis of the wet bulb thermometer method for measuring humidity. The actual rate of evaporation now is not as simply determined and is influenced by wind. The wet bulb temperature is almost independent of wind condition, owing to a convenient accident. Heat conduction is a diffusion process, and the diffusion coefficient for water vapor in air (0.24 sq. cm./sec.) is numerically close to the diffusion coefficient of temperature in air (thermal conductivity/specific heat = 0.20 sq. cm./sec.). Hence, the exact way in which each molecular diffusion process merges into the more rapid eddy diffusion process is not important because no matter how complex the transition is, it must be quantitatively similar for the two processes.

Calculation of the balance of inward heat diffusion and outward vapor diffusion leads to Equation 1:

$$\Delta T = (1 - H)\,\frac{\lambda D C_o}{K + \alpha\lambda D C_o} \qquad (1)$$

where ΔT is the difference in temperature between dry and wet bulbs, H is the relative humidity of the outer air, C_o is the SVC of the evaporating substance at the temperature of the outer air, D is the diffusion coefficient of the vapor in air, K is the thermal conductivity of air, and λ is the latent heat of evaporation referred to the unit used in concentration (*i.e.*, if C_o is in grams/cc., λ must be in cal./gram); α is the relative variation of C_o with temperature, $\alpha = \frac{\lambda M}{RT^2} - \frac{1}{T}$, where M is the molecular weight if the gas constant R is expressed (as usual) in cal./mole. [Relative humidity is introduced only for evaporation of water since this is the only case when the air is already partly loaded to a significant extent with vapor. The correction for prior partial saturation of other substances is not usually important. If it were, it could not be treated as simply because the diffusion coefficient of other vapors is considerably less than that of temperature.]

The $\frac{1}{T}$ term in α allows $\frac{\lambda}{RT^2}$ to determine $\frac{d \log p}{dT}$ (p = vapor pressure), whereas we expect diffusion rate to be determined by concentration and therefore $\frac{d \log C}{dT}$ to be required. This is arguable since complications arise in any diffusion process in a temperature gradient. For more accurate discussion, a treatise such as that by Fuchs (*15*) should be consulted. We are concerned only with approximate values, note that $\frac{1}{T}$ is much smaller than $\frac{\lambda M}{RT^2}$, and ignore it.

We can then show that for rate of evaporation through a stagnant layer of thickness l,

$$\text{Rate} = \frac{C_o(1-H)}{l} \Big/ \left[\frac{1}{D} + \frac{\lambda^2 C_o M}{KRT^2}\right] \qquad (2)$$

For water and an ambient temperature of 20°C. Equation 1 gives $\Delta T = (1 - H)/0.084$, consistent with the Smithsonian tables, and Equation 2 gives:

$$\text{Rate} = \frac{C_o(1-H)}{l} \Big/ (4.17 + 10.84) \qquad (3)$$

Equation 3 shows that if water must evaporate from a surface which can receive heat only from air through the same surface, it will evaporate at only about 0.27 of the rate which obtains under isothermal conditions (where there is no second term in the denominator). The thermal component of the total resistance is thus about four times the mass-diffusion component.

The thermal term, being proportional to C_o, becomes relatively less important at lower temperatures and with less volatile substances. It is greater for ether than for water, and for ether the temperature drop is so great that another factor enters—namely, condensation of water from the air on the evaporating surface. For xylene at 20°C. the thermal term reduces the evaporation rate from an isolated surface to about 0.6 of the isothermal value (*cf.*, to 0.27 for water), and for most pesticides (except the fumigants) the reduction is negligible.

In applying Equation 2 to pesticides, therefore, we can set the second term in the denominator equal to zero; however, since we want to use this equation mainly for comparison with other substances (since *l* can only be measured by this equation), we have a complication—*i.e.*, the best known comparison substance, water, may have any value for this second term between 0 and 4 times the first (at 20°: at 10°C., *ca.* 0 to 2.3). The first condition could apply to a smear of water on a copper plate provided with vanes below to conduct heat as quickly as possible from the air, the second to an isolated drop or a wet cloth or paper. Practical surfaces, leaves, soil, etc. will be somewhere in between. Insofar as significant heat is received on such surfaces by radiation or supplied by conduction from the soil, its effect will be nearly the same on water and pesticide and does not therefore disturb the comparison.

Laboratory Comparison of Evaporation Rates

Some indirect method of measuring evaporative loss is needed because of the difficulty of direct measurements. Total amounts in random crop samples at various times after spraying can be measured by residue analytical methods (radioactive tracer or otherwise). The rate of loss so determined is subject to large statistical errors and includes losses by chemical and biochemical reaction and perhaps translocation in the crop as well. Exposure of typical test surfaces treated with some model substance, preferably less volatile than water but sufficiently volatile for simple gravimetric procedure, would seem the most suitable. We will see, however, how successful water is as a model for providing rough estimates.

Crude experiments were performed in the laboratory with substances unlikely to show significant weight change by adsorption of water or oxygen and sufficiently volatile for loss to be recorded conveniently on an ordinary balance. Petri dishes (41 sq. cm. area) were used to contain the substances, mostly liquids and used in the pure state. Two solids were included: *p*-dichlorobenzene and naphthalene. These were layered in coarse powder form, and the surface was sprayed with a solution of low molecular weight polyisobutene in petroleum ether until it was sticky enough to prevent blowing of the powder in the wind it was intended to use.

Not all measurements could be conducted together because the loss of weight rates covered a range of over 1000-fold. Moreover, it was desirable to use three replicates of each substance and arrange the dishes on a grid through which the draught from an ordinary room fan could blow, occupying a sufficiently small area for the wind to be reasonably uniform. Dishes were removed for weighing at intervals and replaced in different positions to randomize ventilation. The experiments were conducted in three groups over different time intervals according to volatility, with anisole and *n*-octanol forming the common compounds linking the groups.

Mean room temperature was 20°C., and no thermostatic measures were taken, but the rates were recorded relative to that of one of the standards. Water and xylene received closer study (described below) to illustrate particular points. For the most volatile group three ventilating conditions were used: (1) no deliberate ventilation, (2) gentle fanning, (3) more violent fanning with the wind directed about 45° downward onto the grid of dishes. The third condition visibly disturbed the liquid surfaces. The wind velocity at dish level was about 10 m.p.h. (used only for the less volatile groups).

Table I. Laboratory Determination of Evaporation Rates

Ventilation	*Substance*	*Vapor Pressure* (p), *mm. at 20°C.*	*Molecular Weight* (M)	*Rate of Loss* (W) *grams/ min.* $\times 10^4$	$W/p\sqrt{M}$
Still	Water	17.5	18	59	1.12[a]
	2,2,4-Trimethylpentane	37	114	540	1.37
	m-Xylene	6.2	106	76	1.19
	Anisole	2.8	108	30	1.03
Slow wind	Water	17.5	18	93	1.79[a]
	2,2,4-Trimethylpentane	37	114	717	1.82
	m-Xylene	6.2	106	174	2.72
	Anisole	2.8	108	102	3.50
Stronger wind	Water	17.5	18	108	2.07[a] [7.45]
	2,2,4-Trimethylpentane	37	114	1186	3.01
	m-Xylene	6.2	106	267	4.18 [6.7]
	Anisole	2.8	108	158	5.04
Stronger wind	Anisole	2.8	108	158	5.04
	p-Dichlorobenzene	0.80	147	54	5.6
	N,N-Dimethylaniline	0.66	121	41	5.6
	n-Octanol	0.073	130	4.1	4.9
Stronger wind	*n*-Octanol	0.073	130	4.1	4.9
	Naphthalene	0.049	128	3.3	6.0
	Exp. compound	0.022	162	1.5	5.4

[a] Corrected for 30% relative humidity of ambient air. Figures in brackets allow for full wet bulb depression.

The data available on the molecular diffusion coefficient of organic vapors in air are meager, but they indicate (in accordance with approximate theory) an inverse proportionality to the square root of molecular weight. The rate of mass transfer by molecular diffusion will be proportional to the diffusion coefficient and to the SVC, itself proportional to vapor pressure times molecular weight (M). We should expect, therefore, under standard conditions of ventilation, that the rate of loss will be proportional to vapor pressure × $\sqrt{M}$. The ratio of observed rate to this product is listed in the last column of Table I. For anisole and compounds less volatile in the strong wind, the ratio is as constant as the crudity of the measurements and assumptions would allow us to expect.

The mechanism of deviation of the ratio from a constant value for the more volatile substances has already been indicated. For these substances the heat demand slows evaporation. This effect is greater when the high wind blows on the evaporating surface because the heat exchange through the base of the dish is relatively less important. The water evaporation rate has been corrected, in forming the product in the last column, for the ambient air being at 30% relative humidity (RH).

We wish only to show that we can reasonably predict evaporation rate on the basis of vapor pressure if the data for a model substance which is not too volatile are known.

Results reported by Phillips (*19*) for evaporation of aldrin (labeled with ^{36}Cl) from a 20-sq. cm. area on a flat plate are six times greater than predicted from Table I, taking the vapor pressure as 4×10^{-6} mm. Hg, from Martin (*18*).

The rates calculated for xylene and water (into 30% RH) diffusing through a 1 cm. depth of stagnant air over an area of 40 sq. cm. are (in units of 10^{-4} gram/min.) 84 and 70 under isothermal conditions and 52 and 19 when heat can diffuse only by the same route by which vapor diffuses out.

Comparison with experimental results shows that the higher the ventilation rate, the more closely the ratio approaches that expected for the isolated condition, but it does not fully reach it. The values in brackets in the last column of Table I are corrected on the assumption that full temperature difference was built up. Clearly an intermediate condition still prevailed, and in fact the water temperature in this condition was found to be 5.1° below ambient compared with 8.3° below for a wet bulb.

Under field conditions water evaporation normally occurs from the same surfaces as evaporation of pesticide. Any temperature effect caused by the former will therefore affect the latter, and in this repect the state of affairs is simpler. On the other hand, leaves can restrict water evaporation, and the soil surface is very complex; hence, other complications appear under field conditions. All these factors, however, will make the pesticide evaporation rate (if the pesticide is fully exposed on an outer surface) faster than that calculated from the water rate.

Comparison with Table I shows also that the effective depth of the stagnant air layer above the liquid is of the order of 10 mm. in still air and 3 mm. in strong wind. van den Honert (*16*) quotes figures for outside conditions ranging from 10 to 0.4 mm. in a much stronger wind.

An important factor in laboratory "still air" evaporation of volatile liquids is self-stirring caused by the difference in density between saturated and "clean" air. Dry air at 20°C. becomes 1.05×10^{-5} gram/cc. (about 0.85%) lighter when it is saturated with water vapor at the same temperature. When, however, it is saturated at the temperature of the wet bulb—*i.e.*, in contact with a surface of isolated water, it becomes about 3% heavier. Self-stirring above water therefore depends on the heat transfer conditions. Air saturated with xylene vapor is 2.4% heavier than clean air when both are at 20°C., and in this case any temperature drop increases the difference. From a flat vessel, therefore, the xylene vapor tends to spill over the edge and thus to limit the stagnant layer depth. In a deep vessel, the density gradient stabilizes the air layer for xylene but ceases to do so for water if heat conduction through the vessel walls is important.

Vessels of the same diameter as those used for the experiments reported in Table I but of greater height were filled to various depths with water and xylene, and measurements in still air were repeated (Table II). Where the evaporation rate of xylene is reduced in approximate proportion to the height, that of water is much less influenced.

Table II. Evaporation of Water and Xylene through Different Heights

Substance	*Loss (grams/min. $\times 10^4$) when Vertical Distance between Liquid Level and Vessel Rim is:*			
	1 cm.	*5 cm.*	*10 cm.*	*20 cm.*
Xylene	56	14	7.5	4.3
Water	48	39	28	22

In field conditions this complication would not occur. We are not likely to be concerned with a pesticide with as heavy a vapor as xylene (except in fumigation work), and convection from wind and local heating will always be more important than that produced by the vapor itself. This experiment is quoted as an example of a complication to avoid in laboratory work.

Decrease of Evaporation Rate with Time

The rate of loss of substance from a complete surface of constant area is independent of the depth of the layer below the surface. Under constant conditions of ventilation, therefore, the rate will be constant until so little substance remains that it can no longer cover the surface. The way this rate then falls off will be complex. There is no reason whatever, from theory or experiment, to suppose that the loss will be exponential. There is a tendency to assume that the natural form of any rate of decay is exponential, but this is only true of a uniformly distributed noninteracting population. For evaporation, exponential loss can be expected only for a volatile dilute component of an otherwise involatile and stirred solution, where the vapor pressure will be proportional to concentration. This could correspond to some field conditions of residues but not without other complications.

Evaporation from glass plates must always be quoted in absolute terms, and the conditions must be specified. Statements, which could be quoted from the literature, such as "23% of the deposit is lost in 24 hours" (density of deposit not stated) are meaningless.

The factors which decrease evaporation rate with time are (1) retreat of an initially continuous deposit into discrete small areas as it gets too thin to be coherent, (2) influence of adsorption or solution in the porous, oily, or wet surface, (3) retreat of a deposit, initially lying on the outer surface, into deeper capillary spaces.

The third factor introduces some important additional ones, especially for loss from the soil, and is discussed separately below. The second factor, for water-soluble substances, is associated with the third. Solution in superficial leaf oils and applied solvents is also considered separately.

There is already a well-known parallel to the influence of the first factor in the control of evaporation from leaves by the stomata. Much work has been done since the classic researches of Brown and Escombe (8). It is not possible here to summarize it adequately, but it is generally agreed that the stomata, which are present (if at all) at a high population density of many per square millimeter, have little effect under normal wind conditions until they become nearly closed. For the resistance of a pattern of holes to be important compared with that of the gross stagnant layer, the width of the holes must be very small compared with their distance apart, or their distance apart must be large compared with the effective thickness of the stagnant air layer. The latter condition is not met by stomata. The first condition is not likely to be important for pesticide deposits because small particles are usually grouped together within the coarser pattern of the spray droplets or the drainage pattern determined by the leaf structure.

It is therefore reasonable to assume that the evaporation rate of residue is proportional to the gross area of spray deposit for a pesticide remaining exposed on a leaf surface. The pesticide will be lost at a constant rate, under constant conditions of ventilation, until the contaminated area decreases significantly.

Evaporation from Solution

At the surface of a solution, equilibrium exists between the uppermost layer of liquid and the vapor in the lowest layer of air. The evaporation rate is determined by the stirring condition in both air and liquid and diffusion in the stagnant layers. Since diffusion coefficients in air are of the order of 10^4 times those in liquids, one might at first expect the more important resistance to be located in the liquid, but this is more than compensated by two other factors. First, the concentrations (and therefore gradients) are usually many times greater in the liquid. Secondly, the viscosity of water is about 60 times that of air, while the density is some 850 times. A given velocity is therefore more slowly arrested in water than in air; it is in fact easier to agitate water than air close to a fixed surface. Self-stirring of liquids by composition changes is greater than the corresponding effect in air, and the same would apply to temperature changes were it not for the great difference in specific heat. A 1°C. difference at 20°C. makes a 2×10^{-4} gram/cc. difference in the density of water but only 6×10^{-7} gram/cc. in the density of air, but the same amount of heat absorbed in the same volume makes 12 times as much difference in air density as in water density.

Benzene and carbon tetrachloride are about equally volatile. From solutions of equal concentration in methylnaphthalene they are lost, at first, at about the same speed, but while the rate of loss of benzene from an unstirred vessel remains constant, that of carbon tetrachloride falls rapidly. Loss of benzene leaves the surface solution heavier, and self-stirring occurs; loss of carbon tetrachloride leaves it lighter, and a concentration gradient is stabilized.

During evaporation from soil or field crops, the stirring of liquid layers is not important, but it should not be neglected in laboratory comparisons. Pesticide solutions subject to evaporation in the field occur in three main situations:

(1) Where the pesticide is dissolved in the superficial oils or cutin of the leaf.

(2) Where it is dissolved in plant sap (*e.g.*, systemic insecticides).

(3) Where it is dissolved in soil water.

In the first case, the layer of solution is so thin that diffusion within it is probably unimportant. In the case of the mesophytes, to which group nearly all crops belong, surface oils and waxes rarely amount to as much as 100 μgrams/sq. cm. of leaf surface (*i.e.*, mean thickness less than 0.5μ on each side) (*3, 13*). Internal oils, much less accessible, may be present in about the same amount (*9*). Some fruits may have more superficial oils or soft waxes—*e.g.*, on apple skin there is about 400 μgrams/sq. cm. (*3*). The polymeric cutin itself, highly lipophilic but not too swollen by fatty solvents, is generally 1—3μ thick (200–600 μgrams/sq. cm. taking both sides) (*4*). One pound of a pesticide uniformly distributed over a flat acre leaves a deposit of 11 μgrams/sq. cm. Pesticides are rarely applied as uniformly. There is more likely to be about one-tenth of a flat acre actually covered, in which the deposit density will be correspondingly higher. It is therefore unlikely that much of an oil-soluble pesticide will be dissolved in superficial oils except on fruits. Such solution may delay the later stages of evaporative loss (approximately exponentially) because the rate of equilibration within the thin oil layer will be rapid (about 1 sec. for 1-μ thickness at $D = 10^{-8}$ sq. cm./sec.—*i.e.*, 1/100 of rate in normal liquids). Within the crosslinked cutin, D could be much lower, and a long delay in the release of a small "tail" fraction of pesticide could be expected.

In the third case, we are concerned with a considerable depth of water distributed in fine channels and small pockets where there is negligible stirring. Since the result is important and its explanation is often misunderstood, it is discussed separately under wick-evaporation.

Steam Distillation

Where a solution of a moderately volatile organic substance in water is distilled, the distillate is often richer in organic substance than the residue and may form two separate phases. The evaporation of pesticide along with water from wet soil is often referred to as steam distillation or codistillation. The implication that the pesticide evaporates more rapidly because of the presence of the water is entirely correct, but to imply that steam distillation is the explanation directs attention to the wrong part or the total process.

The word distillation in the chemical laboratory is usually confined to a process in which the liquid or mixture in the boiler actually reaches the pressure allowed within the apparatus so that rapid bulk flow of vapor takes place from boiler to condenser. The speed of transfer rises enormously when this pressure is reached. If water were not present in a steam distillation, the other components would not reach the necessary pressure at the same temperature, and only slow diffusive transfer in the gas phase would occur. The presence of water does not assist diffusive transfer but only lowers the temperature at which diffusion gives place to bulk flow. The use of steam as a carrier gas allows easy collection.

During evaporation from moist soil, there is no distillation in this sense. Evaporation of both water and pesticide occurs purely by diffusion. The mechanism in a laboratory apparatus by which water accelerates diffusion into a bulk flow distillation is not operative here.

Loss of DDT during evaporation of water from very dilute solutions or suspension has been investigated by Bowman *et al.* (*2, 7*), who refer to co-distillation to explain the loss of DDT accompanying the loss of water, without any real evidence that the water has any influence. No parallel experiments on vessels without water are reported, and only in one comparison trial was distillation involving gas flow carried out. In all other cases water and DDT were diffusing together, probably with no mutual influence, through air. In fact, in the earlier paper the ratio of rates of evaporation was found to be close to those predicted from the known vapor pressures. Unfortunately, the rates were assumed to be proportional to the product of vapor pressure and molecular weight, true for flow distillation only, whereas for diffusive distillation the square root of molecular weights (*see above*) is more likely to be relevant. This correction reduces the predicted DDT/water ratio to about 0.23 of the authors' calculation. In the later paper the experimental ratio is revised upward so that we have DDT evaporating about 10 times faster than expected.

In these experiments the DDT would almost certainly be in the supercooled liquid state, which persists for a surprisingly long time in much more concentrated suspensions than those used. The vapor pressures quoted from Balson (*5*) and the later, higher figures of Dickinson (*10*) refer to crystalline DDT. The supercooled liquid would be expected (since the solubility of the solid in best solvents corresponds to about one-ninth on a mole fraction basis) to have about nine times the vapor pressure at room temperature of the crystals. There is little discrepancy left. In view of the facts that all measurements had to be made at less than 1 p.p.m. concentration, that DDT loss had to be obtained by difference, and that adsorption on vessel walls is difficult to allow for, this work leaves me with no anxiety for the validity of classical physicochemical theory. Distillation from supercooled droplets on a glass plate to growing crystals has been demonstrated by Feichtmeir (*12*).

Wick Evaporation

There is abundant evidence that water can accelerate the evaporation of pesticides from the soil. Two mechanisms operate: one which depends on the evaporation of water, the other requiring only its presence. The first is best called wick evaporation and is the phenomenon which should be referred to by the agronomist when he speaks of steam distillation.

When evaporation occurs from the exposed surface of a wick dipping into the liquid in an otherwise closed vessel, liquid moves up the capillaries of the wick to replenish that lost at the top by evaporation. The diffusive escape in the vapor phase causes an actual mass flow in the wick. It is easy to show that at practical rates in the field diffusion in the liquid phase competes poorly with this mass flow. If the liquid contains a low concentration of a less volatile solute, the latter will increase in concentration near the evaporating surface and cannot diffuse back down the wick as quickly as it accumulates.

One of three results follows:

(1) The solute increases to such a high concentration at the surface that water evaporation is greatly reduced. This happens in a glycerol–water solution.

(2) The solute increases to a concentration at which its rate of evaporation balances its rate of arrival.

(3) The solute increases to a concentration limited by its solubility, leading for example to the "efflorescence" of salt crystals seen on the surface of crumbs on a fertile soil after drying.

These results are not mutually exclusive, and actual results may be a combination of these effects.

The second effect can greatly increase evaporation of a moderately volatile, moderately water-soluble pesticide. The pesticide will tend to be lost along with the water in the ratio present in the undisturbed soil water, not because of any peculiarity in the evaporation process but because the bulk flow of the solution up the capillaries is too fast for diffusion in the soil water to compete. Surface concentrations are automatically adjusted until evaporation occurs in the ratio supplied. A mixture of water, alcohols, ketones, etc., allowed to evaporate only from the top of a wick 30 mm. or more long, does so without any change of bulk composition. The phenomenon is exploited in the odor-masking devices sold. If excessively involatile constituents are avoided, any mixture can be evaporated automatically at constant composition if allowed to do so only through a wick.

If the rate of evaporative loss per unit gross area of surface—"negative" rainfall—is v (cm./day) and the effective total cross-sectional area of water in continuous soil capillaries is s, the mean linear rate of upflow in the soil water is v/s. If diffusion coefficient of the solute is D (sq. cm./sec.), it can be shown that the concentration at the steady state falls off with distance x (cm.) from the surface according to

$$C = C_o \exp\left[-\frac{vx}{sD \times 8.6 \times 10^4}\right] \tag{4}$$

Inserting reasonable (*see below*) values ($v = 0.15$, $s = 0.2$, $D = 3 \times 10^{-6}$), the value of the exponent is about $3x$. This enforces about a 20-fold increase of concentration at the surface compared with original concentration for 1-cm. depth or 400-fold for 2-cm. depth.

An efficient wick is woven so that most of its fibers are parallel to its length; hence the capillaries are uninterrupted as far as possible. Soil is mostly particulate rather than fibrous, and the capillaries are easily and frequently interrupted; hence, soil is a poor wick. Soil scientists know that evaporation from soil surface is approximately constant and rapid as long as the surface remains wet—*i.e.*, as long as water is flowing up capillaries to compensate for evaporative loss. The capillary transport breaks down when it has to conduct more than a few centimeters upward, depending on soil type. The surface soil then dries, and the rate of evaporative loss falls sharply since the limiting vapor-phase diffusion must now operate over a much greater depth. It is during—and only during—the initial rapid water-loss phase that evaporation of water indirectly accelerates that of the pesticide. Many experiments have confirmed this acceleration (*11, 17*).

The growing plant itself may be likened crudely to a wick. Water is taken up by cellular flow, transported by channel flow in the continuous xylem vessels, and evaporated from the leaf surface. Unquestionably systemic insecticides supplied to the soil are concentrated in the leaves in this way. They are not, however, concentrated in the epidermal cells of the leaf as much as we might expect from the passive-wick model, for two reasons. Protoplasmic streaming in the leaf cells accelerates diffusion and so reduces the concentration gradient. Also the general direction of flow before final evaporation is perpendicular to the large leaf area, so that the final linear flow rate is much less than in the xylem vessels. The distance traversed in this final flow is small—about half the leaf thickness. This is about 100μ in most crop leaves. One is tempted to speculate that if it were much greater (*cf.* Equation 3), lethal concentrations of various substances would accumulate as long as transpiration were rapid. Is this why leaves of rapidly transpiring plants are thin, and fleshiness is only possible if transpiration is restricted?

Adsorption Displacement

The second effect of water on evaporation, requiring only the presence of water, arises from the fact that many clay surfaces (and some organic ones) are strongly hydrophilic but also capable of adsorbing other molecules. The pesticide may therefore be held sufficiently strongly on a dry soil for its evaporation to be greatly reduced. When the soil is wetted, however, the stronger affinity of the water displaces the pesticide.

EPTC (*S*-ethyl di-*N*,*N*-propylthiocarbamate) is about the most volatile of the common herbicides, and evaporation limits its persistence under normal conditions and makes incorporation rather than surface application desirable. Nevertheless, it can be reactivated by rain many weeks after application under arid conditions.

Other examples are known from the work of Barlow and Hadaway (*6*) on insecticides in porous wall materials, who note examples of reactivation by moisture for cellulosic materials. The direct observation is recovery of insecticidal activity, but undoubtedly when the insecticide becomes available to the insect, it also becomes available for diffusion in the vapor phase.

Evaporation from Crystalline Deposits

Table I lists two materials evaporating from the crystalline solid. There is nothing very inhibitory about the solid state. Ice evaporates much faster than lubricating oil and naphthalene much more rapidly than glycerol. However, when we have a substance which can exist for sufficient time in the supercooled liquid state (*e.g.*, impure DDT in thin films), it is significantly more volatile and more soluble in this form. As a rough rule, a crystalline substance becomes about one-third to one-fourth as volatile and as soluble as the supercooled liquid for each 50°C. below the melting point.

Deposits which start as liquids may crystallize after exposure, and their evaporation rate will fall. Supercooling is more likely to occur and lead to this complication when the deposit density is extremely low, as often happens with radiotracer methods.

The Quantitative Picture

In the mild summers of England, moist soil can easily lose as much as 6 tons of water per acre per day by evaporation. This is more than the average rainfall in the driest month in the driest part of the country and a little less than the year-round average, consistent with the fact that the soil, in the driest area, dries out in the summer and wets up again in winter.

Over most of the United States the potential evaporation is higher. That it may not in fact be higher only serves to emphasize the fact that the soil surface is wet only for a small part of the summer. Only by one mechanism (wick evaporation) does evaporation of water assist that of the pesticide. If the pesticide is on the surface and water is not, the surface is hotter than it would be if the water were there, and the evaporation rate of pesticide is therefore greater with respect to water.

A value of 6 tons/acre-day as the potential evaporation rate from wet soil is conservative (low). If the pesticide is fully exposed—not dissolved, or adsorbed—its rate of loss will be less than expected by multiplying the 6 tons by the vapor pressure of the pesticide and the square root of its molecular weight and dividing by half this product for water (the half allowing for average 50% humidity of the air initially).

This way we obtain the predicted rates of loss for some pesticides, taking the vapor pressure data recorded from Martin (*18*), Balson (*5*), Dickinson (*10*), or Friedrich and Stammbach (*14*) (for simazine).

Table III.

Substance	*Vapor Pressure, mm. 20°C.*	M	*Predicted Rate of Loss from Acre of Glass Plate*	
			Rate	*Units*
EPTC	0.15	189	768	lb./day
2,6-Dichlorobenzonitrile	5.5×10^{-4}	172	2.7	lb./day
Parathion	3.8×10^{-5}	291	0.24	lb./day
Lindane	9.4×10^{-6}	291	1.8	lb./month
DDT	1.7×10^{-7}	355	1.2	lb./year
Simazine	6.1×10^{-9}	202	0.04	lb./year

Although EPTC is quite volatile under field conditions, the predicted loss seems much too high, and one must doubt the quoted vapor pressure, which is about the same as that of a saturated paraffin of the same molecular weight (tridecane, *M*- 184, v.p. at 20°C., *ca.* 0.14 mm.).

Obviously evaporation is a potentially important factor in loss of deposit for any except the very involatile pesticides.

Fate of Evaporated Residues

When 6 tons of water evaporates from an acre in a day and from many contiguous acres, where does it go? Let us assume that each cubic meter above the crop can hold, in addition to what was initially present, half the SVC of water at 20°C. This is about 8.6 grams, corresponding to about 35 kg. or 77 lb. per acre. A depth of nearly 200 meters is therefore necessary to accommodate the 6 tons. In fact a greater depth still is affected in the upper part of which condensation (cloud formation) may occur at a temperature reduced by adiabatic convection. Although molecular diffusion near the evaporating surface determines locally the rate of evaporation, a very deep layer of air is necessary to accommodate the total amount evaporated.

Because rate of loss is roughly proportional to $p\sqrt{M}$, but the capacity of a given volume of air is proportional to $p \times M$, a smaller depth of air is necessary to accommodate the predicted evaporation of pesticide, around 50 meters instead of 200 meters. This is still substantial, but two qualifications are necessary.

First, a pesticide evaporating from spot-wise deposits within a crop will largely be adsorbed on other parts of the crop. This does not happen with water since if one leaf is transpiring, so are the others. This must accelerate the predicted rate of loss from each local deposit but will delay the total loss at low application rates, by reducing the available vapor pressure.

Secondly, much of any pesticide vapor escaping to 50 meters or more above the crop will ascend even higher by eddy diffusion and eventually reach the highly photochemically active ionosphere. I suggest that except for the destructive reactions occurring in the upper atmosphere, all life would probably have succumbed to intoxication by its own waste products, let alone by-products of the chemical industry.

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12

Evaluation of Spray Drift Potential

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A small, low speed wind tunnel was used to measure the proportion of a flat-fan spray occurring as small, drift-susceptible droplets. In-flight evaporation of the falling droplets was accounted for. Comparison of the volume percentage of a spray occurring in a selected droplet size range with similar data for sprays formed from various thickened liquids was taken as indicative of potential spray drift in the field. The method appeared to be sufficiently precise to allow selection of candidate spray liquids for field evaluation. Liquids imbibed in sized particles of lightly crosslinked polymers ("particulate" sprays) were found to form sprays having a very small volume percentage of droplets in the very small droplet size range.

Spray drift from agricultural sprays is determined by many factors, including nozzle design, spray pressure, air velocity past the nozzle, fluid properties, and meteorological factors (*1, 2, 5*). It is apparent that the proportion of the spray occurring as small droplets is of paramount importance, and methods for studying spray drift have been based largely on the size of droplets produced in the spray (*2, 3, 4, 20*).

Several investigators have measured the number of droplets occurring in each of several size ranges, either by collecting the droplets on prepared flat surfaces or by photographic methods (*8, 9, 11, 18*). In this approach, the droplet size distribution curve is obtained. It is then easy to calculate the fraction of droplets in the smaller size ranges and any of the several mean droplet diameter values. Fraser and Eisenklam (*8*) proposed a dispersion value as a measure of droplet size uniformity. Their approach is simple but suffers from the considerable difficulty of adequately observing the very small droplet component (*5*). All direct observation methods require measuring and counting large numbers of droplets.

An alternate approach is to use an air-classification procedure (*4*). Only the amount of spray collected at certain sampling sites need be determined, and the droplet sizes represented are selected by the choice of sampling sites for a given experimental technique. Adequate design of a spray sampling system, coupled with an air-classification method for separating the several droplet sizes, appeared to be a promising approach for assaying the relative abundance of small droplets produced by a hydraulic spray nozzle.

Experimental

Wind Tunnel Design and Operation. A small wind tunnel was built, incorporating the following features: (a) a variable speed exhaust fan to allow selection of air movement in the 0–3 m.p.h. range; (b) an air-alignment system to ensure laminar flow of the moving air; (c) an air-pad spray reservoir and attendant regulators and valves; (d) elevation of the spray nozzle above the wind tunnel proper to allow the smaller droplets to reach terminal velocity before entering the moving air stream (*10*) and to prevent the spray itself from introducing significant turbulence; (e) a spray-sampling arrangement to permit only a selected segment of the spray fan to enter the air stream, patterned after the design used by Courshee (*3*); (f) a droplet-sampling scheme to allow comparison of the droplet size distribution from different types of liquid systems. A schematic of the design is shown in Figure 1. Air alignment plates were necessary to orient the entering air stream and prevent displacement of the droplet trajectories. Window screen baffles were effective in minimizing small eddy currents, as recently reported by Skelland and Cornish (*17*). Air flow pattern was observed with smoke plumes. Absolute air speed calibration was accomplished by timing the movement of a puff of smoke through a measured distance (an accurate, sensitive anemometer could be used).

The spray fan formed by the 6503 flat atomizing nozzle (Spraying Systems Co., Bellwood, Ill.) in the spray chamber was assumed to elevate relative humidity in the chamber so that droplet evaporation was negligible before entrance into the wind stream. The possible effect of droplet coalescence was neglected. Careful telescopic observation of the spray impinging on the spray-dividing knives revealed no evidence of drops shattering. It appeared that the drops either passed through the aperture or were deflected by the sharply inclined knives.

Droplets were collected on 1-inch ethylcellulose strips, placed laterally across the wind tunnel floor at various distances downwind, and on 11-mm. glass rods located 40 inches downwind from the spray nozzle. The effective fall distance for droplets impinging on the wind tunnel floor was 2 feet. Droplet sizes that reach the glass rods will not all impact efficiently, and the efficiency varies with droplet diameter (*2, 4*). Nonetheless, the size droplet reaching a given glass rod was approximately

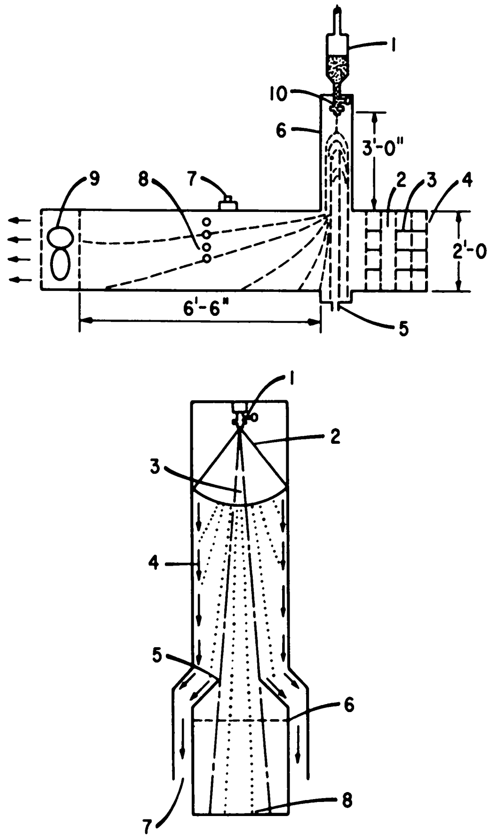

Figure 1. Wind Tunnel Design

Top: general side view

1. *Spray container*
2. *Vertical baffles*
3. *Horizontal baffles*
4. *Window screen*
5. *Drain*
6. *Spray introduction chamber*
7. *Fan speed regulator*
8. *Air sampling rods*
9. *Exhaust fan*
10. *Spray nozzle*

Bottom: spray introduction chamber

1. *Spray nozzle*
2. *Spray fan*
3. *Spray segment entering wind tunnel*
4. *Wall drainage of unused spray*
5. *Spray dividing knives*
6. *Top edge of wind tunnel*
7. *Waste drainage*
8. *Wind tunnel floor*

the same for any type spray used. Equal impaction efficiency could then be assumed for a given site, so the data allowed reliable comparisons even though the true percentage of droplets of the indicated size remained in doubt.

Alternate sampling methods include various impingers and filters. These require that the air velocity entering the sampling device be the same as the air velocity in the wind tunnel to prevent disturbance of the droplet trajectories and to ensure accurate sampling. Floor samples can be taken with paper or other materials which allow droplet counting techniques to be used. For example, Koenig and Sypers-Duran (*9*) observed that Eastman No. 890 Linograph paper provides a convenient method for examining aqueous spray deposits. This paper is sensitized by light and developed by water, providing a semipermanent record of the location and approximate size of water droplets collected. We have found this method useful for qualitative observation of wind-tunnel results and uniquely useful for recording aerial spray swath patterns and for semiquantitative drift studies in the field.

The amount of spray collected at each sampling site was conveniently determined fluorometrically when a suitable tracer was included in the spray liquid. Fluorescein was found to extract quantitatively from most deposits and could be determined easily to ±0.1 p.p.b. This sensitivity allowed calculation of the fraction of spray collected at each sampling site if the amount of spray passing through the slit system and entering the wind tunnel in a given time period were known. Results from different sprays on the basis of equal droplet size then allowed us to make quantitative comparisons.

Results and Discussion

In-Flight Evaporation of Spray Droplets. Droplet diameters collected at each sampling site may be determined experimentally or calculated from Stokes's law if evaporation of the falling droplet can be neglected. Unfortunately, in-flight evaporation significantly affects the trajectory of aqueous sprays and must be accounted for.

In an apparently neglected paper published in 1934, Wells (*19*) calculated the interrelationship between fall distance, fall time, and droplet diameter for water droplets falling in air. However, he neglected the effect of fall velocity on evaporation rate, as did Eisner *et al.* (*7*) and Derjaguin *et al.* (*6*) in more recent papers. Sherwood and Williams (*16*) accounted for the effect of droplet fall velocity on evaporation rate but unfortunately based their calculations on the assumption that the temperature of the evaporating droplet surface was equal to the air temperature. This assumption has since been shown to be invalid (*7, 13*).

To arrive at equations accounting for the simultaneous variation in droplet diameter, fall velocity, and evaporation rate, Stokes's law for the fall of small spheres is fundamental. The terminal fall velocity v, is given by:

$$v = \frac{(\rho_d - \rho_a) g D^2}{18\,\eta_a} \tag{1}$$

where

ρ_d = droplet density

ρ_a = air density

η_a = air viscosity

D = droplet diameter

g = gravitation constant

Marshall (*12*) observed that the rate of change of surface area is constant for a pure liquid droplet evaporating in still air. Similarly, examination of his equations shows that droplet evaporation in moving air varies with D^2—*i.e.*, the rate of change of surface area is constant for a given air velocity. At the steady-state condition,

$$\frac{\delta A}{\delta t} = -K\,\frac{\Delta p}{P} \tag{2}$$

and that

$$v = 0,\ K = 4\pi C_v.$$

where

A = droplet surface area

t = time

C_v = diffusivity of water vapor in air at prevailing temperature

K = effective transfer coefficient at instantaneous v

Δp = vapor pressure-gradient between the surrounding air and the droplet surface

P = partial pressure of air

Cunningham *et al.* (*5*) questioned the relationship of evaporation rate to surface area, but their observation appears valid only for the period before the steady state is reached. Ranz and Marshall (*13*) found this period to be quite short. Observing that

$$\frac{\partial A}{\partial t} = 2\pi D\,\frac{\partial D}{\partial t} \tag{3}$$

Equation 2 becomes

$$\frac{\partial D}{\partial t} = - \frac{K}{2\pi D} \frac{\Delta p}{P} \tag{4}$$

Ranz and Marshall (*13*) carefully studied the evaporation of water droplets in still and moving air. They found that the steady-state temperature at the surface of a small evaporating drop was the wet bulb temperature of the surrounding air. Marshall considered the dependence of the effective mass transfer coefficient on air velocity to be determined largely by the boundary layer of less mobile air at the droplet surface, and he reported correlations which show that K_v varied linearly with $v^{1/2}$. Ranz and Marshall's data clearly show this relation, which we may write as Equation 5.

$$K = k_o + kv^{1/2} \tag{5}$$

where

$k_o = K$ at $v = 0$

$k =$ correction to K for $v > 0$.

To recalculate their data for the present purpose, observe that

$$\frac{\partial V}{\partial t} = \frac{\pi D^2}{2} \frac{\partial D}{\partial t} \tag{6}$$

where $V =$ droplet volume.

From Equation 4

$$\frac{\partial V}{\partial t} = - \frac{KD}{4} \frac{\Delta p}{P} \tag{7}$$

and

$$K = - \frac{4 \dfrac{\partial V}{\partial t}}{\mathrm{D} \dfrac{\Delta p}{P}} \tag{8}$$

Equation 8 allows evaluation of k_o and k from Ranz and Marshall's data. This relationship is shown in Figure 2.

Consider the effect of simultaneous variation in v and K. Solving Equation 1 for water droplets falling in air at 25°C. and substituting in Equation 5,

$$K = k_o + 548\, kD \tag{9}$$

This corrects K for instantaneous fall velocity as determined by droplet diameter. Substituting in Equation 4, the constant velocity restriction is removed, and an ordinary differential equation results.

$$\frac{dD}{dt} = -\frac{k_o + 548\,kD}{2\pi D}\,\frac{\Delta p}{P} \tag{10}$$

Rearranging and integrating,

$$t = \frac{2\pi}{\Delta p/P}\left[\frac{D_o - D_t}{548\,k} - \frac{k_o}{(548\,k)^2}\ln\frac{k_o + 548\,kD_o}{k_o + 548\,kD_t}\right] \tag{11}$$

where

D_o = droplet diameter at $t = 0$

D_t = instantaneous droplet diameter.

Substituting the values for k_o and k from Figure 2,

$$t = \frac{P}{\Delta p}\left[25.2(D_o - D_t) - 0.505\log\frac{8.68 \times 10^{-3} + D_o}{8.68 \times 10^{-3} + D_t}\right] \tag{12}$$

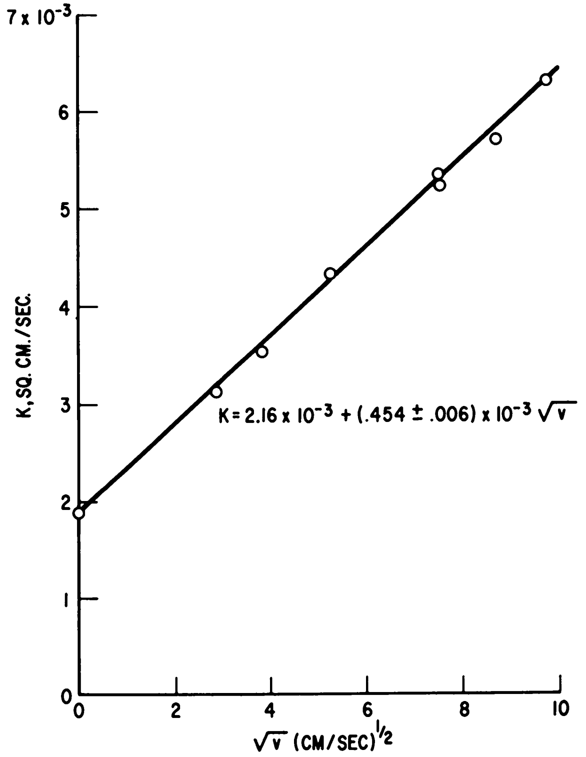

Figure 2. Experimental evaluation of K_v, calculated from data of Ranz and Marshall (13)

For a given relative humidity (RH) and temperature, values are assumed for two of the three variables, t, D_0 and D_t, and the third is calculated. In this way, droplets of various initial diameter can be calculated to evaporate to any assumed diameter D_t after t seconds of fall at terminal velocity. The equation corrects for the effect of fall velocity on evaporation rate and the concurrent effect of changing diameter on fall velocity. It assumes constant air temperature and pressure, a large volume of air per droplet so that the air humidity is relatively unaffected, no air turbulence, and the absence of solutes which reduce vapor pressure or form evaporation-retarding films at the surface of the droplet. It further assumes terminal fall velocity at all times. With these restrictions, the theory appears valid for droplet sizes that obey Stokes's law.

Turning to the relationship of fall distance to elapsed time as affected by in-flight evaporation, a solution of Equation 12 in the form

$$D_t = G(D_0, t) \qquad (13)$$

is required. This expression would be substituted in Equation 1 to give

$$-\int_{h}^{0} dh = \int_{0}^{t} v_t \, dt \qquad (14)$$

The solution is a complex exponential, subject to considerable difficulty in numerical calculation. However, it is appropriate to evaluate Equation 14 graphically by calculating v_t from Equation 1 for values of D_t and t obtained by solving Equation 12 at selected values of D_0. This integration gives the distance the drop has fallen, h, in time t for stated values of D_0 and $\Delta p/P$.

The equations were solved for pure water droplets falling in air at 25°C., 760 mm, pressure, and 30, 50, and 70% RH. Figure 3 shows that falling water droplets decrease in size rather quickly, especially in dry air. Initial diameter appears to affect rate of disappearance to a lesser degree than one might expect. This results from the greater fall velocity of larger droplets, inducing a more rapid rate of evaporation. As a droplet is reduced in size, it passes through the air more slowly and consequently evaporates less rapidly per unit surface area.

Figure 4 shows the calculated fall distance for water droplets of various initial diameters as a function of fall time. Most of the fall distance for an evaporating droplet is apparently accounted for during the initial period when both fall velocity and evaporation rate are high.

Spray Drift Aspects. The above calculations have significant implications relating to spray drift. Qualitatively, evaporative effects have been recognized for some time (*4*, *21*). The small droplet-fall behavior

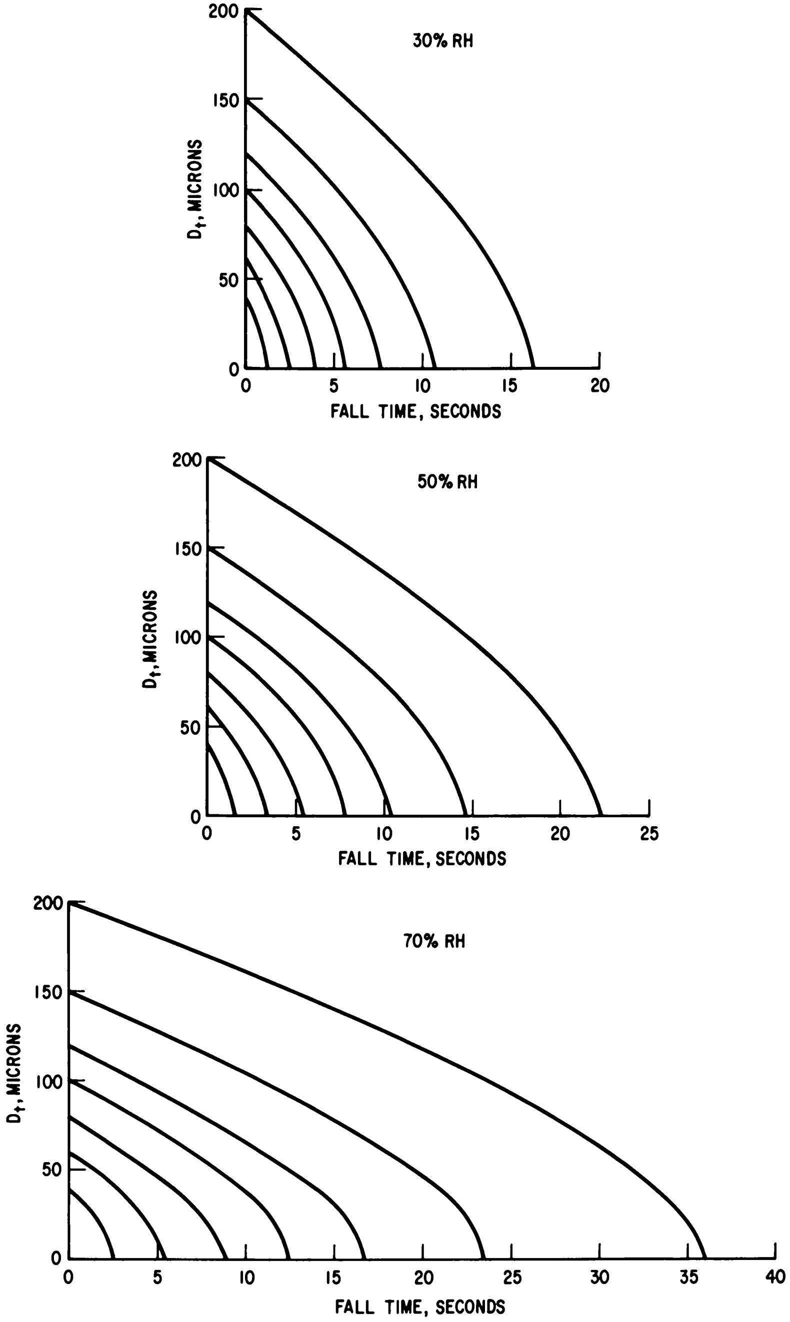

Figure 3. Instantaneous droplet diameter vs. fall time for water droplets falling in air at terminal velocity (25°C., 760 mm. Hg)

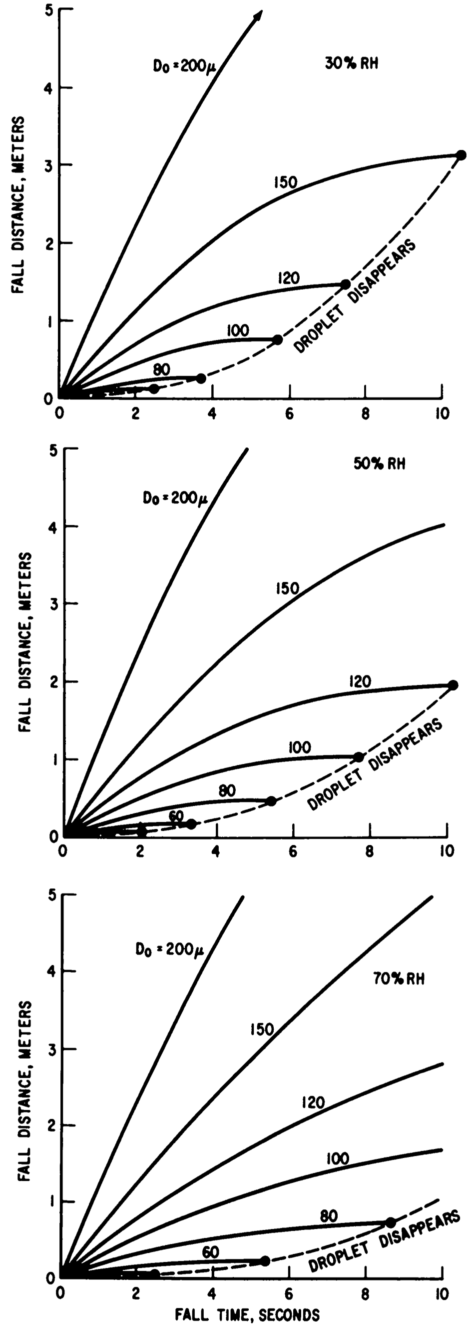

Figure 4. Fall distance vs. time for water droplets falling in air at terminal velocity (25°C., 760 mm. Hg)

in agricultural sprays is visualized as lying between two boundary conditions. A spray sheet or cloud probably raises the humidity to near the saturation point, and local evaporative effects are minimized. The boundary condition for negligible evaporation from small droplets in the main body of the spray is then described by Stokes's law (ignoring turbulent effects). In this region the spray swath may be displaced by wind, with some segregation of smaller droplets; therefore, the applicability of Stokes's law appears limited to the main spray swath and immediate vicinity. Many droplets become segregated from the main body of the spray, either by wind action or by the trajectory imparted by the breakup of the spray sheet, or both. Droplet concentration in the air is then low, and humidity of the surrounding air is less affected by the evaporating droplets. Further segregation or mixing with fresh air at the prevailing temperature and humidity causes the in-flight evaporative behavior of these drifting droplets to approach the conditions described by the in-flight evaporation equations. The present theory then represents the evaporating droplet boundary condition and approximates the behavior of droplets not in the main spray sheet or cloud, and which comprise the major drift hazard.

It is apparent that effects of eddy currents and general air turbulence might be approximated by modifying Equations 10 and 14. Modifications of the basic equations could possibly account for solute effects. Extension of the theory to nonaqueous solvents requires the appropriate evaluation of Δp and K. Momentum imparted by vertical spray nozzles affects the time required for droplets to reach terminal fall velocity (*11*). Helicopter and fixed-wing aircraft impart a downward vector to the bulk of the spray and also produce a turbulent effect on the time of droplet fall and should be accounted for.

The calculations appear to provide useful guides to selecting minimum droplet sizes for certain spray operations. Aqueous sprays of oil-in-water emulsions, wettable powders, and solutions of insecticides, fungicides, and herbicides are widely used. The surfactants, salts, and inert ingredients apparently affect initial droplet evaporation rates only modestly (*12*, *13*). Consequently, the falling droplets will lose much of their volume by evaporation of the water present, leaving a very small oil droplet, moist dust particle, or concentrated solution. The residual particles or droplets will generally be so small that their fall velocity is negligible in a practical sense. The effect of droplet evaporation on lateral displacement of the falling droplet is illustrated in Figure 5 for pure water droplets and laminar air movement. It is apparent that free-falling droplets 100μ or smaller in diameter constitute a major drift hazard at most practical spray distances above the vegetation level, and even quite large droplets (by normal agricultural spray standards) may constitute a drift hazard for agricultural sprays. (Droplets as large as 200μ are beyond the range of applicability of Stokes's law. However, the deviation from calculated fall rate is probably insufficient to change the over-all conclusions.)

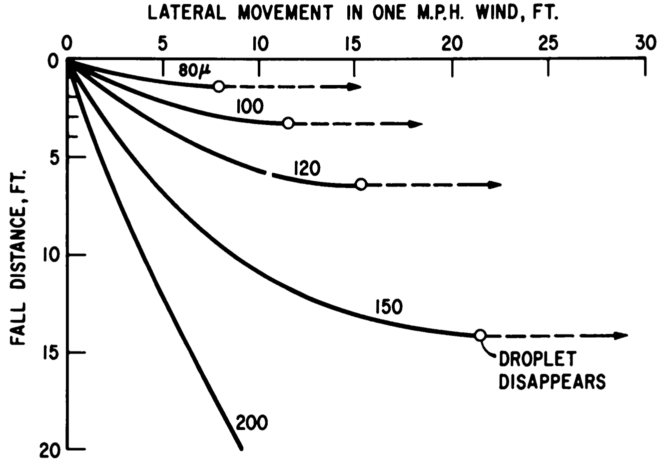

Figure 5. Relation of fall distance through air to lateral movement for water droplets falling at terminal velocity in a 1-m.p.h. wind. Calculated for 25°C., 50% RH, 760 mm. Hg, and laminar air movement

It follows that the spray drift potential for a specified liquid system may be defined in terms of the volume fraction of the spray which has a high probability of contributing to drift under conditions normally encountered during field applications. Selection of the maximum droplet size considered susceptible to drift should allow for the type and effectiveness of the active ingredient, an estimate of the amount of downwind contamination or injury considered tolerable, as well as the several mechanical and meteorological factors concerned. Such quantitative estimates are obviously not yet possible. It is possible, however, to measure the volume fraction of a spray system occurring in a specified droplet size range and to express the results relative to similar data for a different liquid spray system. This comparison should then have value in predicting which spray system would have the greater drift susceptibility if used under identical field conditions. Additionally, the relative extent of drift under field conditions could be estimated from laboratory data. In this sense, the present wind tunnel method attempts to estimate the potential drift hazard from a liquid spray by measurement, under controlled spray conditions, of the volume fraction of droplets in selected size ranges.

Interpretation of Wind Tunnel Data. As spray droplets enter the moving air stream in the wind tunnel described, droplets smaller than about 150μ in diameter are falling at approximately the terminal fall velocity. Little evaporation has occurred because the entire spray was initially confined to a small volume of air. These small droplets have only a small momentum as they enter the air stream; hence they attain the lateral airstream velocity quickly (*4*). Taking the size of a droplet at the point where it enters the air stream as D_o, it impacts on the floor of the wind tunnel or arrives at the air sampling site with instantaneous diameter D_t. The time elapsed is given directly by the air velocity. The fall distance, h, is the vertical distance from the upper surface of the moving air stream to a particular sampling point. It is then possible to predict the initial and impacting diameter of droplets which will be collected at a given site when the indicated correction is made for air temperature, relative humidity, and barometric pressure and assuming a planar spray sheet.

Water droplets were collected by the immiscible liquid method of Fraser and Eisenklam (*8*) at 2.4, 3.9, and 5.9 feet downwind from the spray nozzle. The observed impacting droplet sizes showed excellent agreement with the predicted sizes (Table I), thus lending confidence to the use of in-flight evaporation theory as a tool for interpreting wind tunnel spray drift data.

Table I. Diameter of Water Droplets Impinging on the Wind Tunnel Floor

Downwind Distance from Nozzle, inches	*Droplet Diameter (D_t), μ*	
	Calculated	*Observed*[a]
27	121	121 ± 10[b]
45	89	78 ± 15
69	62	57 ± 14

[a] Number average.
[b] Standard deviation.

Figure 6 shows the calculated initial droplet sizes D_o which impact at each of the several sampling sites, as determined by the prevailing temperature, humidity, and barometric pressure ($\Delta p/P$). Having determined the volume fraction of the spray collected at each of the several sampling sites as previously described, interpolation from Figure 6 gives

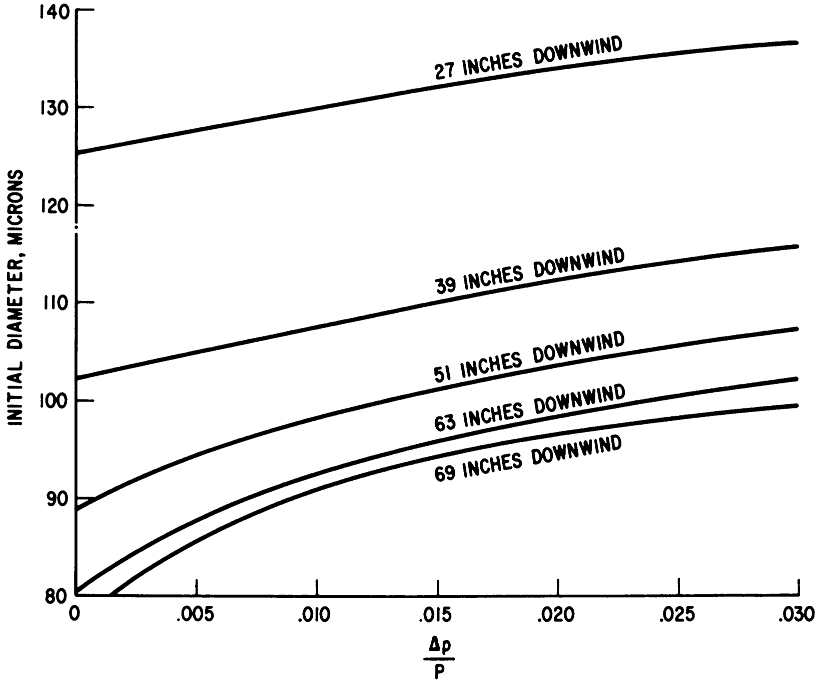

Figure 6a. Variation in initial size of droplets which impinge on selected wind tunnel sampling sites with changing psychometric conditions. Floor samples

the corresponding mean droplet diameter, D_o, present in the spray. For liquids other than pure water, this treatment provides "equivalent droplet diameters,"—*i.e.*, that fraction of the spray which behaved as pure water droplets of the computed size.

One may plot the data as shown in Figure 7 for water sprays and for a particulate spray (*14*). [A "particulate" spray is formed from a liquid imbibed in sized particles of a lightly crosslinked, swellable polymer.] Air (glass rod) and floor samples are treated separately because of the uncertain impaction efficiency on the rods, as previously discussed. The large apparent error for the particulate spray data of Figure 7b results from the proximity to the detection limits of the analytical method used.

Alternately, one may graphically integrate the floor sample data, obtaining the total fraction of spray collected as droplets in a selected size range. Similar treatment of the air samples is not valid, but interpolation of the data allows summing over the four samples at selected droplet sizes. A single value is thus obtained for the air samples. Tabulation of the values for air and floor samples allows comparison of the small drop component of different sprays, or the graphic method can be used for more detailed comparison of a few sprays. Table II shows the tabular data for the sprays represented in Figures 7a and 7b. The error of estimate was obviously significant but probably less than the uncertainties concerned in using droplet size data to predict spray drift in the field. Moreover, the results appeared capable of distinguishing between apparent drift potential from sprays differing by a factor of about 2 or more. The precision observed would then allow comparison of sprays with at least as much precision as would time-consuming field experiments.

Conclusions

Evaluation of the small drop component of flat fan sprays by the wind tunnel method is sufficiently reproducible to allow comparison of

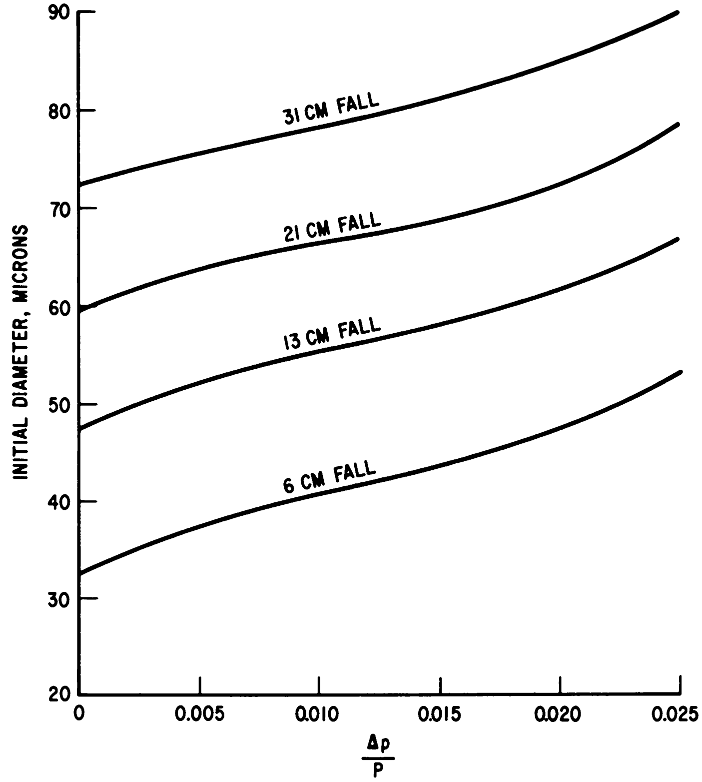

Figure 6b. Variation in initial size of droplets which impinge on selected wind tunnel sampling sites with changing psychometric conditions. Air samples

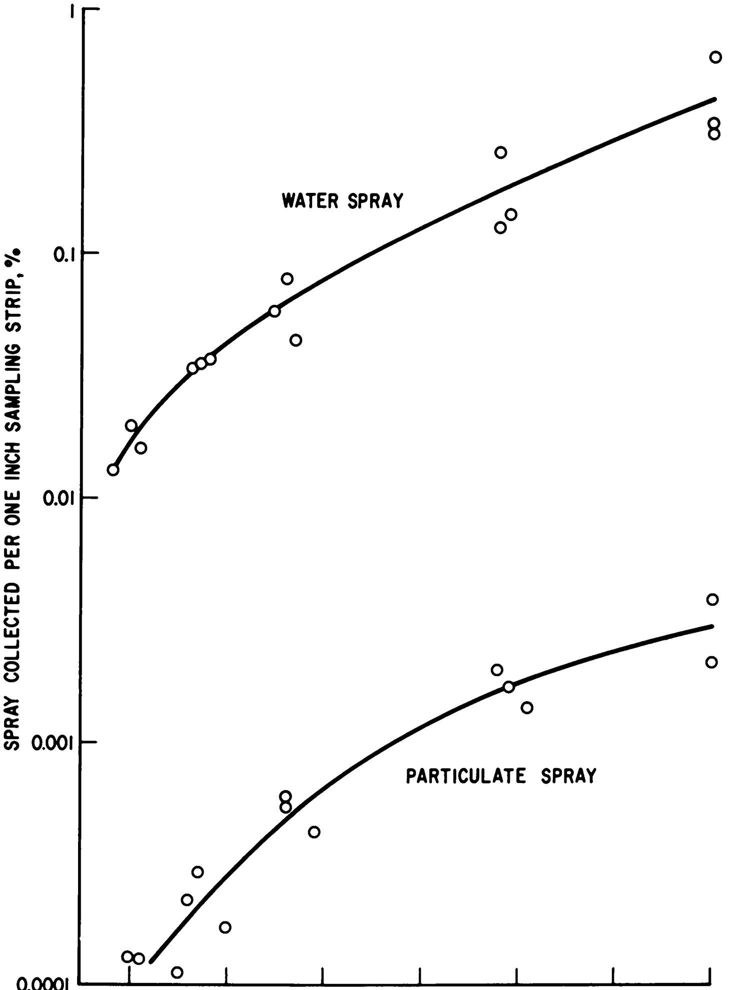

Figure 7a. Droplet size data as measured in the wind tunnel for a water spray and for a particulate spray. Floor sample data

the drift potential from different sprays. The information obtained does not predict actual levels of drift expected from a given field application. Rather, it permits comparison of the relative drift potential expected from different spray liquids. For example, the drift potential from particulate sprays was found to be less than for sprays of aqueous liquids thickened by other means. For these comparisons, each material was made up to the apparent optimum viscosity before spraying. Optimum in this case was taken as the highest viscosity that would form a spray pattern from the spray nozzle employed with an applied pressure of 50 p.s.i.g. (Table III). Similar evaluations were attempted for sprays of nonaqueous liquid systems (*15*). For this purpose an oil-soluble fluorescent tracer (Black-Ray gasoline additive A-680) was employed and the liquid chosen (Insecticide base oil, Shell Chemical Co.) was substantially nonvolatile, eliminating the need for in-flight evaporation corrections. The results indicated that the unthickened oil spray produced a somewhat greater proportion

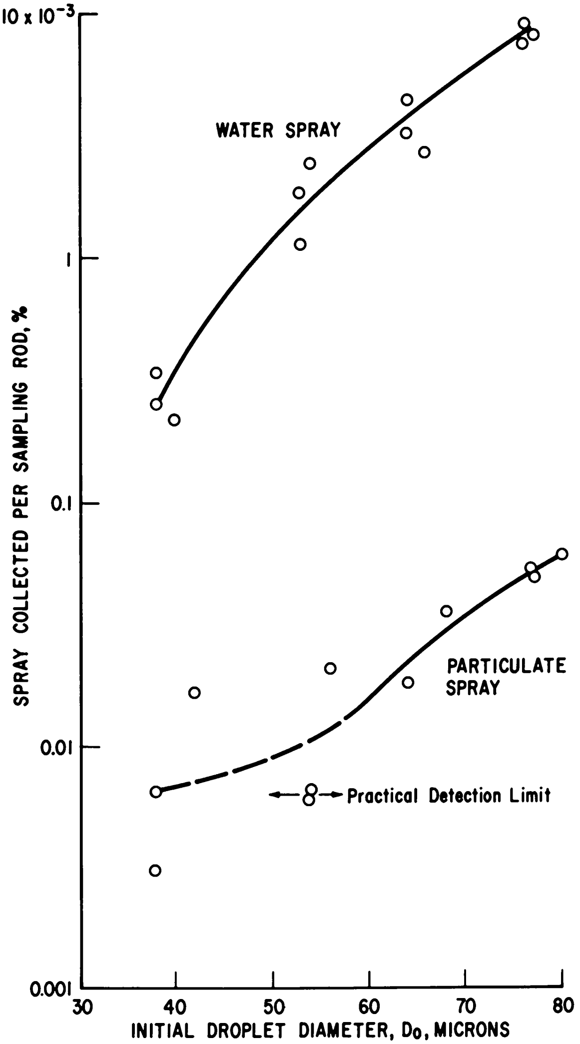

Figure 7b. Droplet size data as measured in the wind tunnel for a water spray and for a particulate spray. Air sample data

of very small droplets than had been found for water (Table IV). Particulate oil system sprays may be produced in a manner analogous to aqueous particulate systems but using a lightly crosslinked polymer compatible with the solvent used. Such a system was observed to reduce greatly the proportion of drift-susceptible droplets produced in the spray (Table IV).

Table II. Integrated Values for the Spray Data Shown in Figure 7

Type Spray	*Temperature, °F.*	*Relative Humidity, %*	*Floor Sample, % of Spray in 96-132μ equiv. D_0 Range*	*Air Sample, Total % Collected as 44, 56, 69, and 82μ equiv. D_0*
Water	71	80	1.59	16.2×10^{-3}
	81	68	1.90	17.3
	84	78	2.92	20.2
Particulate	86	73	0.021	0.10
	78	67	0.021	0.11
	91	63	0.014	0.14

Table III. Drift Potential of Thickened and Particulate Aqueous Sprays

Liquid		*Apparent Viscosity (Brookfield), cp.*	*Sample, %*	
			Floor[a]	*Air*[b]
Water		1	1.6–2.9	$16\text{–}20 \times 10^{-3}$
Sodium alginate[c]		4,700	0.4	3.3
Hydroxyethylcellulose[d]		800	0.2	3.2
Invert emulsion herbicide[e]	(a)	*ca.* 50,000	0.2	1.4
	(b)	50,000	0.6	2.0
Particulating agent[f]			0.03	0.3

[a] Integral values for % of spray in the 96–132μ equivalent initial droplet diameter size range.

[b] Sum of deposit on 11-mm. glass rods, 44, 56, 69, and 82μ equivalent initial droplet diameters.

[c] Keltex FF Brand, Kelco Co.

[d] Cellosize QP-52000 brand, Union Carbide, New York, N. Y.

[e] (a) Verton CE herbicide, Dow Chemical Co. (data not corrected for evaporation). (b) Commercial sample.

[f] Norbak particulating agent, Dow Chemical Co. (maximum observed for approximately 100 tests representing various lots of particulating agents).

The low speed wind-tunnel method for evaluating spray drift potential from various liquid systems was found to estimate relative amounts of small, drift-susceptible droplets produced in the spray with sufficient precision for choosing candidate systems for field evaluation. The data do not estimate the irrelevant mean droplet diameters, eliminating possible confusion of the separate questions of spray drift potential and degree of surface coverage by the spray. Particulate sprays formed from either aqueous or nonaqueous liquid systems were found highly effective in reducing spray drift potential.

Table IV. Drift Potential of Oil Sprays

	Wind Tunnel Sample, %	
Spray Liquid	*Floor*[a]	*Air*[b]
Unthickened solution	1.4	35×10^{-3}
Particulate (*see* text)	0.014	0.01×10^{-3}

[a] Integral values for % of spray in the 96–132μ equivalent initial droplet diameter size range.

[b] Sum of deposit on 11-mm. glass rods, 44, 56, 69, and 82μ equivalent initial droplet diameters.

The effect of reasonable variations in nozzle design, spray pressure, and to a limited extent, variations in field application technique could probably be evaluated. Such comparisons should be based on the relative proportion of the sprays which occur in selected droplet size ranges. In actual field situations the effective droplet fall distance is the vertical distance moved relative to the surrounding air. For turbulent air, this may be several times the height at which the spray is released. Knowledge of the in-flight behavior of selected droplet sizes and of the micrometeorological factors concerned should then allow significant improvement in predicting relative drift potential from agricultural spray operations.

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The Formation of Spray Drops from Viscous Fluids

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The effect of viscosity on the formation of spray drops from fan-jet and cone nozzles has been examined using Newtonian liquids and water-in-oil (w/o) emulsions. Atomization can be described in terms of four ranges of Reynolds numbers for the flow of the liquid through the nozzle. Comparison of Newtonian liquids with w/o emulsions shows that the limiting viscosity of the emulsions at high rates of shear is a suitable viscosity parameter to describe their spraying properties. This viscosity depends on the disperse phase ratio, the method of mixing, and the constituents of the emulsion. Theoretical expressions have been developed which describe the formation of drops from slow moving nozzles, and the use of these to establish the relationship between drop size, operating conditions, and liquid properties is illustrated.

In applying pesticide sprays, the first problem is that of distributing a small quantity of active material over a large target area. The uniformity and extent of the distribution required depend on the type of pest to be controlled and the mode of action of the toxicant; a patchy distribution may be satisfactory to control mobile insects or to apply systemic pesticides to foliage, whereas for static pests and contact pesticides, a more uniform spray deposit may be required. The degree of distribution attained depends on:

(1) The effective area of the target surface
(2) The shape of the targets
(3) The method of spray application
(4) The volume of spray applied to the target surface
(5) The droplet size of the spray

(6) The extent to which the spray is capable of spreading over the target surface

(7) The extent to which the deposit is subsequently redistributed by rain or dew

Some of these factors are invariable (*e.g.*, 1 and 2), while others may be varied either by the spray operator (3, 4, and 5) or by the formulator (5, 6, and 7). The drop size of the spray is the one factor which can be controlled to some extent by both the person applying the spray and by the person formulating the spray. Before such control is possible, it is essential that the effect on drop size of variations in the operating parameters of spray equipment and variations of the properties of the spray fluid be understood, and it is with this aspect that the present paper is concerned.

During recent years, the tendency to apply smaller and smaller volumes of spray per hectare has necessitated the use of small drops to maintain adequate distribution. However, the size of the drops cannot be reduced indefinitely without affecting their ability to impact on the target, and in any case, as the drop size is reduced, the tendency of the spray to drift from the target is increased. Thus, there is an optimum drop size for most spraying operations which represents the smallest drop size consistent with satisfactory impact efficiency. To determine this optimum size for any particular application, one must take into account the mode of action of the toxicant, the nature of the crop, the type of spray equipment, and the volume of spray to be applied.

It is necessary to know how the optimum drop size can be achieved. The drop size will be governed by the equipment used, particularly by the type and size of nozzle and by the conditions of pressure and liquid output under which the nozzles are operated. It will be governed also by the physical properties of the spray fluid, such as density, surface tension, and viscosity. For fan-jet nozzles, one of the commonest types of atomizing equipment used in pesticide sprays, Yeo (25) has shown that a simple expression can be used to relate the various parameters governing drop size. For static or slow-moving nozzles, this takes the form:

$$D_S V_E \propto \left(\frac{Q\gamma}{\rho_L}\right)^{1/3}$$

where

D_S — Sauter mean diameter (*SMD*) of the spray (cm.)

V_E — velocity at which liquid is emitted from the nozzle (cm./sec.)

Q = volume of liquid emitted per second through the nozzle (ml./sec.)

γ = the surface tension of the liquid (dynes/cm.)

ρ_L = the density of the liquid (grams/ml.)

A similar expression was derived by Dorman (*10*), who also introduced the spray angle, θ, into the expression. Both expressions give sufficiently accurate results and are quite useful. Although they cover most of the important parameters that can be varied in the spray and the equipment, they do not include a viscosity term, and in fact, both Yeo and Dorman found this unnecessary over the low viscosity range tested, 1–12 cp. However, in recent years interest has increased in the use of highly viscous sprays. The interest was initiated by fear of the hazard of spray drift, it being assumed that highly viscous spray fluids would provide larger drop sizes than would conventional aqueous-based sprays and would thus reduce the likelihood of drift.

Although it may seem reasonable that an increase in viscosity of the spray fluid should increase the drop size, there is little fundamental information on the relationship between the drop size of the sprays and the viscosity of the spray liquid. Moreover, the information that is available is conflicting. Besides the work of Yeo and Dorman, where a viscosity term was found unnecessary when working with liquids having relatively low viscosities, other workers have found that a function of viscosity was necessary to describe drop size (*16, 17, 20*), but the value of this function has varied from $\nu^{0.1}$ to $\nu^{1.06}$ (where ν is the kinematic viscosity of the liquid). More recently, Dombrowski and Johns (*9*) have examined the breakup of sheets of viscous liquids formed from fan-jet nozzles and have derived a theoretical expression for the size of drops produced. The expression is very complex and includes viscosity terms, but it is difficult to use in a practical fashion to predict drop size and its variation with a particular physical parameter of the spray fluid.

Quantitative data on hollow-cone nozzles, which are also important in pesticide sprays, appear to be even more scanty than the data for fan-jet nozzles. Fraser (*16*) states that the mean diameter for cone nozzles is proportional to $\nu^{0.2}$, and Knight (*19*) has produced an expression:

$$D_8 = 220\, P^{-0.453} \times Q^{0.209} \times \nu^{0.215}$$

where P = operating pressure of the nozzle (p.s.i.g.); this is in general agreement with Fraser as far as the viscosity dependence is concerned. On the other hand, Consiglio and Sliepcevitch (*6*) have produced an expression for the specific surface area of the spray (which is a simple function of D_8) from hollow-cone nozzles involving γ^{-1}, $\nu^{0.4}$, and $Q^{2.4}$.

Further complications arise from the results of field trials on spray drift using water-in-oil emulsion sprays and other forms of viscous sprays containing pesticides. Some workers claim a significant suppression of spray drift (*5, 21, 23, 24*), while others claim no suppression at all (*1, 2*).

Experimental

The highly viscous spray fluids used in pesticide application have been either water-in-oil emulsions or solutions of macromolecules; both systems are non-Newtonian since their viscosity varies with the applied shear. While a viscosity parameter which is suitable for studies on drop formation was subsequently devised for such systems (*11*), it was necessary to use Newtonian liquids in the initial studies on the effect of viscosity on drop size. Sugar solutions behave as Newtonian liquids and provide a suitable means of varying viscosity over a wide range. These were prepared from a commercially available syrup by dilution with distilled water; 1% w/v of a black dye (Nigrosine G140) was added to each solution to render the spray drops visible for sizing.

In extending the work to non-Newtonian systems, a series of water-in-oil emulsions was used. These were prepared using the following formulations:

A: Oil phase, trimethylbenzene containing 1.5% w/v oleic acid and 3.5% w/v of a condensate of dodecylamine with 2 moles ethylene oxide; aqueous phase, distilled water.

B: Oil phase, trimethylbenzene containing 40% w/v of *N,N*-dimethyloleylamine salt of 2,4,5-trichlorophenoxyacetic acid; aqueous phase, distilled water.

C: Oil phase, trimethylbenzene containing 1.5% w/v dodecyldiethanolamide and 6.0% w/v of a condensate of oleylamine with 2 moles ethylene oxide; aqueous phase, distilled water containing 20% w/v dalapon.

Emulsions were prepared by mixing the oil phase with the aqueous phase using a high speed stirrer and stirring until homogenous. Viscosities were measured using a Brookfield RVT Synchroelectric rotating spindle viscometer.

The sprays were formed from a series of hollow-cone nozzles (supplied by Delavale-Watson, Widnes, Lancs, England) and a series of ceramic tipped, fan-jet nozzles (supplied by E. A. Allman Ltd., Chichester, Sussex, England). Their characteristics are listed in Table I.

Table I. Characteristics of Nozzles Used

Nozzle	*Orifice Shape*	*Orifice Dimensions, cm.*	*Emission Rate l/hr. at 30 p.s.i.g.*
Spraycone WG 1158	circular	0.076 diameter	18
Spraycone WG 408	circular	0.062 diameter	10
Spraycone WG 4008	circular	0.222 diameter	100
Allman 000	elliptical	0.096 × 0.048	19
Allman 1	rectangular	0.158 × 0.065	70
Allman 6	elliptical	0.292 × 0.107	159
Allman 9	elliptical	0.340 × 0.126	212
Allman 12	rectangular	0.272 × 0.119	259

The nozzles were fitted into the bottom of a pressurized spray tank mounted on nylon wheels running on a horizontal rail 9 feet above ground level. The tank was driven along the rails by elastic at a known constant speed.

The spray drops of syrup solution were collected on siliconized Perspex plates (*8*). Water-in-oil emulsion drops were collected on glazed photographic bromide paper and were rendered visible by immersing the paper in a 1% w/v solution of Nigrosine G140, followed by rinsing in water and drying (*11*). The stain sizes were converted to the corresponding drop sizes by using previously prepared calibration curves. The collecting surfaces were placed in a continuous strip across the swath, and the drop stains were measured directly using either a Flying Spot Particle Resolver (*15*) or, with the coarser sprays, a low powered microscope and calibrated graticule. Surface tensions were measured by the drop volume method, using the correction factors of Harkins and Brown (*18*).

Results and Discussion

Variation of Drop Size with Viscosity in Hollow-Cone Nozzles. Figure 1 shows the variation in volume median diameter of drops formed from a typical hollow-cone nozzle (Spraycone WG 4008) with increase in viscosity from 1 to about 100 cp. To maintain a constant emission rate, the operating pressure was increased as the viscosity was increased. The variation of drop size with viscosity is similar to that already reported using fan-jet nozzles (*11*), and the results can be considered in terms of three viscosity ranges:

(1) A low range where there is little or no variation of drop size with viscosity;

(2) An intermediate range where the drop size decreases with increase in viscosity;

(3) A high range where the drop size steadily increases with increase in viscosity.

Figure 2 shows high speed flash photographs of the operation of a hollow-cone nozzle. The spray drops are formed from the edges of a conical sheet of liquid produced by the nozzle. Unstable waves appear in the sheet at right angles to the direction of liquid flow. These waves grow in amplitude until they are sufficiently large to cause the sheet to break up into roughly parallel, circular ligaments which then disintegrate into drops. The three viscosity ranges can be distinguished from the flash photographs. In Range 1, the spray sheet is small and turbulent and is rapidly broken up by wave formation. In Range 2 there is a transition to a much smoother spray sheet which extends further from the nozzle before breaking up. The formation of waves can be seen clearly, but since the spray sheet is larger here than in Range 1, it is also thinner at the point of breakup, and hence the drops produced tend to be smaller.

In Range 3, the spray sheet is well developed, but the angle of the cone (α) becomes smaller as the viscosity is increased. This leads to a thicker sheet at the point of breakup, and hence the drop size increases. Eventually, at very high viscosities, a conical sheet is no longer formed.

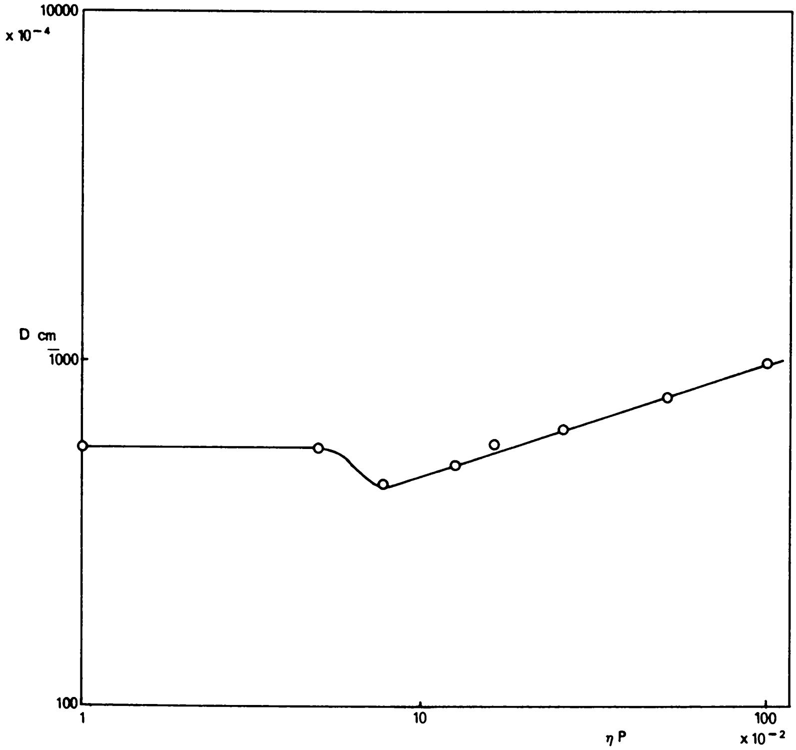


Figure 1. Drop size vs. *viscosity using Spraycone WG 4008*

Thus, the changes in drop size which accompany changes in viscosity (Figure 1) appear to be related to changes in the shape and size of the spray sheet. The relationship between the various properties that govern sheet dimensions may be found from a dimensional analysis in a manner similar to that published for fan-jet nozzles (*12*).

The properties that govern sheet dimensions are viscosity, η, surface tension, γ, and density of the spray liquid, ρ_L, and velocity of the leading edge of the spray sheet, V. The first three are influenced by temperature, and should be measured at constant temperature; apart from this, the limited variations in temperature likely to be encountered in practice would not be expected to have any signiificant direct effect on sheet breakup. From the point of view of drop formation the most suitable parameter to describe sheet dimensions is the length of the leading edge of the sheet, $l \sin \alpha/2$, where l is the length of sheet from nozzle to the point of breakup, and α is the angle subtended at the nozzle by the leading edge of the sheet.

Thus, the following expression can be postulated:

$$f\left(\eta, \gamma, \rho_L, l \sin\frac{\alpha}{2}, V\right) = 0$$

The parameters in this equation can be combined to form two dimensionless functions:

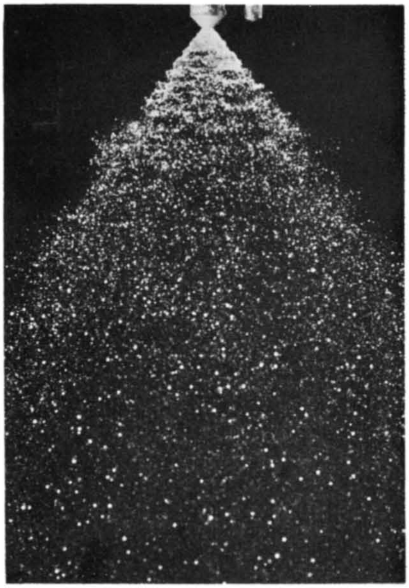
$$\Pi_2 = \left(\frac{\gamma}{l \sin\frac{\alpha}{2}\, \rho_L V^2}\right)$$

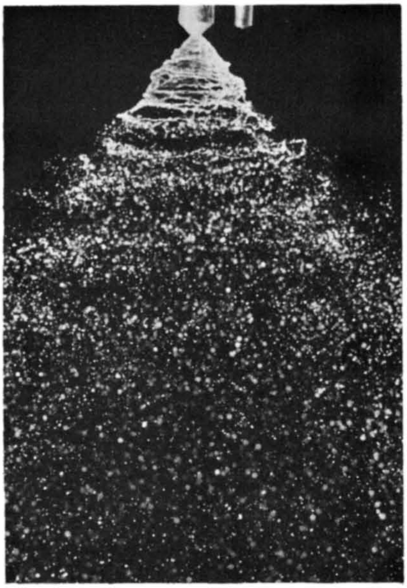
$$\Pi_1 = \left(\frac{\eta}{l \sin\frac{\alpha}{2}\, \rho_L V}\right)$$

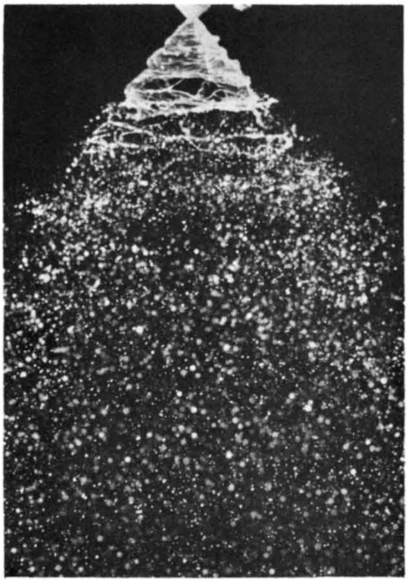
Using the method of dimensional analysis described by Buckingham (*4*), these functions are related by:

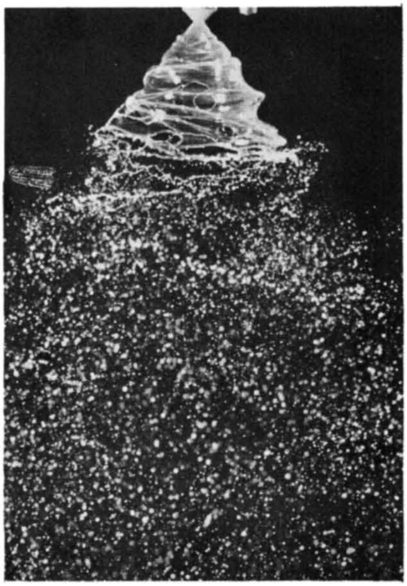
$$\left(\frac{\gamma}{l \sin\frac{\alpha}{2} \rho_L V^2}\right) = \psi \left(\frac{\eta}{l \sin\frac{\alpha}{2}\, \rho_L V}\right) \qquad (1)$$

To determine the value of the functions in Equation 1, an assumption must be made regarding the value to be used for V. If V is the velocity of the sheet at the point of breakup, then π_2 is a ratio of the viscous energy of the spray sheet to its inertial energy and is thus the inverse of the Reynolds number (Re) for the liquid flow in the sheet at the point of breakup. It is reasonable to assume that the velocity at the point of breakup is directly related to the velocity with which the liquid is emitted from the nozzle (V_E), and therefore π_2 could be replaced by 1/Re for flow through the nozzle orifice. Then, the V term in π_1 should also be replaced by V_E. Making these assumptions, Equation 1 has been plotted in Figure 3; the curve obtained is identical in form to the plot of D *vs.* viscosity shown in Figure 1. This suggests that the variation in drop size with viscosity can be related to three ranges of Re numbers for flow through the nozzle orifice. An examination of these ranges in conjunction with flash photographs of the type shown in Figure 2 shows that Range 1, where drop size does not change with viscosity, covers the range of Re numbers for turbulent flow in the nozzle orifice. Range 2, where there is a tendency for the drop size to decrease with increase in viscosity, represents the critical region of Re numbers for the transition from turbulent to laminar flow, and Range 3, where drop size increases progressively with increase in viscosity, represents the range of Re numbers for laminar flow in the nozzle orifice.









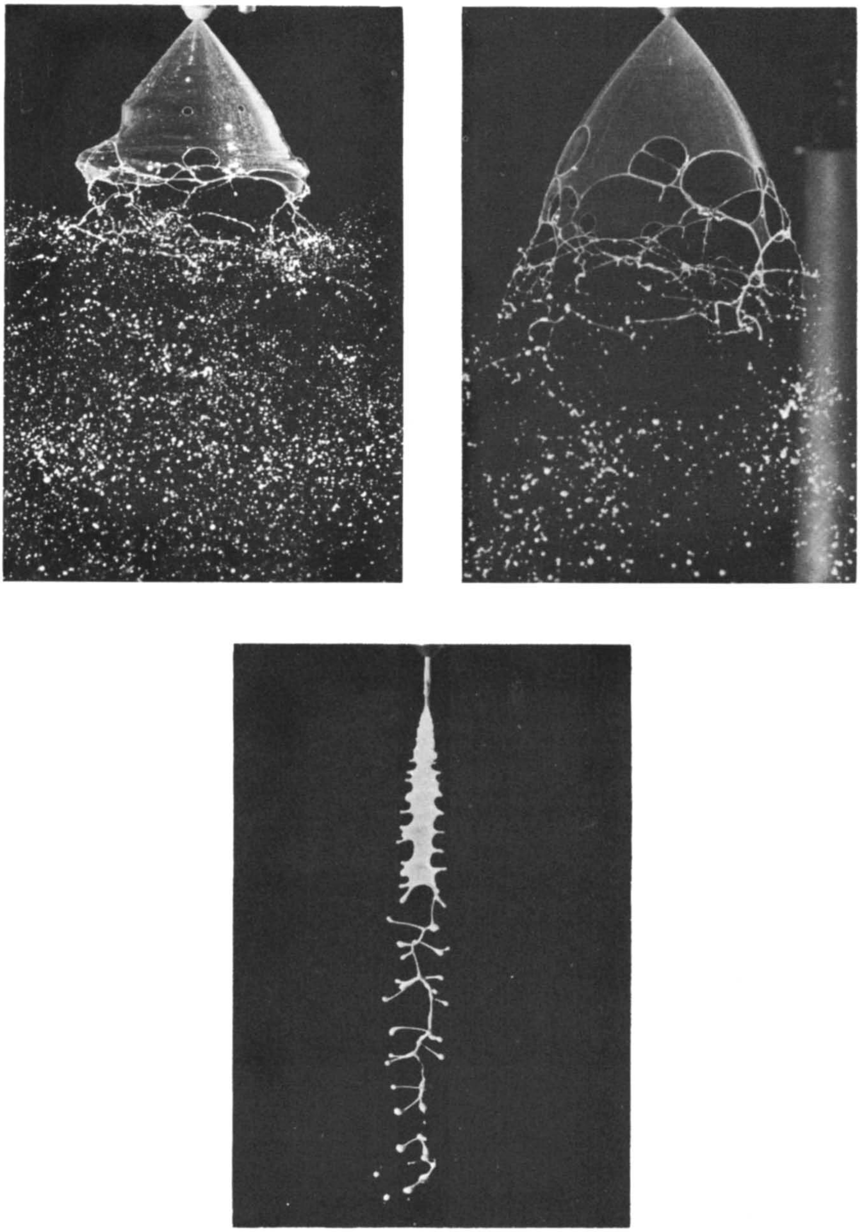


Figure 2. High speed photographs of a hollow-cone nozzle in operation

It is now plausible to relate the factors responsible for controlling the size of the drops formed from the spray sheet by a further dimensional analysis as follows:

$$f\left(D, \rho, \frac{Q}{l \sin \frac{\alpha}{2}}, \gamma, V\right) = 0$$

where D is the volume median diameter of the drop, and ρ is a density term that includes both ρ_L and ρ_A.

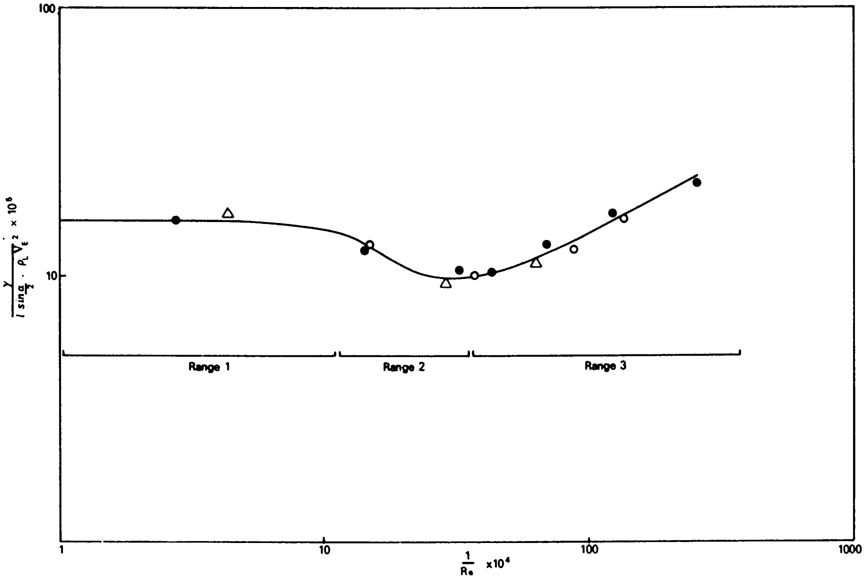


Figure 3. Plot of $1/Re$ vs. $\frac{\gamma}{l\ sin \frac{\alpha}{2} \cdot \rho_L V_E^2}$

○ Spraycone WG 1198
● Spraycone WG 4008
△ Spraycone WG 408

There is no need to include a separate viscosity term since it is implicitly included as a result of Equation 1 and Figure 3. The term $\frac{Q}{l \sin \frac{\alpha}{2}}$ governs the thickness of the sheet at the point of breakup and is directly proportional to the volume of liquid crossing unit length of the leading edge of the sheet in unit time. Again, these parameters can be expressed in terms of two dimensionless function, and the functions must be related as follows:

$$\frac{D_\gamma}{\rho}\left(\frac{l \sin \frac{\alpha}{2}}{Q}\right)^2 = \psi\left(\frac{\gamma\, l \sin \frac{\alpha}{2}}{\rho V Q}\right) \tag{2}$$

As with any dimensional analysis, the validity of this equation depends entirely on the assumption made during its development. The assumptions are that the properties responsible for variation of drop size are all covered in the equation and that the drop size is not influenced significantly by dimensionless factors which cannot be introduced in a dimensional analysis.

Before Equation 2 can be tested experimentally, certain assumptions must be made regarding the values assigned to ρ, V, and γ. Although ρ must include a function of the air density, pesticide spraying operations are usually carried out under normal atmospheric conditions. Thus, it may be assumed that any variation in the air density will be small compared with variations that may be introduced in liquid density and with the considerable variations that may occur in the other parameters in Equation 2. Consequently, the density of the liquid, ρ_L, has been used in place of ρ in Equation 2, and as discussed before, V_E has been used in place of V.

For a pure liquid there is no problem in assigning a value to γ, but this is more difficult with solutions of surface-active agents. Under static conditions, such solutions have a surface tension considerably below that of the solvent, but under dynamic conditions the surface tension will depend on the age of the surface and will lie between that of the pure solvent and that of the solution under static conditions. According to Fraser (*16*) the life of the spray sheet is too short for the surface tension to be lowered sufficiently to alter the process of droplet formation from that of the pure liquid. In the present work where the spray contained no surface-active agents, the values of the surface tension obtained under static conditions have been used. However, the static value may not be applicable with spray fluids containing highly surface-active materials.

Making these assumptions, the results obtained from the breakup of the spray sheet from several nozzles, moving at approximately 10 m.p.h., have been plotted in the form of Equation 2 in Figure 4. They all lie on or near a straight line whose slope is 5/3; thus, the expression may be written as:

$$DV_E \propto \left(\frac{Q\gamma^2}{l \sin \frac{\alpha}{2} \cdot \rho_L{}^2 \cdot V_E{}^2}\right)^{1/3} \tag{3}$$

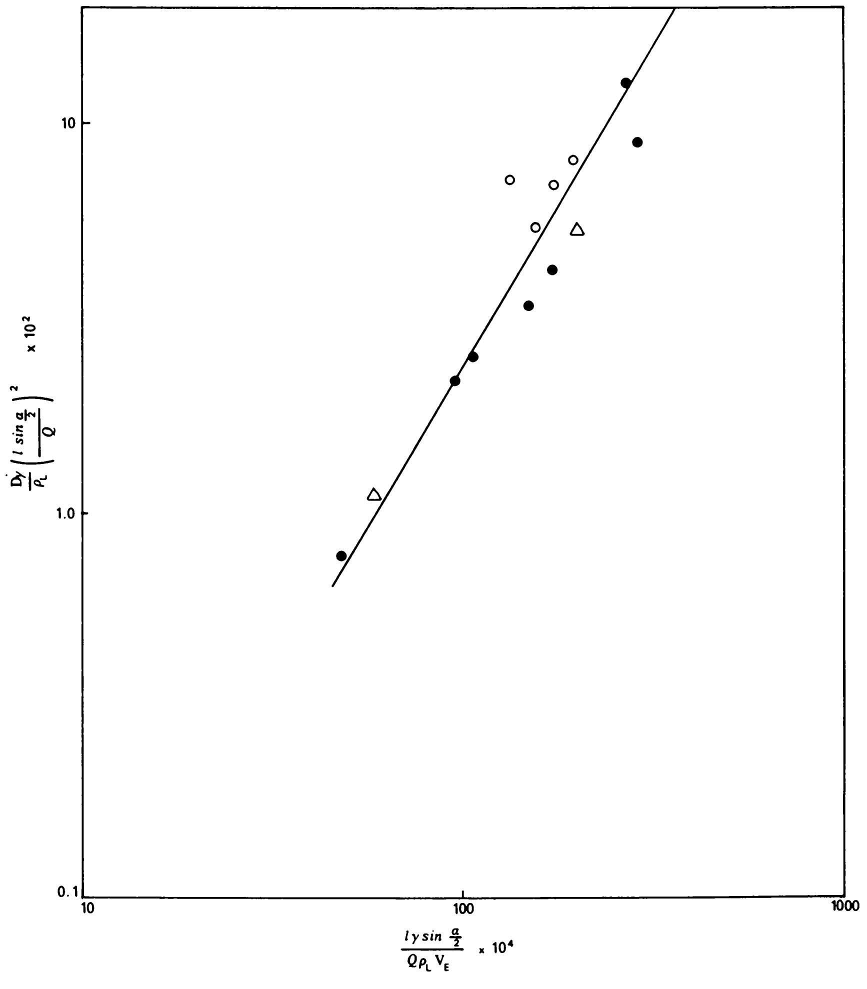


Figure 4. Plot of $\frac{D\gamma}{\rho_L}\left(\frac{1 \sin\frac{\alpha}{2}}{Q}\right)^2$ vs. $\frac{1\gamma \sin\frac{\alpha}{2}}{Q\rho_L V_E}$

○ *Spraycone WG 1198*
● *Spraycone WG 4008*
△ *Spraycone WG 408*

Since this expression has been derived by an empirical fit of experimental data, it is unwise to assume that it is generally applicable when the various parameters are varied beyond the limit tested. It has given satisfactory results for various sizes of hollow-cone nozzles operating under the range of conditions shown in Table II.

Table II. Range of Parameters Used in Deriving Equation 3 for Hollow-Cone Nozzles

Parameter	*Range*
Q	5–40 ml./sec.
γ	70–85 dynes/cm.
V_E	500–1500 cm./sec.
ρ_L	1.0–1.40 grams/ml.
η	1–150 cp.
l	1.0–10.0 cm.
α	30°–80°C.
P	20–50 p.s.i.g.
Orifice area	0.005–0.04 sq. cm.

Variation of Drop Size with Viscosity in Fan-Jet Nozzles. The effect of viscosity on the size of drops produced from fan-jet nozzles has been examined in a way similar to that described for hollow-cone nozzles. The theoretical treatment of the breakup of the flat sheet was carried out in the same way, and an analogous equation has already been published (*11*). However, the behavior of fan-jet nozzles is somewhat more complex than that of hollow-cone nozzles because of the possibility of ligament formation at the edges of the flat spray sheet formed. Photographs of fan-jet nozzles spraying liquids of different viscosities (Figure 5) showed that while the change in shape of the flat sheet with change in viscosity paralleled the change in shape of the conical sheet from cone nozzles, there was also a tendency for the amount of liquid entering the edge ligaments to increase considerably as the viscosity was increased. Confirmation of the importance of these edge ligaments in affecting the drop size of the spray was obtained by examining the distribution of drop sizes within the spray when using liquids of various viscosities. Over the range of low viscosities a single modal distribution was found, and the only effect of change of viscosity was to move the over-all distribution to higher or lower sizes. Over the high viscosity range a bimodal distribution became apparent. Thus, it appeared essential to treat the breakup of the edge ligaments separately from that of the liquid sheet. By collecting the drops from nozzles moving slowly (10 m.p.h.) over the stationary collecting surfaces, it was possible to separate reasonably well the drops which were formed from the ligaments from those formed from the sheet.

SHEET BREAKUP. Using the same treatment as that described for hollow-cone nozzles a similar expression has been developed (*11*):

$$DV_E \propto \left(\frac{Q_S\gamma^2}{r\theta\rho_L{}^2V_E{}^2}\right)^{1/3} \tag{4}$$

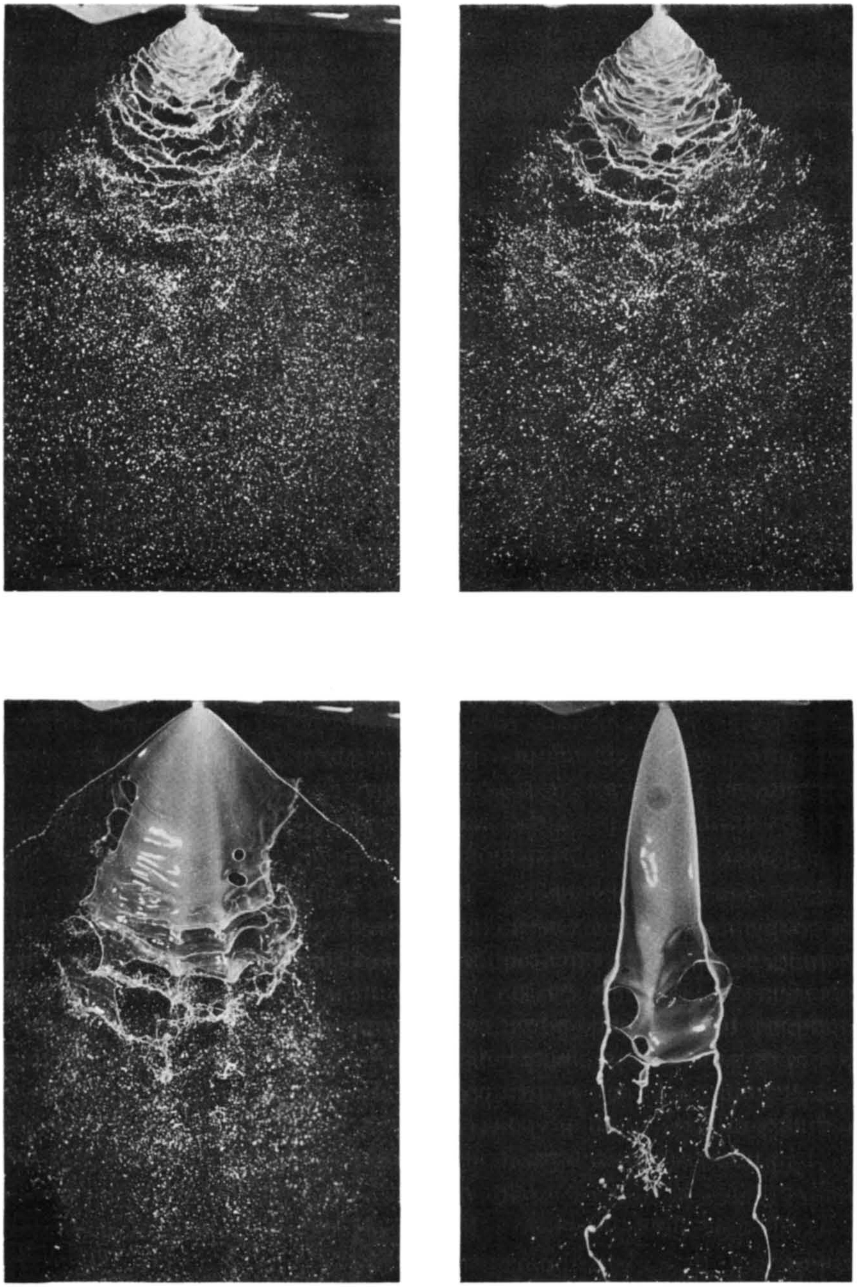


Figure 5. Fan-jet nozzles spraying liquids of different viscosities

This expression has been tested and works satisfactorily using the wide variation of the parameters shown in Table III.

Table III. Range of Parameters Used in Deriving Equation 4 for Fan-Jet Nozzles

Parameter	*Range of Values*
Q	5–125 ml./sec.
γ	35–85 dynes/cm.
V_E	750–5000 cm./sec.
ρ_L	0.95–1.40 grams/ml.
η	1–350 cp.
r	1–15 cm.
θ	20°–60°C.
P	20–100 p.s.i.g.
Orifice area	0.004–0.04 sq. cm.

Equation 4 can be written in the form:

$$DV_E \propto \left(\frac{Q_S\gamma}{\rho_L}\right)^{1/3} \times \left(\frac{\gamma}{r\theta\rho_L V_E^2}\right)^{1/3}$$

This corresponds to the expression derived by Yeo (25) with the addition of the dimensionless term $\left(\frac{\gamma}{r\theta\rho_L V_E^2}\right)^{1/3}$ which is similar to the π_1 term for hollow-cone nozzles introduced in Equation 1. This function is related to the inverse of the *Re* number for flow through the nozzle orifice (Figure 6) in a way similar to that shown for hollow-cone nozzles in Figure 3. Thus, the variation in the size of drops formed by breakup of the sheet from fan-jet nozzles can be described by three similar ranges of Reynolds numbers to those already described for hollow-cone nozzles. This also means that a complete relationship exists between the factors involved in drop formation from liquid sheets (where the drops are formed by disruption of the sheet by wave formation) which takes the form:

$$DV_E \propto \left(\frac{Q_S\gamma}{\rho_L}\right)^{1/3} \times \psi\,(\mathrm{Re}) \qquad (5)$$

Since Equation 3 for hollow-cone nozzles can also be reduced to Equation 5, the latter appears to be a general expression that can be applied to the sheet breakup of all types of fan-jet and hollow-cone nozzles. The function of Re appears to take the same form in all cases, but its value may vary with different designs of nozzle.

LIGAMENT BREAKUP. Columns of liquid break up in air owing to the development of oscillations which increase in amplitude until this exceeds

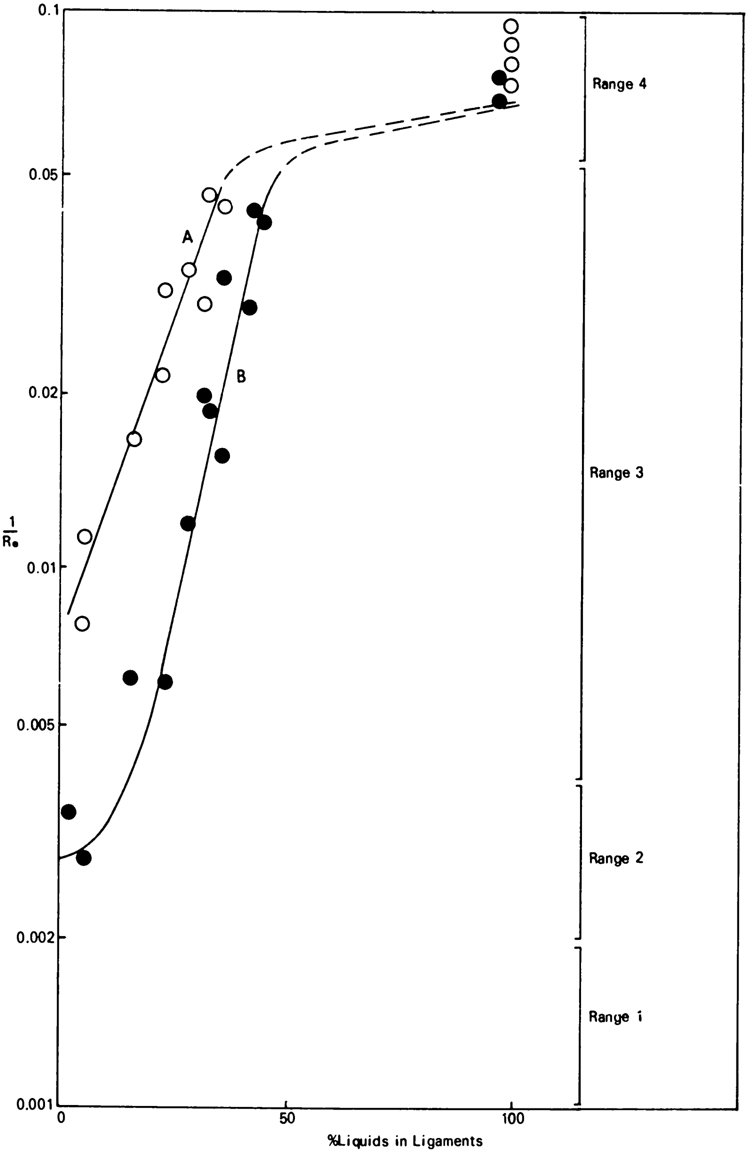


Figure 6. Variation of percentage of liquid entering ligaments with Re

● *Aqueous Newtonian liquids*
○ *Water-in-oil emulsions*

the radius of the column, when a series of regular drops is formed. From the expressions published in the literature on the wavelength of the oscillations produced in liquid ligaments (*22, 26*), a general expression for the variation of drop size with viscosity for drops produced from ligaments has been deduced (*11*). This takes the form:

$$D/d \propto \left(\frac{\eta}{\sqrt{d\gamma\rho_L}}\right)^{1/6} \tag{6}$$

where

$$d = \left(\frac{2Q_L}{\pi V_E}\right)^{1/2}$$

Q_L = volume of liquid emitted into ligaments per second.

This expression gives reasonably good results for the size of drops produced from ligaments using various fan-jet nozzles operating under various conditions (*11*).

Since the breakup of the two regions of the spray—ligaments and sheet—occurs by different mechanisms, the over-all drop-size distribution obtained will depend on the proportion of liquid entering these two regions. The extent to which edge ligaments are formed depends on the nozzle design and operating pressure. The effect of increasing viscosity is similar to that of reducing pressure, both leading to a reduction in the energy available for extending the spray sheet. Thus, it would appear that with any given nozzle design the formation of edge ligaments is related to the flow characteristics of the liquid through the nozzle, which are described by the Re number. The percentage of liquid entering the edge ligaments, determined from the drop size measurements, has been plotted against 1/Re in Figure 7 (Curve A) for liquids of various viscosities sprayed through a number of fan-jet nozzles. Edge-ligament formation starts at Reynolds numbers of 250–300. Between Reynolds numbers of approximately 20–250 the proportion of liquid entering the edge ligaments varies directly with the log (1/Re), and this range corresponds to Range 3 of Re numbers as already defined. At Re numbers below about 20, formation of a sheet is rapidly suppressed, and drop formation is wholly caused by ligament breakup. Thus, there is a fourth range of Re numbers which is important in describing the spray characteristics of liquids from fan-jet nozzles. Effectively, this range represents the flow conditions where the nozzle ceases to operate as a fan-jet nozzle; similarly, a fourth range of Re numbers applies to hollow-cone nozzles under conditions where the conical sheet cannot be formed.

Figure 7 also shows the effect of the surface tension of the spray liquid on ligament production. Whereas Curve A was obtained using sugar solutions of surface tension *ca.* 75–80 dynes/cm., Curve B was obtained by spraying water-in-oil emulsions whose static surface tension was 35 dynes/cm.

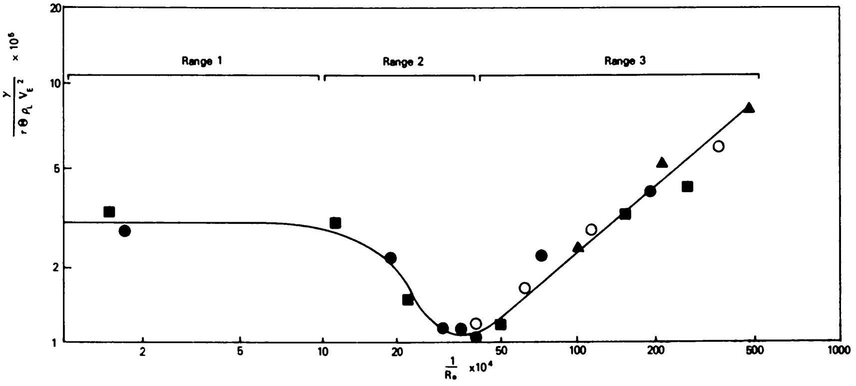


Figure 7. Plot of $\frac{1}{Re}$ vs. $\frac{\gamma}{\tau\theta\rho_L V_E^2}$ *for fan-jet nozzles*

○ *Allman No. 6, 20 p.s.i.g.*
● *Allman No. 9, 20 p.s.i.g.*
■ *Allman No. 9, 30 p.s.i.g.*
▲ *Allman No. 12, 20 p.s.i.g.*

The ligaments were not as pronounced with the lower surface tension, but the proportion of spray entering the ligaments still varied directly with log (1/Re).

Practical Application of the Theory. The practical difficulty in using Equations 3 and 4 is in measuring the sheet dimensions: l and α for hollow-cone nozzles; r and θ for fan-jet nozzles. Unlike the remaining parameters in Equations 3 and 4, these dimensions and angles cannot be measured in the field. However, they can be measured from flash photographs in the laboratory using a nozzle design similar to that to be used in the field. From the laboratory results, a plot of the appropriate π_1 function *vs.* 1/Re can be drawn, where Re is calculated from:

$$\mathrm{Re} = \frac{4m\rho_L V_E}{\eta}$$

where m = hydraulic mean depth of nozzle orifice (cm.), the nozzle area/perimeter.

The appropriate curve for hollow-cone nozzles is shown in Figure 3 and that for Allman fan-jet nozzles with elliptical orifices is shown in Figure 6. The 1/Re *vs.* π_1 function curves are the same for all sizes of any given nozzle design so that once the curve is plotted, it is not necessary to measure the sheet dimensions to calculate the drop size from any similar nozzle operating under any conditions of pressure and throughput. Once Re is calculated for the nozzle under the appropriate operating conditions, the π_1 function can be read from the graph and the cube root of this value can be substituted for the ψ (Re) term in Equation 5.

The values of the four Re ranges found for the types of nozzles used in this work are listed in Table IV.

Table IV. Approximate Limits of the Four Ranges of Reynolds Numbers for the Nozzles Used

	Reynolds Numbers			
Nozzle Types	*Range 1*	*Range 2*	*Range 3*	*Range 4*
Allman elliptical fan jet	>1000	250–1000	20–250	<20
Allman rectangular fan jet	>1200	300–1200	20–300	<20
Watson hollow cone	>1100	250–1100	30–250	<30

Besides varying with the design of the nozzle, these limits will be affected by roughness and imperfections in the nozzle orifice; thus, the values in Table IV are approximate.

Since the limiting values of Re are constant for a given nozzle design, the variation of drop size with viscosity will be more pronounced with a small nozzle (where relatively small increases in η will cause Re to be reduced to pass through the various ranges) than with larger nozzles. For example, with an Allman 000 nozzle spraying water at 30 p.s.i.g., a *VMD* of 275μ will be obtained, and a *VMD* of twice this value will be obtained with a spray liquid of viscosity 40 cp. An Allman 9 nozzle operating at 30 p.s.i.g. gives a *VMD* with water of 600μ, a spray liquid with a viscosity of 40 cp. produces an even smaller drop size (495μ), and to double the drop size obtained with water would require a spray liquid with a viscosity of 250 cp.

In view of these observations and the theory developed above, it is not surprising that there are many conflicting reports on the effect of viscosity on drop size. It is possible that all the reported observations are correct within the narrow limits in which the measurements were carried out. Unfortunately, these limits are not fully reported in much of the published work.

The equations for sheet and ligament breakup have been derived using results obtained from nozzles which were static or moving only slowly. In practical spraying operations, the nozzles may be moving more rapidly, particularly in aerial spraying. In such cases a more complex velocity function will be required than the simple emission velocity term (V_E) that appears in Equations 3, 4, and 6. Working with aircraft sprays, Yeo (25) showed that his expression for drop size needed to be modified by including the dimensionless function:

$$\chi\left(\frac{V_E}{V_o}\right)$$

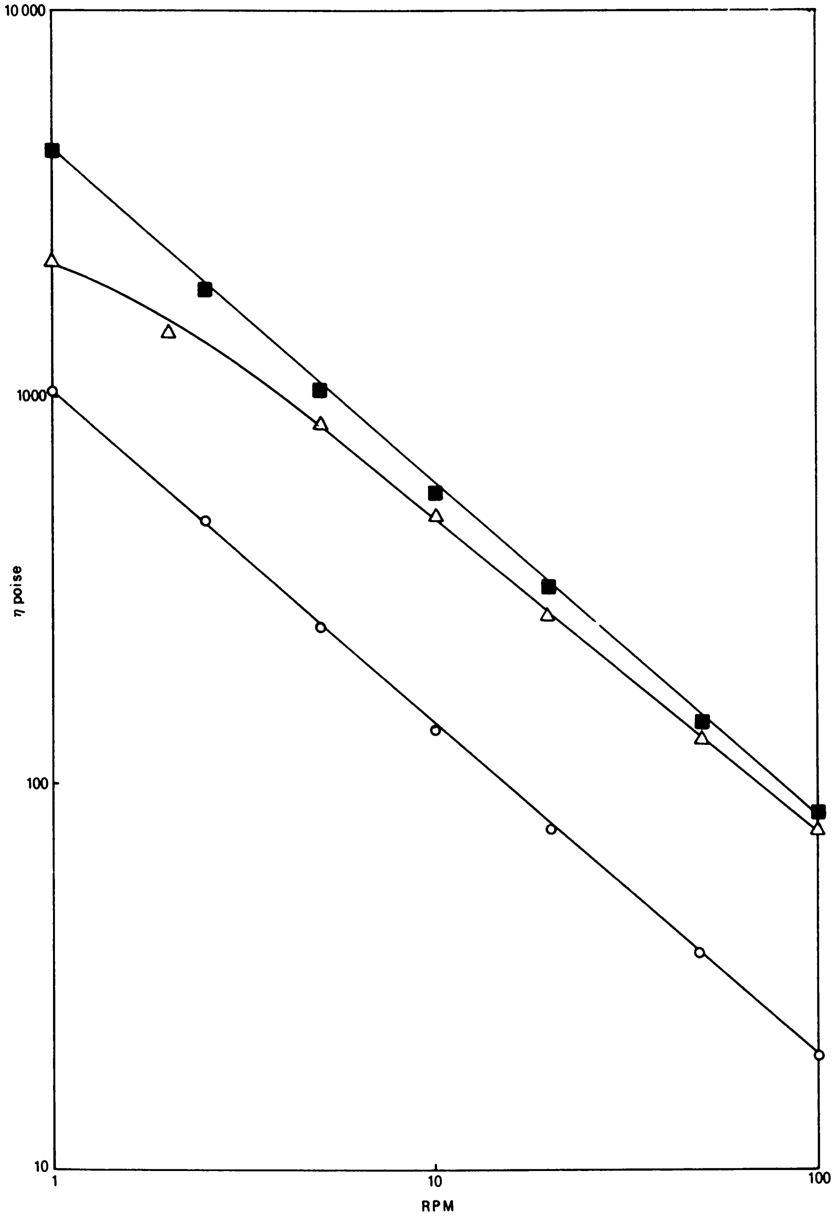


Figure 8. Viscosity of water-in-oil emulsions

■ *Formulation B,* η_∞ *2.91 poise*

△ *Formulation A with the addition of 20% w/v endrin in the oil phase,* η_∞ *2.62 poise*

○ *Formulation C,* η_∞ *0.59 poise* where V_o was the velocity of the emerging liquid relative to stationary air. Therefore, in cases where air flow past the nozzle is appreciable when compared with the velocity of emission from the nozzle, Equations 3, 4, and 6 should include a similar factor.

Application of the Theory to w/o Emulsions. Since concentrated w/o emulsions are non-Newtonian fluids, the viscosity of the emulsion is meaningless unless it is related to shear rate under which the measurement is made. The viscosity of concentrated emulsions decreases as the shearing forces to which they are subjected increases; this is shown in Figure 8 for three typical water-in-oil emulsions. However, at very high and very low shear rates they have limiting shear-independent viscosities, which may be designated η_∞ and η_0, respectively.

It is difficult to measure the shearing forces to which a liquid is subjected when passing through a spray nozzle, but a rough idea of the order involved may be made by calculating from the velocity of emission of liquid and the dimensions of the nozzle. Assuming that no slippage occurs between the liquid and the orifice sides, the rate of shear in an Allman No. 9 nozzle operating at 20 p.s.i.g. is around 1600 sec.^{-1}. With such high shear forces arising in spray nozzles, η_∞ seems likely to be the most suitable parameter for relating viscosity to spraying characteristics. However, since it is impossible to measure viscosities under such high rates of shear using simple laboratory viscometers, one must be able to calculate η_∞ from data obtained under lower shear rates. Further complications arise in measuring viscosities since the viscosity of emulsions containing high disperse phase ratios increases owing to the high shearing forces in the nozzle, and hence viscosity measurements must be made on samples collected after the emulsions have been sprayed.

Cross (*7*) has recently investigated the viscosity of concentrated solutions of macromolecules and suspensions of clays by considering the interactions between solute molecules or suspended particles. He deduced a theoretical expression for viscosity:

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + ks^n}$$

where η is the viscosity at shear s (sec.^{-1}), and k and n are constants for a given fluid.

The systems investigated by Cross all fitted this equation when $n = 2/3$. However, the use of this equation with data from water-in-oil emulsions gives incompatible values for η_∞, and $n = 4/5$ should be used (*12*) for such systems.

When using simple rotating cup or spindle viscometers, the modified Cross equation can be simplified and rearranged (*12*) to the form:

$$\eta = \eta_\infty + \frac{(\eta_0 - \eta_\infty)\Omega^{-4/5}}{K}$$

where Ω = speed of rotation of rotating cup or spindle viscometer (r.p.m.)

If η is plotted against $\Omega^{-4/5}$, a straight line is obtained with an intercept at η_∞, and most of the values of η_∞ used to study the spraying characteristics of w/o emulsions were obtained this way.

When these values of η_∞ were substituted in the drop size equations for sheet breakup and the drop size was calculated and compared with the size measured from spraying w/o emulsions, good agreement was found (*12*). However, with drops formed from the ligaments there was a tendency for the measured drop size to be somewhat greater than that predicted. This is caused by the relaxation of the shearing forces in the ligament once it has left the nozzle which permits the viscosity to rise. Photographs of sprays of very viscous water-in-oil emulsions show that the formation of waves in the ligaments, which is their normal mode of breakup, is considerably suppressed. Thus, although η_∞ is a suitable parameter to use for predicting the *VMD* of drops formed from the breakup of liquid sheets, it is not suitable when considering drop formation from ligaments of water-in-oil emulsions. From the results so far obtained it appears that the effective viscosity governing ligament breakup is approximately twice η_∞.

VISCOSITY OF W/O EMULSIONS. The viscosity of water-in-oil emulsions at infinte shear depends on several factors:

(1) The water-to-oil phase ratio

(2) The methods of mixing and the degree to which the two phases are mixed.

(3) The type of emulsifier system employed.

(4) The nature of the toxicant and solvent used.

Factor 1, the disperse phase ratio, has a considerable effect on η_∞ as shown by the results for three typical water-in-oil emulsion formulations (Table V).

Table V. Variation of η_∞ with Disperse Phase Ratio

Phase Ratio Water:Oil (v/v)	*η_x, poise*		
	Formulation A	*Formulation B*	*Formulation C*
12:1	2.76	5.55	0.74
10:1	2.28	2.62	0.61
8:1	1.35	1.70	0.44
5:1	1.05	1.04	0.39
3:1	0.41	0.51	0.21

The disperse phase ratio can be critical if significant increases in drop size are required to suppress spray drift. Using fairly large nozzles, such as Allman No. 9, a w/o ratio of about 10:1 will be required with Formulations A and B, while Formulation C is unlikely to suppress drift, even at the highest phase ratio used.

The extent to which mixing of the phases may affect the viscosity of w/o emulsions is shown in Figure 9, using Formulation A at a w/o ratio of 9:1. Curve A shows the viscosity obtained by hand mixing (shaking in a cylinder), Curve B, the viscosity of similar emulsions prepared by slow-speed paddle stirring, and Curve D, the viscosity found after high-speed mixing. As the degree of dispersion improved, the viscosity increased.

Such variations in viscosity are important only in terms of the ease of handling of premixed emulsions before spraying. During spraying, further mixing occurs owing to the shearing forces imposed on the emulsion as it passes through the nozzle. Thus, Curve C shows that the emulsions prepared by either hand mixing or paddle stirring have similar and much increased viscosities after spraying through an Allman No. 9 nozzle at 20 p.s.i.g. The emulsion prepared in the high speed mixer was initially more viscous than the other emulsions after spraying, and it was only slightly affected by passage through the nozzle (Curve E). Several important practical points emerge from these results:

(a) Although it is possible to vary the initial viscosity of w/o emulsions considerably by varying the mixing method, the spray operator cannot effect any significant control over the spraying characteristics of w/o emulsions by this means. The spray nozzle acts as an efficient mixing device and will tend to increase the emulsion viscosity up to a limiting value determined by its own characteristics.

(b) Since spray characteristics are governed by the viscosity of the spray fluid in the nozzle and in the emerging spray sheet, the value of the viscosity used for predicting the behavior of w/o emulsions should be the value measured immediately after spraying. Also, since the size and shape of the nozzle may influence the viscosity of the spray fluid, the viscosity measurements should always be made after spraying through similar nozzles to those that are to be used in the field.

(c) Besides the nozzle, pumps, valves, and narrow spray booms may also affect viscosity of w/o emulsions. Thus, it is possible to start with a fairly thin premixed emulsion in the spray tank, but this may become progressively more viscous as it is passed through the equipment. This is one of the major difficulties of using premixed w/o emulsions and led to the development of the bifluid spraying system.

Of the other factors which influence the viscosity of w/o emulsions, the effect of emulsifiers and solvents is well established (3). Although

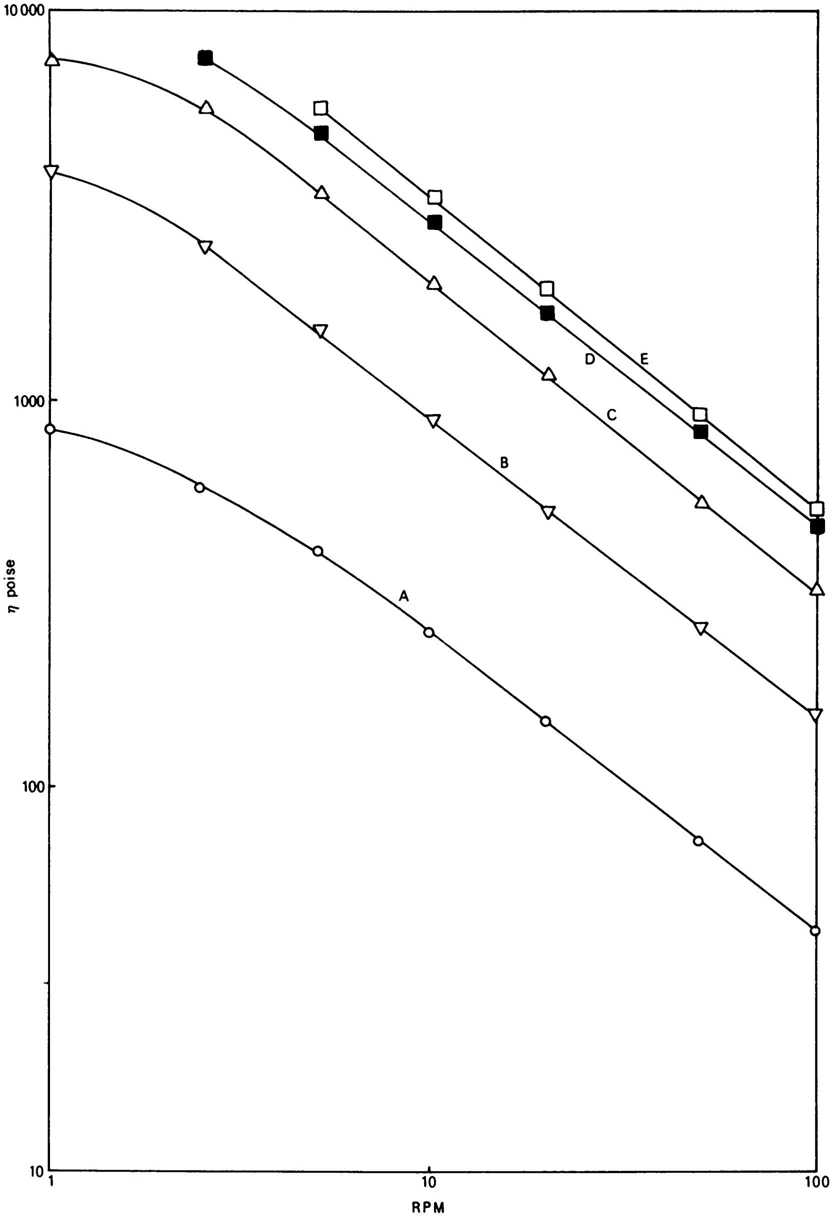


Figure 9. Viscosity of water-in-oil emulsions—effect of method of mixing

A. Hand mixing
B. Slow speed stirrer
C. Hand mixing or low speed stirring followed by passing through Allman No. 9 nozzle
D. High speed mixing
E. High speed mixing followed by passing through Allman No. 9 nozzle

the types of emulsifiers that can be used to produce w/o emulsions under the conditions encountered in practice are limited (*13*), considerable variations in viscosity by using different emulsifiers have been found (*14*). However, of particular importance here is the effect of the toxicant (*14*); it may be present in either the water or oil phase.

Table V shows that Formulation C had a much lower viscosity than the other two and contained 20% w/v dalapon (the sodium salt of 2,2-dichloropropionic acid) in the aqueous phase. In the absence of dalapon, the viscosity of the emulsion was increased threefold, being similar to the viscosity of Formulations A and B. This effect is presumably caused by interaction between the salt and the emulsifier present. The presence of toxicant does not always reduce viscosity; in fact, the presence of 20% w/v endrin in the oil phase of Formulation A will increase its viscosity slightly.

Control of Drop Size w/o Emulsions. Although the control of the drift of herbicide sprays was the initial reason for renewed interest in water-in-oil emulsion sprays, there are other interesting and novel ways of applying pesticides. The physical properties of w/o emulsions are considerably different from those of more conventional types of spray liquids, and the emulsifiers required to form and stabilize w/o emulsions are different from the usual materials employed in oil-in-water and wettable powder sprays. These differences can affect all aspects of spray performance, and a thorough study is required to appreciate the advantages and disadvantages which w/o emulsions may possess over aqueous-based sprays.

For w/o emulsions to be used in applying all types of pesticides, one must be able to control the drop size over fairly wide limits to ensure that the optimum drop size for any application can be achieved.

For any spraying operation, it is necessary to specify the amount of toxicant required per unit area, the volume of liquid per unit area, and the drop size. To control these, the operator has three main variables at his command—operating pressure, nozzle size and type, and phase ratio of the emulsion. Each has some effect on all the factors specified. In addition, in aerial spraying the orientation of the nozzles in the air stream may also be varied to control drop size.

The volume applied per unit area is fixed by the pressure and the size of the nozzle (assuming that the number of nozzles per unit length of boom and the speed of the sprayer are constant), and in combination with the phase ratio of the emulsion, this determines the toxicant deposit per unit area. The phase ratio in turn is the main factor which determines the viscosity of the spray liquid. The viscosity, the size and type of

Table VI. Effect of Nozzle Type and Water-to-Oil Phase Ratio on Drop Size and Emission Rates for Water-in-Oil Emulsions Applied through Fan-Jet Nozzles

Approx. Drop Size Required, μ	*Allman Nozzles*		*Ratio Required w/o Phase Formulations*			*Approx. Emission Rate per Nozzle of Formulation A*[a]	
	No.	*p.s.i.g.*	*A*[a]	*B*	*C*	*IG emulsion/hr.*	*lb. endrin/hr.*
250	000	30	1:1	1:1	1:1	4.3	4.3
	1	20	1.7:1	1.7:1	1.5:1	11.5	8.6
	9	30	1.9:1	1.9:1	2.8:1	43.0	29.6
350	00	45	3:1			9.1	4.6
	1	20	1:1	1:1	1:1	11.5	11.5
			2.8:1	2.3:1	4.5:1	11.0	5.8
	1	65	4:1			22.7	9.1
	6	50	1:1			45.5	45.5
	9	20	2:1	2:1	2.5:1	35.0	23.3
	10	100	1:1			92.0	92.0
450	000	50	2:1	2:1	2.2:1	5.2	3.5
	1	65	6:1			22.7	6.5
	3	30	4:1			22.0	8.8
	9	20	1:1	1:1	1:1	37.0	37.0
			3:1	3.5:1	8:1	34.0	17.0
600	000	20	1.7:1	1.7:1	1.5:1	3.0	2.2
	1	65	9:1			22.0	4.4
	3	30	6:1			22.0	6.3
	12	20	1:1	1:1	1:1	44.4	44.4
800	3	30	9:1			21.0	4.2
	4	85	13:1			42.0	6.0
	5	65	9:1			42.0	8.4
	12	20	8:1	7:1	—	41.0	9.1
1000	8	40	9:1			42.0	8.4
	9	70	14:1			63.0	8.4
1250	9	30	13:1			40.0	5.7
	12	20	16:1	13:1	—	40.0	4.7

[a] Oil phase contained 20% w/v endrin in addition to the emulsifiers.

nozzle, the volume emission rate and the velocity of emission (both of which depend on the pressure and nozzle size), and the surface tension together determine the drop size of the spray. Thus, the situation is different from that with water-based formulations, where at least the toxicant content can be varied within certain limits simply by altering the dilution of the formulation, without seriously affecting its other spraying characteristics. However, using the information given here it is possible to calculate the relationship between the three main variables for any given spray application. These calculations provide the framework within which the characteristics of the spray may be varied; additional variations in the distribution of the spray may be made by altering the number of nozzles and changing the speed of the sprayer. Obviously, such calculations cannot be carried out in the field, and it is necessary for the operator to have the appropriate data for each formulation. The data should be sufficiently extensive to allow the effects on drop size of varying phase ratio, pressure and nozzle to be clearly seen.

A limited example of such data is given in Table VI. These data do indicate the wide ranges of drop sizes and emission rates that can be accommodated with a water-in-oil emulsion spray. Thus, although the application of these emulsions is more complicated than that of aqueous-based sprays, it is possible to provide a wide range of toxicant dosage, volume applied, and drop size. The extra complications entailed in applying w/o emulsions must be offset by improved performance of the spray, either in terms of drift control or improved biological activity, for the spraying of w/o emulsions to be worthwhile.

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Formulations for Controlled Release of Abate in Water

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The organophosphorus insecticide Abate has a very low mammalian toxicity, yet it is extremely effective as a mosquito larvicide in concentrations as low as 0.005 p.p.m. The introduction of Abate into potable water stored in cisterns and drums to control Aedes aegypti *larvae has been investigated. To reduce the frequency of application and still maintain concentrations in the range 0.005–0.1 p.p.m., new formulations have been developed; the most promising is in a foamed plastic which releases the insecticide at a controlled rate over a long time. The rate of release depends upon toxicant and surfactant concentration as well as polymerization conditions of the plastic matrix. Formulations have produced lethal concentrations to larvae in reservoirs for 20 weeks.*

Some of the more troublesome breeding sites for *Aedes aegypti* (Linneaus), the mosquito vector of yellow fever, include cisterns, metal drums, and other man-made containers which store water for drinking and household uses in tropical areas. Several larvicidal compounds have been investigated for possible use in treating these containers by Jakob (*4*) and Brooks and Schoof (*1*). To be considered for such application, the toxicant must have extremely low mammalian toxicity and should be effective in very low concentrations. One of the more promising compounds investigated was Abate (*O,O,O′,O′*-tetramethyl-*O,O′*-thiodi-*p*-phenylene phosphorothioate, manufactured by the American Cyanamid Co., Princeton, N. J.) which is reported to have an oral LD_{50} to rats and mice greater than 4000 mg./kg. (*3*) and is lethal to *Aedes aegypti* larvae in concentrations below 0.005 p.p.m. A concentration of 1.0 p.p.m. or less of Abate has been accepted as a safe level for treating reservoirs of potable water as a control measure.

In the work described above, the larvicides were applied as emulsifiable concentrates or granules. There are two disadvantages with emulsifiable concentrates: (1) they produce a turbidity in water which is objectionable to the householders, and (2) the total dosage applied is released instantly. This seriously limits the quantity which can be applied at any given time and makes it necessary to re-treat frequently if the concentration is to be kept low. Granules do not impart turbidity to the water but do release one-third to one-half the applied dose within the first few days. Fortunately, Abate hydrolyzes slowly in water, and larvicidal concentrations can be maintained for long periods of time in clean water with granular applications. Abate also tends to deposit on solid surfaces. This decreases its effectiveness because it migrates to the walls of the container or to debris or organic matter if present in the container with a resulting decrease in aqueous concentration. If lethal concentrations of the toxicant are to be maintained over a time, losses to these surfaces must be replaced. It would be desirable, therefore, if a formulation were available that would release small amounts of Abate into the water over a long time.

Several years ago Miles *et al.* (*6*) reported on work with wax and plastic formulations of DDVP (dimethyl dichlorovinyl phosphate), which were designed to release the toxicant into air or water over long times. The plastic formulations described were similar to those proposed by Leeds (*5*). According to Leeds, if poly(vinyl chloride) and a plasticizer are mixed with a third material to form a paste and if the third material is incompatible with the resin product upon polymerization, a microreticulated structure will be formed which will entrap the incompatible ingredient. It is believed that this type of structure is formed when DDVP is formulated in a PVC resin formulation. When the product is exposed to air or water, DDVP slowly passes from the matrix into the environment. Although the physical properties of Abate are quite different from those of DDVP, it was thought that a PVC resin formulation might prove to be a suitable vehicle for introducing Abate into water.

Experimental

The first experimental plastic formulations were prepared in the same manner as the early DDVP formulations. Typical combinations of ingredients are shown in Table I. The ingredients were mixed thoroughly

Table I. Typical Non-expanded Plastic Formulations, %

	No. 1	*No. 2*	*No. 3*
PVC	67.5	67.5	48.75
Dibutyl phthalate	30.0	29.8	48.75
Surfactant (Dow FC172)	—	0.2	—
Abate	2.5	2.5	2.5

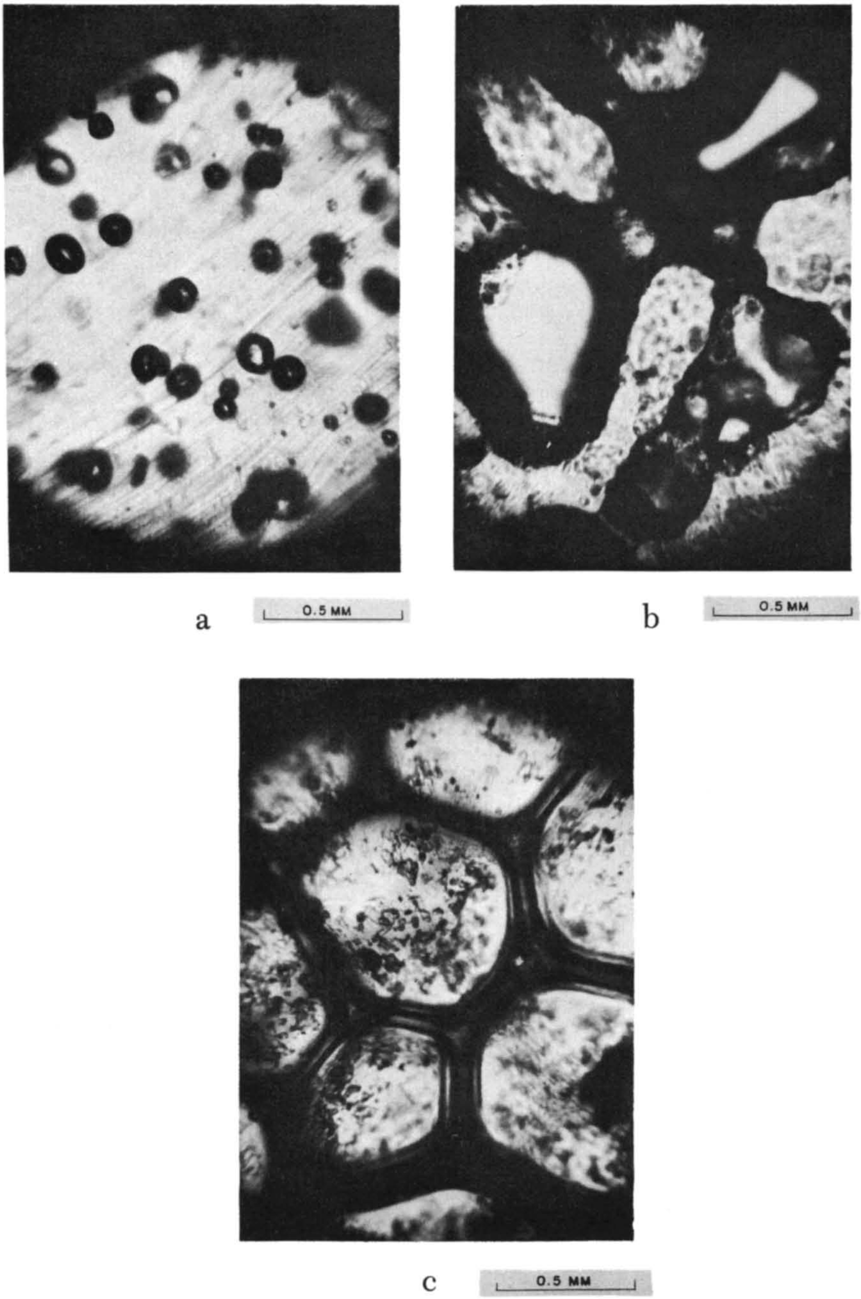

Figure 1. Photomicrographs of thin sections of Abate–PVC formulations

(a): Non-foamed
(b): Foamed with CO_2
(c): Foamed with azodicarbonamide plus foam stabilizer

and poured into aluminum molds to a depth of about 1/4 inch, then polymerized in an oven for 12 minutes at 130°C. The product was a firm, tough, plastic solid with a somewhat disagreeable odor of Abate. A photomicrograph of a thin section of the plastic formulation is shown in Figure 1a.

To test the new formulations, approximately 12 grams of each were placed individually in steel drums containing 35 gallons of water. This was equivalent to about 2 p.p.m. of Abate. Water was withdrawn periodically and analyzed for Abate, and bioassays were conducted simultaneously with third instar *Ae. aegypti* larvae of the Charlotte Amalie strain (DDT-dieldrin resistant). The tests were conducted for 3 weeks after introducing the toxicant, but during this period no larvae kill was observed in any of the drums.

The following procedure was used for chemical analysis for Abate. A 500-ml. sample of water was made slightly alkaline with dilute NaOH and extracted three times with 25-ml. portions of $CHCl_3$. The $CHCl_3$ extracts were combined in a 250-ml. beaker and evaporated to near dryness on a hot plate. The residue was transferred quantitatively to a 22 × 175-mm. test tube and evaporated to dryness in a water bath. The Abate residue was oxidized by adding 0.3 ml. 60% $HClO_4$ and 0.1 ml. HNO_3 and heating the test tube in an aluminum block at 200°C. for 1 hour. The test tubes were placed in the block cold, and the temperature was raised gradually to prevent spattering. The resulting orthophosphate was determined colorimetrically by the method of Chen *et al.* (*2*) with modifications (*8*). The Abate concentration in all cases was found to be less than 0.005 p.p.m., which is about the limit of detection by this method.

The results showed that the rate of release of Abate by these formulations was too slow to be practical. To increase the release rate, the formulation was modified in two ways. A blowing agent was added to foam the product to increase the surface area, and varying amounts of surfactant were added to increase the rate of solution of the Abate into water. The basic formula for the expanded formulation is shown in Table II.

Table II. Typical Expanded Plastic Formulations

	Percent
Abate	5.0
PVC	40.0–45.0
Dibutyl phthalate	40.0–45.0
Triton X-100	10.0– 0.0
Ammonium carbonate	1.0
Citric acid	3.0
Water	1.0

The organic materials were mixed thoroughly in a mortar, and ammonium carbonate was added and ground with a pestle into a smooth paste. Finally, the citric acid was dissolved in the water and stirred into the formulation. The product was poured into aluminum molds to a depth of about 1/4 inch and heated in a forced draft oven for 20 minutes at 130°C. Upon cooling, the material formed a tough stable foam.

To compare the rate of release of the various formulations, 3 grams of each product were placed individually in gallon jars filled with water. In this experiment the total amount of Abate added to the water was equivalent to about 40 p.p.m. Weights were attached to the expanded formulations to hold them on the bottom of the jars. Samples were taken periodically and analyzed for Abate. Fresh water was added to replace the samples taken. Data from these tests, given in Table III, show that the release rate is increased markedly when the product is foamed as well as with increasing surfactant content.

Table III. Effect of Surfactant and Foaming on the Rate of Release of Abate

Abate Concentration, p.p.m.

	Not Expanded		*Expanded*			
Days	*0% TX-100*	*10% TX-100*	*0% TX-100*	*3% TX-100*	*6% TX-100*	*10% TX-100*
1			.012	.036	.085	.083
2	.009	.050	.026	.173	.272	.372
3	.013	.072		.171	.278	.364
4	.041	.118	.034	.204	.333	.375
7	.042	.156	.045	.256	.265	.430
11	.057	.123	.046	.266	.320	.499
15			.028	.095	.236	.413

Table IV. Rate of Release of Abate by Plastic and Granular Formulations in Water

Formulation[a]	*Treatment Level, p.p.m.*	*Abate Found, p.p.m. (average)* *1st mo.*	*2nd mo.*	*3rd mo.*	*4th mo.*	*5th mo.*	*Weeks of 100% Kill*	*Highest Conc. Observed, p.p.m.*
A	1.3	.017	.019	<.01			10	.036
B	2.6	.019	.031	<.01			9	.040
A	4.0	.023	.049	.015	.010	<.01	17	.051
B	8.0	.023	.044	.029	.023	.018	20	.068
Sand (1%)	1.0	.190	.070	.058	.062	.057	18[b]	.348
Sand (1%)	2.5	.204	.060	.047	.039	.059	18[b]	.510

[a] Formulation A. 2.5% Abate. Formulation B, 5.0% Abate.
[b] Experiment terminated.

Additional quantities of the more promising formulations were prepared for simulated field tests and for comparison with granular formulations. In this series of tests the expanded formulations were prepared with 10% Triton X-100 to produce maximum release. The blowing agent was CO_2 from the ammonium carbonate, citric acid reaction, and the Abate concentrations were 2.5 and 5.0%. Tests were conducted in 55-gallon steel drums, with biological assessment and chemical analyses

Table V. Foam Stabilized Abate Formulation

	Percent
PVC	36.0
Dioctyl phthalate	32.4
Kempore SDA-200	9.0
FS-100[a]	3.6
Triton X-100	9.0
Abate	10.0
	100.0

[a] A foam stabilizer manufactured by Air Products and Chemicals, Inc., Allentown, Pa. Curing conditions: Heat at 198°C. for 8 minutes.

Table VI. Abate Formulation Foamed with Low Temperature Blowing Agent

	Percent
PVC	47.6
Dioctyl phthalate	16.2
Diisodecyl phthalate	16.2
Ferro 707-X[a]	2.0
Triton X-100	9.0
Nitrosan	4.0
Abate	5.0
	100.0

[a] A vinyl stabilizer manufactured by the Ferro Corp. Curing conditions: Heat at 133°C. for 12 minutes.

Table VII. Concentration of Abate Found in 55-Gallon Drums

Sample No.	*Size, grams Sample*	*Percent Abate*	*Stabilizer[b] Foam*	*Blowing Agent*
1	15	10	FS-100	SDA-200
2	15	10	707X	Nitrosan
3	15	10	—	CO_2
4	15	10	FS-100	66-M-1[a]
5	30	5	FS-100	SDA-200
6	30	5	707X	Nitrosan
7	30	5	—	CO_2
8	30	5	FS-100	66-M-1
9	30	5	763	SDA-200
10	30	5	760	SDA-200

[a] The product 66-M-1, furnished by Air Products and Chemicals, Inc., is a plastisol containing azodicarbonamide and FS-100 stabilizer.

made at weekly intervals. The biological test methods are described elsewhere by Smith and Brooks (7). Table IV compares the results obtained with applications of 1.3–8.0 p.p.m. Abate in expanded plastic formulations and 1.0 and 2.5 p.p.m. Abate applied as sand granules.

Discussion

For plastic formulations the rate of release was slow, and the peak concentrations were not reached until the second month of the experiment, whereas peak concentrations were reached during the first week for granular formulations. Peak concentrations were also much higher in the drums treated with the granules, where values above 0.5 p.p.m. were observed in drums treated at 2.5 p.p.m. The highest concentration observed in the drums treated with the plastic formulation was 0.068 p.p.m.

Although the results obtained in the above tests were promising, a number of variations in the ratio and type of ingredients were tried in an effort to improve the efficiency of the plastic formulation. The primary variables investigated were changes in the type of blowing agent and the addition of foam stabilizers. During the study, the blowing agent Nitrosan (*N,N′*-dimethyl-*N,N′*-dinitrosoterephthalamide, du Pont Co.) and Kempore (azodicarbonamide, National Polychemicals, Inc.) were compared with CO_2 produced by the reaction of citric acid with ammonium carbonate. Examples of the formulations prepared are given in Tables V and VI.

A photomicrograph of a thin section of a formulation foamed with CO_2 (Figure 1b) is compared with that of a similar product foamed

of Water Treated with Various Foamed Plastic Formulations

Triton X-100, %	*Abate Conc., p.p.m.*			
	2 Weeks	*4 Weeks*	*8 Weeks*	*12 Weeks*
10	.039	.031	.018	.020
10	.056	.027	.012	.015
10	.046	.037	.015	.013
0	.029	.015	<.01	.014
10	.029	.023	.018	.027
10	.047	.028	.024	.016
10	.101	.045	.017	.011
10	.033	.039	.034	.035
10	.036	.025	.017	.025
5	.012	<.01	<.01	<.01

[b] Foam stabilizers FS-100 (Air Products and Chemicals, Inc., Allentown, Pa.). Foam stabilizers 707X, 760, and 763 (Ferro Chemical Co., Belford, Ohio).

with azodicarbonamide with the addition of a foam stabilizer (Figure 1c). The large nonuniform cell structure is typical of the product foamed with CO_2.

A variety of foamed plastic formulations containing 5 and 10% Abate were prepared with the various blowing agents described above. Foam stabilizers were added to those formulations which were expanded with azodicarbonamide or Nitrosan. To compare the efficiency of the various formulations, samples of each type were placed in 55-gallon drums of water which were sampled at biweekly intervals and analyzed for Abate. All drums were treated at the 8 p.p.m. level. Results of chemical analyses are given in Table VII. There was no significant difference in release rates by products foamed by high and low temperature blowing agents. Although a more uniform product was produced when foam stabilizers were used with conventional organic chemical blowing agents, the non-stabilized products foamed with CO_2 performed about as well even though their cell structures were extremely poor. Formulations with low surfactant content did not release the Abate as well as those with high percentages of surfactant.

Summary and Conclusions

Abate can be formulated with poly(vinyl chloride) to form a stable plastic product which will slowly release the toxicant when placed in water. The rate of release of Abate is very low when the insecticide is cured with PVC and a plasticizer to form a solid rubberlike product, but it increases with the addition of a surfactant. The rate of release can be improved further if the product is foamed to increase the surface area. The uniformity of the cellular structure of the product can be improved by adding foam stabilizers, but this does not improve the performance. In fact, products with poor cell structures seemed to be superior to those with small uniform cells. Formulations containing higher percentages of Abate produced higher concentrations in water and were effective for longer periods. The rate of release of Abate from foamed formulations also increased with increasing surfactant content. The range of concentrations prepared was 2.5 to 10.0% Abate. Drums of water treated with plastic formulations of Abate at a rate of 8 p.p.m. (1.5 grams of Abate in plastic in 50 gallons of water) were effective against *Ae. aegypti* larvae for as long as 20 weeks, and the concentration in the water never exceeded 0.068 p.p.m. Granular formulations of Abate are also effective for long times, but the concentrations in the water during the first week of treatment are 4 to 5 times higher than those obtained with plastic formulations.

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15

Formulation and Structure of Residual Insecticides for Bark Beetle Control

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The potential of "surface" and "tissue" (subsurface) deposits of synthetic organic insecticides to control bark beetles was investigated. The contact toxicity and deposit structure of surface deposits on fiberboard panels of six insecticides were studied in the laboratory: DDT, dieldrin, dinitrocresol, endrin, heptachlor, and lindane. Each insecticide was characterized by spontaneous crystallization after application in solution form. In field studies of lindane and dieldrin, tissue deposits appear to offer the greater promise. They were slightly but consistently more effective than surface deposits in killing beetles in infested bark and in protecting green logs. Fundamental research is needed on tissue deposits to clarify their properties and behavior in the bark and their effect on the bark beetle. Only then can formulation be lifted from its present empirical state.

Chemical control of the primary forest insect pest—the bark beetle—is achieved mainly by spraying insecticide on the bark of the host tree. This strategy is dictated by the behavior of these insects, which spend all their life in or under the protective cover of bark except for a brief flight period as adults. Control is defined as (1) suppression or the destruction of beetle populations in trees or logs (postattack sprays), and (2) the protection of green trees or logs from beetle invasion (preattack sprays). Broadcast sprays as used on defoliators have not proved feasible. Systemic insecticides, though theoretically appealing, have not been successful in combating these pests (*23*, *35*, *38*).

Bark sprays should be used only after a thorough evaluation of the need (*24*). They are expensive and must be skillfully applied to be effective (*46*). They are best suited for use on valuable trees which occur on cabin sites, in naval stores stands, or in seed production areas.

Historically, the first bark sprays to be used widely were fumigants (*18, 41*). Called penetrating sprays, they are applied in high volumes (2 to 6 gal./100 sq. ft. of bark surface) to penetrate the bark and kill the bark beetles in their galleries. Through the years the fumigant ethylene dibromide in oil or water emulsion was developed and adopted for suppression of several bark beetle species as a penetrating spray (*15, 19, 29, 30, 42, 45, 47*).

The development of synthetic organic insecticides in the 1940's and thereafter stimulated research on their use as an alternative to the more expensive penetrating sprays. The promise of these modern insecticides lay in their potential for use at low volumes as postattack sprays for suppression but also, because of their residual properties, as preattack sprays for protection of green trees or logs (*32*). A recent review (*27*) indicates that the single insecticide lindane, either pure or as the active ingredient of benzene hexachloride (BHC), is the preferred chemical for bark beetle control. EDB (ethylene dibromide) is still used in some places, but such penetrating sprays are being replaced by the residual organic insecticides. This trend probably will continue. Indeed, lindane (or BHC) is gradually becoming a "universal" chemical for bark beetle control.

Comparison of Formulations

Our present understanding of formulation of the synthetic organic insecticides for bark beetle control is sketchy. The literature reveals only a few examples of formulation research. Field studies have emphasized the chlorinated hydrocarbon insecticides.

Compared with other compounds, lindane has usually performed well in the field (*1, 14, 20, 40, 43*) and has ranked at or near the top in laboratory tests of contact toxicity (*13, 26, 27, 31, 32, 33, 39*). It has received more attention than any other insecticide, and most of the discussion that follows, by default, pertains mainly to this chemical. The very success of lindane has probably played a leading role in discouraging research on formulation of bark sprays.

In a few studies, the major types of formulations have actually been compared in the same test at the same time. When this was done, solutions in diesel oil or No. 2 fuel oil, without exception, have been superior to emulsions (*10, 22, 40, 43*). Wettable powder suspensions were reported to be least effective in one study (*40*) and intermediate in another (*22*). A single report of the use of a dust (BHC) showed it least effective of all (*22*).

At a given spray concentration and application rate, solutions are more reliable. Emulsions of lindane usually work well enough, however, if applied in larger volume or at higher concentration. Elimination of the oil carrier reduces the cost and also the hazard of phytotoxic reactions where living trees are sprayed for protection. Several early studies report the excellent control afforded by lindane emulsions (*4, 5, 12, 14, 20, 23*), and reports on the excellent performance of lindane emulsions on a wide assortment of bark beetle species have recently grown (*6, 7, 8, 9, 10, 17, 37, 40, 44*). Massey (*28*) has reported on the successful use of an emulsion of DDT to protect living trees.

Formulations of lindane now used for various bark beetle species are quite similar. They are usually 0.5–1.5% (w/w) and are applied either to bark wetness or to runoff, amounting to 1/2 to 2 gallons/100 sq. ft. of bark surface. The higher volumes are more often used (application to the point of runoff) and give only a slight cost advantage over penetrating sprays. This procedure does not fully exploit the low volume potential of lindane and other residual insecticides. Doane (*14*) reported that lindane killed 98% of emerging elm bark beetles [*Scolytus multistriatus* (Marsham)] when a 6% emulsion was applied at the low volume of less than 1 pint per 100 sq. ft. of bark surface. Moore (*32*) found in preliminary tests with fogging equipment that a light coating of 6 or 12% DDT or 10% lindane gave very high kills of bark beetles. We know of no examples in the literature of a concerted study of the potential of such low volumes.

Deposit Structure

A crucial omission in the research on residual insecticides for bark beetle control has been the absence of corollary studies relating control effectiveness to the physical structure of insecticide deposits on and in bark. The importance of deposit structure has been well documented (*3, 21, 36*). The structure of the deposit affects its availability to the insect contacting it and governs its toxicity. On an absorbent surface like bark, two major types of residues can be created: deposits on the surface and deposits in the bark tissue. Henceforth, these will be referred to as "surface" and "tissue" deposits, respectively. Dusts and wettable powders form surface deposits. Solutions and emulsions penetrate and form mainly tissue deposits, though they may not remain in the tissue. The insecticide may crystallize out of solution, forming a deposit of fine crystals on the bark surface.

A study of the structure of surface deposits of residual insecticides aimed specifically at bark beetle control was undertaken between 1956 and 1962 at the U.S. Forest Service's Pacific Southwest Forest and Range

Experiment Station (*27*). Portions of that work relevant to the present discussion are cited here.

Crystal Blooms. A preliminary examination of crystal blooms of selected insecticides on various species of conifer bark (*32*) soon demonstrated a wide variation and high unpredictability in crystallization patterns. Because of this variation and the difficulty of bioassay with irregular bark surfaces, fiberboard panels were chosen as the test surface. Fiberboard is not a substitute for bark and does not simulate bark except in a general way and so was used mainly for convenience in studying the potential toxicity of crystal blooms and the broad aspects of crystallization patterns.

Acetone was the primary choice of solvent because of the rapid and spontaneous crystallization characteristics of low boiling solvents (*3*) from which insecticides may crystallize within a few hours after application. The California five-spined ips [*Ips confusus* (Le Conte)] was used as the experimental bark beetle for most of the study. The probit method of Finney (*16*) was used to analyze time–mortality relationships.

The best deposits of all six insecticides studied—dieldrin, lindane, endrin, dinitrocresol, heptachlor, and DDT—produced 50% mortality with exposure periods of less than 2 minutes (LT_{50}). All mortality estimates were based on a 72-hour post treatment holding period at about 70°F. and 60% relative humidity. Lindane and dieldrin were the most toxic. One percent solutions produced 50% mortality with less than 2-seconds' exposure (Table I). [1% solutions: weight/volume: 10 mg./ml. = 1%; this applies to all further references to concentration.] This left little doubt that surface deposits could be made toxic enough by contact to kill bark beetles in nature even though they may be in contact with the bark surface of their host trees for as little as 1 minute or less.

Table I. Contact Toxicity of Crystalline Deposits on Fiberboard to *Ips confusus*[a]

	Exposure Time for 50% Kill (LT_{50}), min.	
Insecticide	*Median*	*Standard Error*
Dieldrin	<0.02[b]	—
Lindane	0.02	± .01
Endrin	0.73	± .10
Dinitrocresol	1.28	± .18
Heptachlor	3.91	± .72
DDT	9.12	±1.47

[a] 1% (10 mg./ml.) solution; applied 16 ml./sq. ft., thus 160 mg. active ingredient per sq. ft.

[b] Deposits too toxic to give less than 100% kill with shortest exposure time used (2 seconds).

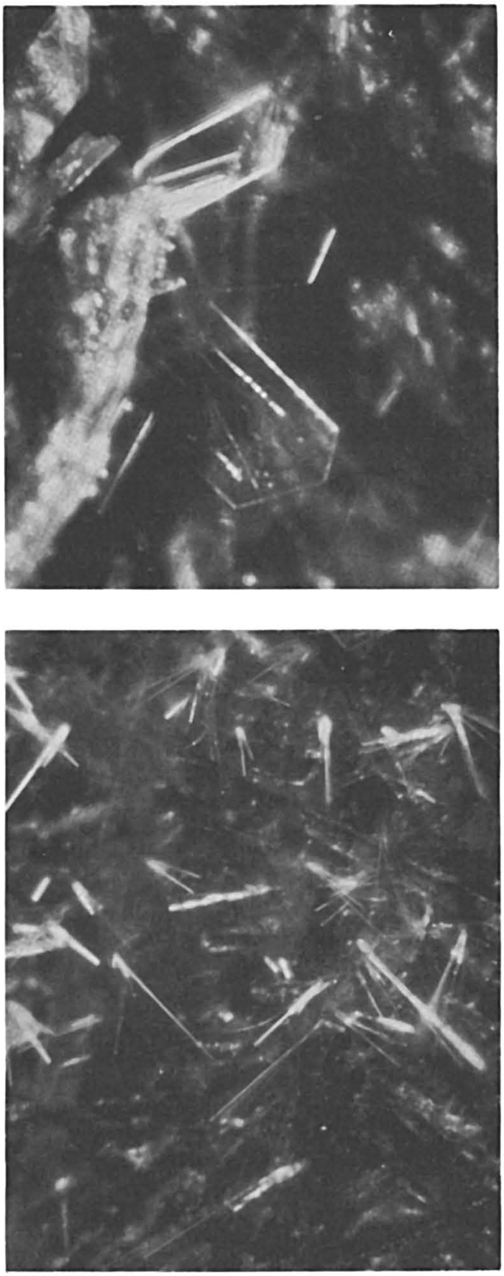

Figure 1. Insecticide deposits on fiberboard showing typical crystal form
Top: platelike crystals of lindane (35 ×)
Bottom: fine acicular crystals of dieldrin (31.5 ×)

The crystals composing the deposits of lindane and dieldrin were upright and easily dislodged by the insect, though markedly different in structure (Figure 1). Lindane crystals were platelike, usually 20–200μ wide and 50–300μ long. Dieldrin crystals were extremely fine and needlelike, usually 20–500μ long and less than 5μ wide.

Toxic Life. Surface deposits must have an extended residual life to be useful for bark beetle control. A lethal dose must be picked up by all beetles during the prolonged emergence or attack period. The toxic life needed may be several weeks when aiming for the destruction of adult beetles as they emerge or when protecting logs from attack, or it may be several months or more when the aim is to protect green trees from beetle invasion.

Lindane, having a relatively high vapor pressure (0.03 mm. Hg at 20°C.; *34*), sublimes readily, and deposit toxicity rapidly fails even when aged indoors. One percent deposits 2 weeks old required a 16.6 ± 5.6-fold longer exposure time to kill 90% (LT_{90}) of a test sample of beetles compared to 4-day-old deposits. Aging outdoors is even more destructive of lindane surface deposits. After aging only 5 days in bright sunshine, fresh deposits that produced 100% kill in 0.05-minute exposure were nontoxic —even with 10-minute exposures.

Dieldrin has a relatively low vapor pressure (1.8 mm. Hg at 25°C.; *34*) and remains toxic for long periods outdoors. Spray concentration appears to play a critical role. Solutions of 8% actually increased about 16-fold in toxicity with 6 weeks of aging in sunlight (Table II). A similar phenomenon was noted with endrin and DDT. The explanation may be that heavier deposits have more insecticide available to crystallize. The heat of the sun drives off more solvent, permitting more crystallization than on deposits kept in shade. This characteristic can more than compensate for evaporative losses of the insecticide. A few of the heaviest 8% dieldrin deposits were held for 53 weeks in full sun and yet remained

Table II. Effect of 6-weeks' Weathering on Toxicity of Crystal Deposits of Dieldrin to *Ips confusus*

Applied Dieldrin		*Contact LT_{50}, min.*			*Effect of Sun on Toxicity*[a]	
% Concentration (w/v)	*Residue, mg./sq. ft.*	*Fresh*	*Aged in Shade*	*Aged in Sun*	*Loss*	*Gain*
0.5	80	0.21	0.09	2.5	−11.9×	—
2.0	320	.10	.15	.54	− 5.4×	—
8.0	1280	.82	.72	< .05	—	+16.4×

[a] Ratio of $\frac{LT_{50}\text{ fresh}}{LT_{50}\text{ aged in sun}}$.

extremely toxic. The entire sample of 300 beetles was killed with 2 seconds' exposure time. Many workers have shown the residual life of surface deposits to be inversely related to vapor pressure of the insecticide generally (*27*).

Variations in Crystal Deposits. An outstanding characteristic of insecticide blooms is the extreme variation in the crystal stand, in the density of crystals, in their size and shape, and the percent of total area covered (Figure 2); much of this variation is unexplained. The bark of conifer trees is complex in its microscopic structure (*11*), and after erosion by weathering becomes an even more complex surface on which crystallization of insecticides is almost totally unpredictable (*32*).

One quality readily measured is the completeness of crystallization or "coverage." Coverage is strongly affected by the solvent used, the concentration of insecticide, and the total applied dose. Nevertheless, the resulting influence on toxicity is surprisingly slight. For example, with both dieldrin and DDT, the mortality response from 1-minute exposures of test beetles reached maximum at 10% coverage or less and remained almost constant from 10–100% coverage. It would seem that upright needle crystals typical of DDT and dieldrin are so readily available to the insect and dislodge and attach so easily to the body parts that the insect is quickly saturated with crystals at low coverage. Lewis and Hughes (*25*) have noted that insects can be quickly saturated with insecticide crystals, at which point loss from the body balances uptake.

Another readily measured characteristic is crystal size and shape. It can be strongly affected by the concentration of the applied insecticide. Concentration, in turn, controls the total residue deposited per unit area. Lindane and dieldrin serve as good examples. The optimum concentrations of 1% were extremely toxic (Figure 3). Correlated with this high activity was a peak development of fine needlelike dieldrin crystals and broad platelike crystals of lindane, all upright and easily detached. However, concentrations less than 1% crystallized poorly or not at all; in those greater than 1%, very small granular particles—usually $< 5\mu$—firmly attached to the substrate, were intermingled with crystals. They predominated at 4% and finally entirely replaced the upright crystal forms at 8%. Xylene deposits on bark showed a similar relationship. Barlow and Hadaway (*3*) have also noticed this concentration phenomenon on fiberboard.

DDT and dinitrocresol behaved similarly. On the other hand, endrin and heptachlor steadily increased in toxicity throughout the same concentration range. Crystal size and shape did not change with concentration as with the other insecticides. Instead, increasing concentration was followed by more complete crystallization.

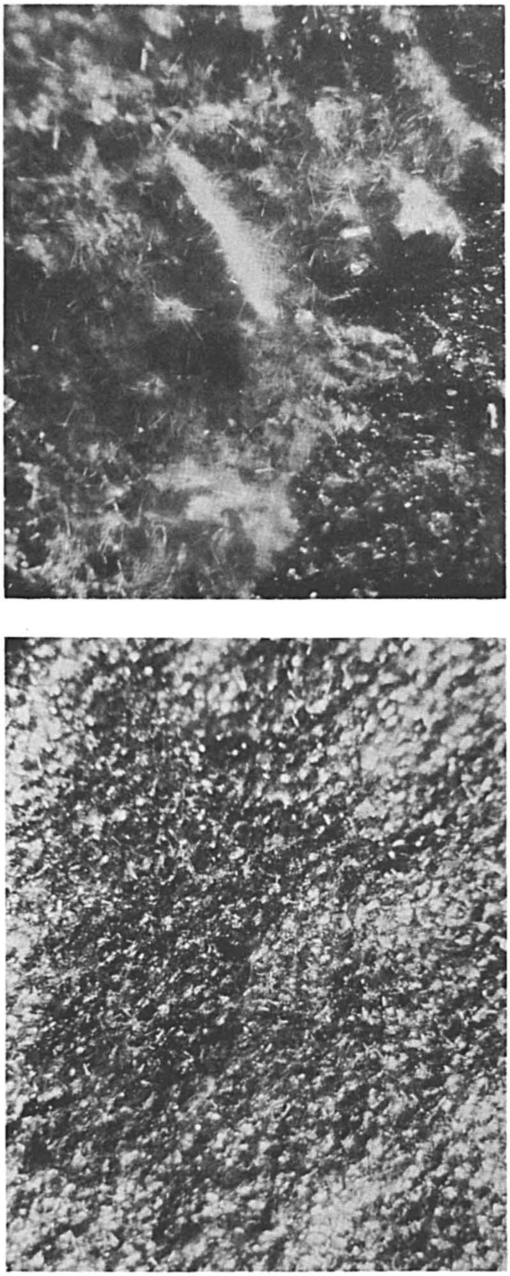

Figure 2. Extreme variation in crystallization of DDT applied to bark in xylene
Top: dense needle bloom
Bottom: very sparse needle growth on the same piece of bark a few inches away (18.9 ×)

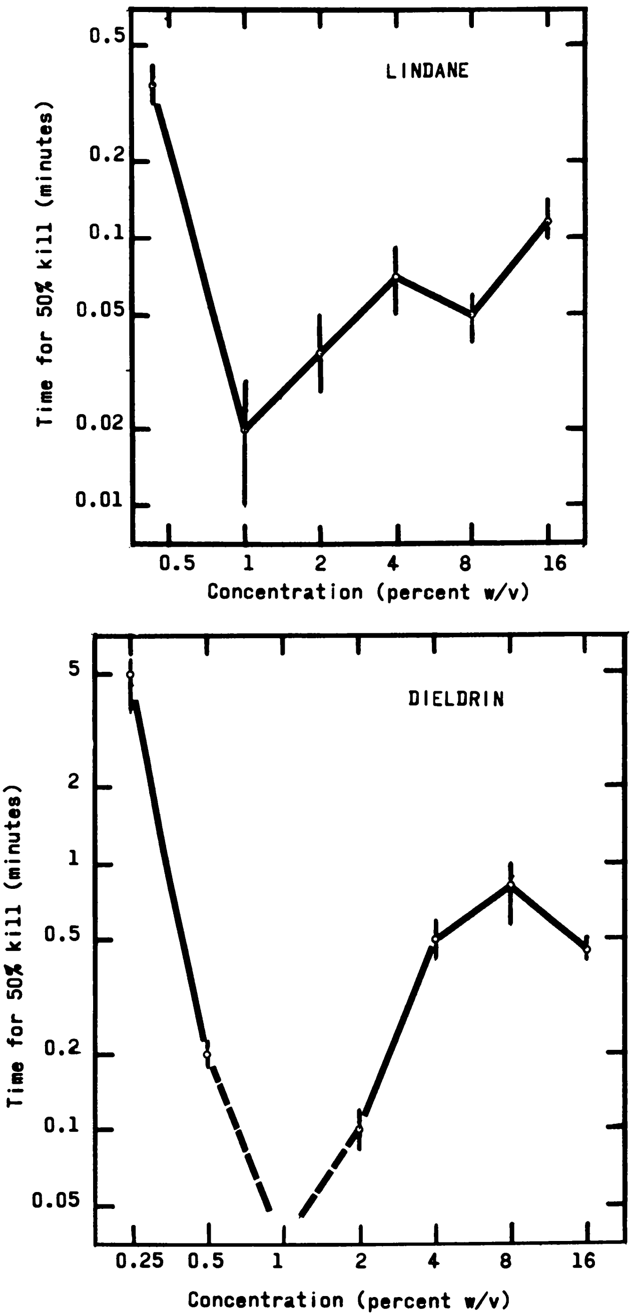

Figure 3. Contact toxicity to Ips confusus *adults of lindane and dieldrin surface deposits on fiberboard; LT_{50} and standard error*

Field Studies of Surface and Tissue Deposits

The high activity of surface deposits to bark beetles led to the question of whether surface or tissue deposits were more toxic when actually applied to infested logs. Lindane in xylene, a good crystallizing carrier, was applied lightly to pine bolts infested with *I. confusus*. It killed from 94–100% of emerging beetles at all concentrations, even those where no crystallization occurred (Table III).

Table III. Mortality of *Ips confusus* Emerging from Bolts Sprayed with Lindane in Xylene

Concentration, %	*Observed Mortality,[a] %*
Untreated	24
0 (xylene)	31
0.05	95
0.1	94
0.25	100
0.5	96
2.0 (crystallization)	99.7
8.0 (crystallization)	100

[a] Three bolts/treatment; a total of 1199 beetles emerged.

Sprays in this and all following tests were applied to the point of bark wetness only, which amounted to 1 to 2 quarts/100 sq. ft. of bark surface. Treated ponderosa pine bolts, 16 inches long, were caged in 40-mesh, wire-screen cages, 18 inches high and 16 inches in diameter. Each treatment was replicated on three bolts unless otherwise indicated. Beetles were collected twice daily, and observations of mortality were made after holding 72 hours.

We decided to substitute wettable powders for solutions to get surface deposits at the low concentrations needed, that were actually below the crystallization threshold (at 1%) of xylene solutions. When solutions do crystallize on bark, they do so sporadically and incompletely, and much tissue deposit probably remains. Preliminary tests in the laboratory on fiberboard showed the surface deposits from suspensions to be no less toxic than acetone solutions of dieldrin which crystallize well (Table IV). We decided to use wettable powders as a convenient tool to gain insight into the comparative potential of surface and tissue deposits. All of the following tests of surface deposits were made with wettable powders.

Surface and tissue deposits proved about equally effective on *I. confusus* emerging from pine bolts treated with 0.05% wettable powder of lindane (surface deposit) and the same concentration of diesel oil solution. The solution does not crystallize (tissue deposit) or show surface toxicity (Table V).

Table IV. Contact Toxicity of Surface Dieldrin Deposits on Fiberboard to *Ips confusus* Adults

% Formulation, w/v	*Total Insects, No.*	*LT_{90}, min.*
Water suspensions:		
0.1	290	>10.0
0.2	240	2.4
0.5	200	1.5
1.0	260	.5
Acetone solutions:		
0.1	70	Nontoxic
0.2	150	Nontoxic
0.5	160	2.5
1.0	160	1.8

Table V. Mortality of *Ips confusus* Emerging from Bolts Treated with 0.05% Lindane Surface and Tissue Deposits

		Mortality, %		
Deposit Type	*Total Insects*[a]	*Emergent*[b]	*Resident*[c]	*Total*
Tissue	297	35	47	82
Surface	141	62	11	73
Controls	446	9	7	16

[a] From three bolts in each treatment, six in the controls.
[b] Insects that emerged.
[c] Insects that died in the bark.

A similar test with the mountain pine beetle [*Dendroctonus ponderosae* (Hopkins)] showed tissue deposits to be about twice as toxic (Table VI). A possible explanation is that *D. ponderosae* emerged over a 54-day period, allowing the surface lindane to volatilize; *I. confusus* emerged over a period of 15 days.

The limitations of surface and tissue deposits in protecting green uninfested pine bolts and logs from invasion were next investigated. Pine bolts were treated with lindane and dieldrin surface and tissue deposits, weathered for 1 month outdoors, then caged and tested for the protection the deposits afforded against the attack of 100 *I. confusus*

Table VI. Mortality of *Dendroctonus ponderosae* Emerging from Bolts Treated with 0.2% Lindane Surface and Tissue Deposits

		Mortality, %		
Deposit Type	*Total Insects*[a]	*Emergent*	*Resident*	*Total*
Tissue	155	37	21	58
Surface	512	25	5	30
Controls	1374	2	4	7

[a] From three bolts in each treatment; six in the controls.

Figure 4. Method of forcing attacks of ips on sprayed bolts treated with lindane and dieldrin surface and tissue deposits

Table VII. Protection of Caged Pine Bolts by 1 Month Old Weathered Lindane and Dieldrin Surface and Tissue Deposits as Measured by Frass Discharge of Introduced *Ips confusus*[a]

Treatment	*Frass Discharge at Spray Conc., %*			
	0	*0.5*	*1.0*	*1.5*
Diesel oil[b]	49.9 cc.			
Water	46.5 cc.			
Untreated	46.5 cc.			
Lindane-tissue		<0.1	0	0
Lindane-surface		1.5	<0.1	<0.1
Dieldrin-tissue		0.5	<0.1	<0.1
Dieldrin-surface		<0.1	<0.1	0

[a] One caged bolt and 100 adult *I. confusus* introduced per treatment.
[b] Checks were weathered in cages to prevent wild attacks; treated bolts were weathered uncovered to subject them to the full erosive impact of the elements.

adults introduced into each cage (Figure 4). Protection was almost complete for all treatments greater than 0.5% concentration (Table VII).

One percent was taken as the minimum effective concentration for adequate protection and was applied to freshly cut ponderosa pine. The trees were limbed and marked off into six 4- to 5-ft. sections: two for testing lindane surface deposits, two for tissue deposits, and one each for water and diesel oil controls. This test was repeated in two different locales in July. *I. confusus* were plentiful in both areas, as evidenced by heavy attacks on extra trees that were cut and left untreated to provide a strong attraction and, hopefully, submit the treatments to the vigorous pressure of a heavy attack. Short bolts with fresh attacks of *I. confusus* were placed alongside the test trees to enhance further the attraction of wild populations.

In both tests, protection for 13 weeks (end of observations) was excellent, though slightly but consistently better with the tissue deposits (Table VIII).

Table VIII. Protection of Felled Ponderosa Pine Trees from Attack by *Ips confusus* with Lindane Surface and Tissue Deposits

	Total Attacks		*Protection,[a] %*	
Treatment	*Test 1*	*Test 2*	*Test 1*	*Test 2*
Tissue deposit	6	8	96	96
Surface deposit	10	12	94	93
Checks[b]	165	182	—	—

[a] $\frac{\text{Attacks on checks} - \text{attacks on treatments}}{\text{Attacks on checks}} \times 100.$

[b] Checks treated with diesel oil and water were attacked about equally, hence were combined.

A similar test was conducted using sugar pine in an area of heavy current attacks by *D. ponderosae*. The result was an excellent 13-week protection of 99.5% by both lindane surface and tissue deposits (total attacks: checks 193, surface and tissue deposits one each).

Conclusions

The relative merits of surface and tissue deposits based on the meager evidence so far accumulated is not clear cut, but the evidence would seem to favor the tissue deposit. Tissue deposits hold several advantages over surface deposits. Their toxicity to attacking or emerging adults is consistently higher, probably because the opportunity is greater for the beetle to be dosed in diverse ways, as well as increased chances of extended contact with the insecticide. The insect contacts tissue deposits while it chews its way through them, increasing the chances of absorbing a lethal dose; this effect is not only from direct contact, but also from stomach action, and perhaps from fumigant action. Tissue deposits often cause considerable kill in the bark (*see* Table V); surface deposits have never been found to do this.

Tissue deposits are protected from the environment, thus enhancing residual life. Rudinsky *et al.* (*40*) recovered 50% of the lindane from Douglas-fir bark 10 weeks after it had been sprayed with a kerosene:Velsicol AR50 (4:6) solution (tissue deposit), but they recovered only 20% when they applied wettable powders (surface deposit). These estimates are based on bioassays with mosquito larvae. For the less volatile endrin, using the specific phenyl azide method of analysis of Bann *et al.* (*2*), their recoveries were 30 and 19%, respectively. Exposure of adult Douglas-fir bark beetles [*D. pseudotsugae* (Hopkins)] for 40 minutes to the 10-week-old wettable powder surface deposits produced only 7 and 7.5% kills from lindane and endrin, respectively. Solution of insecticides in the resin of bark may extend toxic life of tissue deposits. There seem to be good opportunities for developing special formulations that will extend the residual life of tissue deposits (*9*).

Tissue deposits are less available to bark beetle predators and parasites searching the bark surface for their host. Therefore, they offer more specificity toward the target insect. Further, tissue deposits may be easier to reproduce consistently. Unless we acquire better understanding of the factors that control crystallization, we will find it difficult to control the character of surface deposits obtained from solution. On the other hand, the character of wettable powder deposits seems to be more easily controlled (particle size, density).

The central issue seems to be whether it is better to keep the deposit near the bark surface or have it penetrate. More spray volume is required to gain good penetration, and this raises the cost. Low volume sprays that do not penetrate significantly would be cheaper and would involve a lesser risk of phytotoxicity, where green trees are sprayed for protection.

A large gap in our knowledge concerns the physical condition or structure of tissue deposits, how they act on the bark beetle, and the effect of formulation and other factors on their toxic properties. Until this information gap is closed, we will not be able to raise the scientific level of formulation technology for bark beetle control, and until that level is raised, the problem of controlling bark beetles will be that much more difficult to solve.

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