

uses. Although such wastes are exceptionally low in nitrogen and high in carbon, the additional nitrogen necessary to offset microbial requirements during decomposition is much lower than indicated by the over-all carbon-nitrogen ratio. Accounting for this is the high proportion of resistant lignocellulose.

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Pesticides Effectiveness Is Influenced by Formulation

PESTICIDES FORMULATION

Liquid Concentrates Problems

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In the successful formulation of toxicants as emulsifiable concentrates, several factors are to be considered. The choice of the solvent depends on the toxicant solubility, especially at low temperatures; the solvent should have a moderately high flash point and a low order of phytotoxicity or irritation, and it should be low in cost and plentiful in supply. In choosing the inert ingredients, such as the emulsifying agent, special consideration should be given to its composition, so that its proper hydrophile-lipophile ratio balances effective emulsifying power against sufficient oil solubility. The differences in solubility characteristics in aromatic and aliphatic solvents are discussed and examples are given of multiple-purpose formulations which can be used as aqueous emulsions or diluted with aliphatic solvents. The liquid concentrates are then tested for emulsion characteristics, such as spontaneity, emulsion stability, re-emulsification, and effect of various natural waters. Several of the more commonly used methods are described and special emphasis is laid on the correlation of laboratory test methods with actual field use. The concentrates are also tested for aging qualities by accelerated aging tests at elevated temperatures, and for possible effects of corrosion on different containers. Their compatibilities should be determined with other materials and formulations which are likely to be encountered.

OF THE WORLD CONSUMPTION of benzene hexachloride, only about one third was really used effectively to kill insects, and the remainder might as well have been wasted, is the opinion expressed in an editorial in *World Crops* (12). To remedy this deplorable situation, the editorial urges that it is not enough to consider merely the toxic potentialities of a pesticide, but it is also necessary to take strict account of the

method of application and proper formulation.

Design of Proper Formulation

The design of a proper formulation of liquid concentrates should be based on a sound understanding of the following three questions:

1. What does one desire the formulation to do?

2. What is the best way to incorporate the pesticide into the formulation?

3. How can the desired functions be imparted to the formulation?

The first question involves a knowledge of the proposed use. For instance, is the pesticide intended to be a contact spray or a residual spray (11)? In a contact spray the insects are actually present during the time of spraying, and for this reason one is primarily concerned with

wetting and efficient penetration of the spray through the insect cuticle. In a residual spray, one is concerned with the proper spreading over plant surfaces and the formation of a residual deposit.

Another fundamental difference with respect to the desired functions of the emulsions made from these liquid concentrates is between agricultural crop sprays and animal dips. Generally speaking, in agricultural sprays the emulsion formed should not be too stable (2) to avoid excessive runoff from the surface of the leaves. The stability of the aqueous emulsion in the spray tank need only be sufficient to ensure, under the conditions of available agitation, a uniform dosage of toxicant during the application. On the other hand, in a sheep or cattle dip an extremely stable emulsion is not only desirable but, as recent investigations in Kerrville (10) have shown, essential. Sparr and co-workers have found that the amount of toxaphene deposited on the hair of dipped cattle increases as the particle size of the dispersed oil droplets increases. Mere maintenance of uniform insecticide concentration in dipping vats is not enough, as deposition of toxaphene on animal hair is greater from coarse than from fine emulsions.

The next consideration involves the choice of a suitable solvent. Knowing what properties are desired in a solvent, it is at least theoretically possible to draw up specifications for an ideal solvent. For instance, the solvent should have a relatively high flash point and should not be phytotoxic to the plants on which it is sprayed. But here already it becomes apparent that no one solvent or

even a mixture of solvents can possess all the ideal properties. A compromise will have to be found, balancing lowest possible phytotoxicity against high flash point and solvent power. Many of the other desirable properties are easier to attain. Thus, the solvent should have little odor, be noncorrosive to the container, and for many applications be nonstaining. These requirements can usually be met by various methods of purification. In addition, the solvent should also be cheap, readily available, and uniform.

The most important and at the same time most fundamental requirement is that the solvent must dissolve the toxicant. This is a very easy criterion for many of the readily soluble pesticides such as chlordan, toxaphene, and some of the simple esters of 2,4-D (2,4-dichlorophenoxyacetic acid). They are soluble in practically all the common organic solvents, a fact which provides an almost unlimited selection of solvents from which to choose. But when one deals with the less readily soluble toxicants such as DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, dichlorodiphenyltrichloroethane], the choice becomes much more limited, and the predominantly aliphatic solvents such as kerosene or mineral spirits are no longer suitable. This still would leave available a considerable number of solvent types such as aromatic, ketonic, and chlorinated compounds. However, early investigations by Fleck and Haller (3) have shown that chlorinated hydrocarbons such as chlorobenzene or ethylene dichloride have a deleterious effect, catalyzing the decomposition of DDT in the presence of anhydrous ferric chloride.

The ketonic solvents are considerably more expensive. Arkis and Flint (7) have tabulated interesting comparisons of the cost of various solvents per unit of DDT dissolved. The aromatic hydrocarbons are by far the preferred solvents for DDT.

Even among aromatic solvents there are still variations in suitability. Xylenes and many higher boiling aromatic fractions of petroleum are extensively used. The physical constants of these solvents, such as aniline point and kauri butanol number, give a certain indication of their performance as DDT solvents, although there is no strict correlation. Of special interest are also the boiling range and the rate of evaporation of these solvents which have a bearing on their phytotoxicity and the nature of the crystalline structure of the residual DDT deposit (7).

Now, for toxicants which are even less readily soluble than DDT, such as technical benzene hexachloride or lindane, for instance, even the aromatic solvents are no longer adequate. Many formulations will require the addition of cosolvents, usually ketonic in structure.

Of inestimable value to the formulator are the solubility data which are readily available from many of the manufacturers of solvents and toxicants. Table I is an example of the kind of data published by a manufacturer of solvents, giving the solubility at different temperatures of a large number of insecticides and herbicides in a selected group of aromatic solvents. Table II is an example of the kind of information obtainable from a manufacturer of toxicants, giving the solubility at different tempera-

Table I. Solubility of Various Insecticides and Herbicides in Velsicol AR-Solvents^a

	Per Cent by Weight											
	Velsicol AR-55			Velsicol AR-50G			Velsicol AR-50			Velsicol AR-60		
	77° F.	15° F.	0° F.	77° F.	15° F.	0° F.	77° F.	15° F.	0° F.	77° F.	15° F.	0° F.
Insecticides												
DDT, technical, setting point, 89° C. min.	30	25	20	35	30	30	40	35	35	40	35	35
Lindane	18	7	4	21	10	8	21	11	8
Benzene hexachloride, technical, 36% gamma isomer	24	13	..	24	13	..	26	24	..
Methoxychlor	30	15	..	35	20	..	35	25	..
Chlordan, technical	CM ^b	CM	CM	CM	CM	CM	CM	CM	CM	CM	CM	CM
Dilan, technical	CM	CM	..	CM	CM	..	CM	CM	..	CM	CM	..
Toxaphene	CM	CM	..	CM	CM	..	CM	CM	..	CM	CM	..
Parathion	CM	CM	..	CM	CM	..	CM	CM	..	CM	CM	..
Pyrethrum, standard extracts	CM	CM	..	CM	CM	..	CM	CM	..	CM	CM	..
Rotenone, standard extracts	CM	CM	..	CM	CM	..	CM	CM	..	CM	CM	..
Herbicides												
Pentachlorophenol	15	10	..	20	10	..	30	15	..	25	15	..
2,4-D isopropyl ester	53	53	53 ^d	52.5	52.5	52.5 ^e	51.6	51.6	51.6 ^e	51.6	51.6	51.6 ^e
2,4-D butyl ester	55.8	55.8	55.8 ^e	55.1	55.1	55.1 ^e	54.2	54.2	54.2 ^e	54.2	54.2	54.2 ^e
2,4,5-T isopropyl ester	50.4 ^d	49.7 ^d	48.8 ^d	48.8 ^d
2,4,5-T butyl ester	52.9 ^d	..	37.2 ^e	52.3 ^d	..	44.8 ^f	51.4	51.4	51.4 ^d	51.4	51.4	51.4 ^d

^a Velsicol AR solvents manufactured by Velsicol Corp., Division of Arvey Corp., 330 East Grand Ave., Chicago, Ill.

^b CM indicates complete miscibility in all proportions.

^c % by weight ester required for 4 lb. of 2,4-D acid equivalent per gallon of formulation containing 5% by weight emulsifying agent. Velsicol AR-solvents are completely miscible with isopropyl and butyl esters of 2,4-D.

^d % by weight ester required for 4 lb. of 2,4,5-T acid equivalent per gallon of formulation containing 5% by weight emulsifying agent.

^e % by weight ester required for 2.65 lb. of 2,4,5-T acid equivalent per gallon of formulation containing 5% by weight emulsifying agent.

^f % by weight ester required for 3.34 lb. of 2,4,5-T acid equivalent per gallon of formulation containing 5% by weight emulsifying agent.

Table II. Solubility of Lindane in Certain Petroleum Solvents^a

		Grams/100 Grams Solution	
Solvesso 100 (Esso)		10 at 35° F.	
Solvesso 150 (Esso)		10 at 35° F.	
Heavy aromatic naphtha (Esso)		10 at 35° F.	
Hi Solv 30 (Penn. Ind. Chem.)		20 at 68° F.	15 at 32° F.
Hi Solv 473 (Penn. Ind. Chem.)		9 at 68° F.	6 at 32° F.
AR 50 (Velsicol)		21 at 77° F.	10 at 15° F.
AR 50G (Velsicol)		18 at 77° F.	7 at 15° F.
544 c (Socony-Vacuum)		18 at 80° F.	17 at 68° F.
544 b (Socony-Vacuum)		22 at 80° F.	17 at 68° F.
			13 at 32° F.
			13 at 32° F.

Solubility of Lindane at 68° F.			
	Grams/100 Grams Solution		Grams/100 Grams Solution
Acetic acid, glacial	12.8	Hexanedione	32.0
Acetone	43.5	Hexone	30.2
Acetophenone	39.0	Isophorone	36.4
Benzene	28.9	Mesityl oxide	39.0
n-Butyl alcohol	4.4	Methyl acetate	27.7
n-Butyl acetate	31.5	Methanol	7.4
Isobutyl alcohol	3.0	Methyl propionate	37.8
Carbon tetrachloride	6.7	Monochlorobenzene	23.4
Chloroform	24.0	Naphtha, heavy (230-270)	18.1
Cyclohexane	4.6	Odorless distillate (198-257)	2.0
Cyclohexene	17.4	Paraffin (138-212)	3.2
Cyclohexanol	4.6	Pentane	2.2
Cyclohexanone	36.7	Pentanedione	34.0
Dec decahydronaphthalene	8.7	Perchloroethylene	7.4
Diacetone alcohol	21.0	Petroleum ether 40-60	2.1
Dibutyl phthalate	20.0	Petroleum ether 60-80	2.7
Diethyl carbonate	28.4	Petroleum ether 80-100	2.9
Diesel oil	4.1	Petroleum ether 100-120	3.5
Diisobutyl ketone	22.4	Pine oil	10.0
Diisopropyl ether	6.0	Isopropyl acetate	25.0
Dimethyl acetal	38.7	Isopropyl alcohol	2.8
Dioxane	31.4	n-Propyl alcohol	5.2
Ether	20.8	Propylene dichloride	20.0
Ethyl alcohol	6.4	Toluene	27.6
Ethyl acetate	35.7	Trichloroethylene	14.7
Ethylene dichloride	28.9	White oil	1.9
Ethylene glycol	0.6	Xylene	24.7
Ethylidene chloride	20.2	Distilled water, p.p.m.	10
Glycerol	0.06		

^a Data supplied by Diamond Alkali Co., Newark, N. J.

tures of one specific toxicant (lindane) in a large number of organic solvents.

Having selected the toxicant, the solvent, and the method of application, it remains to make sure that the operation will be a success and that the pesticide will be fully utilized to give the expected control. This is accomplished by the addition to the formulation of surface-active agents which may act as emulsifiers, wetting agents, spreading agents, sticking agents, or deposit builders. Some of these materials have been used for a great many years. The properties and functions of deposit builders, like calcium caseinate, or sticking agents, such as dried blood albumen, gums, and fish oils, have been thoroughly investigated in dust and wettable powder applications. The use of wetting and spreading agents such as glyceryl oleate or alkaline fatty acid or rosin soaps in horticultural spray oils has been well established.

Emulsifying Agents

In the last decade, since the advent of DDT, emulsifying agents have assumed ever-increasing importance in the formulation of the new synthetic toxicants. The physical chemistry of surface-active

agents has been extensively studied and many theories of the fundamental principles of emulsification have been advanced. Discussed here is only the orientation theory of Harkins and Langmuir, which postulated that emulsifying agents are substances that contain within each molecule a fatty group at one end and a polar group at the other end. The emulsifying agent is oriented at the interface between oil and water in such a manner that the hydrocarbon part of the molecule is active in the surface of the oil droplet while the polar group touches the water phase. Based on this orientation hypothesis, Harris (5) worked out the concept of the proper balance of hydrophilic and hydrophobic constituents in a surface-active agent in order to make the compound effective. This concept is an extremely helpful guide to the selection of the proper emulsifying agent in the formulation of liquid concentrates. The choice among currently available or potentially useful chemical compounds is enormous; this is reflected in the vast amount of recent literature. Some of the most interesting emulsifying agents in this field are the ethylene oxide condensation products. The more common types are listed in Table III.

Ethylene oxide is an extraordinarily useful tool. Starting with a suitable hydrophobic compound such as an alkyl phenol or a fatty acid, one can, by simply varying the mole ratio of the reacting ethylene oxide, change many of the surface-active properties of the resulting product almost at will. As a rule, the emulsifying properties improve over a certain range with increasing mole ratio of ethylene oxide. The optimum ratio naturally depends on the hydrophobic portions of the emulsifiers and the systems in which they are used. Obviously, with increasing ethylene oxide content, their oil solubility decreases. Emulsifying agents with a long polyoxyethylene chain usually retain sufficient solubility in aromatic solvents so that there is no serious problem on that account in the formulation of such toxicants as DDT, benzene hexachloride, and dieldrin. But their insolubility in aliphatic solvents, such as kerosene or horticultural spray oil with a high unsulfonated residue, may impose severe limitations on these formulations.

Fortunately, this is not the whole story; for while an emulsifier may be insoluble in kerosene, it may well be perfectly soluble in a solution of the toxicant in kerosene which constitutes the formulation. This fact, for instance, makes it possible to use many excellent emulsifiers in 4-, 6-, and 8-pound-per-gallon chlordan and toxaphene emulsifiable concentrates. However, if the concentration of chlordan or toxaphene in the formulation were reduced below 40% (although such formulations are not very popular for economic reasons), the choice of efficient emulsifying agents which are soluble in such a system would again become very limited. It is often possible to make the emulsifier soluble by the use of so-called coupling agents such as glycols or glycol ethers, but these agents add to the cost of the concentrate but do not contribute anything to its function. Besides, unless they are used in considerable amounts, they give no assurance that the emulsifying agent will not eventually settle out as a sludge. While considerably more difficult, it is usually a better practice to attain the proper oil solubility by careful blending and balancing of the constituents of the emulsifier itself.

Emulsifier solubility becomes of particular importance in dealing with what may be called multiple-purpose formulations. As an example, certain low volatile 2,4-D ester formulations recently have attained considerable popularity. An emulsifiable concentrate containing 4 pounds of 2,4-D acid equivalent as, say, the butoxyethanol ester, should meet the following three entirely different requirements:

1. For foliage spray, the concentrate is

Table III. Emulsifying Agents

Based on condensation with ethylene oxide

Type	Example
$R-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2-\text{CH}_2\text{O})_n\text{H}$	Triton, Antarox
$\text{RS}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	Nonic
$\text{RO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	Brij
$\text{RCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	Ethofat
$\text{RCON} \begin{cases} (\text{CH}_2\text{CH}_2\text{O})_x\text{H} \\ (\text{CH}_2\text{CH}_2\text{O})_y\text{H} \end{cases}$	Ethomid
$\text{RN} \begin{cases} (\text{CH}_2\text{CH}_2\text{O})_x\text{H} \\ (\text{CH}_2\text{CH}_2\text{O})_y\text{H} \end{cases}$	Ethomeen
$\text{HO}-(\text{C}_2\text{H}_4\text{O})_a(\text{C}_3\text{H}_6\text{O})_b(\text{C}_2\text{H}_4\text{O})_c\text{H}$ (Polyoxyethylene-polyoxypropylene-polyoxyethylene glycol)	Pluronic
$(\text{RCOO})_a\text{P}(\text{O}[\text{CH}_2\text{CH}_2\text{O}]_n\text{H})_b$ P = polyhydric alcohol such as Sorbitan	Tween

poured into water to give readily formed emulsions of good stability.

2. For mesquite control, the concentrate is first diluted with 5 to 7 times its volume of Diesel oil and then poured into water, when again it should give a readily formed emulsion of at least moderate stability.

3. For basal-stem treatment, the concentrate is diluted with up to 100 times its volume of Diesel oil and applied as such to the lower part of the tree. It is not mixed with water and emulsification is no longer required.

In other words, the emulsifier must be sufficiently potent to give not only normal performance in application 1, but also adequate emulsification even when diluted to about 6 to 8 times its original level with inert oils in application 2. Obviously, the use level of emulsifier in such a multiple-purpose formulation will have to be somewhat higher than in a conventional formulation, but it is also imperative for application 3 that the emulsifying agent should be sufficiently oil-soluble to remain in solution on almost infinite dilution with Diesel oil. To achieve all these requirements in one emulsifier requires extremely careful balancing and blending of the ingredients.

One of the main difficulties in formulating is the highly reactive nature of some of the chemical compounds involved. This is not surprising, because this reactivity is, in many cases, the reason for the effectiveness of the pesticides. Therefore, in selecting the emulsifier, not only must its solubility in the concentrate be considered, but also complete compatibility with the toxicant must be achieved. This, for instance, will eliminate the use of soaps and other alkaline materials in formulations of chlorinated hydrocarbons, such as DDT, which readily split off hydrogen chloride, and similarly in formulations of toxicants, such as pyrethrum, which contain ester linkages.

Even more critical is the formulation required for chemicals like the miticide DMC [di-(*p*-chlorophenyl)methylcarbinol], which readily hydrolyze under acidic conditions. In such cases the system must be carefully buffered to a neutral pH. In other words, the emulsifier, whether it be a simple chemical compound or a blend of several components, must be fully compatible with all other constituents.

Blending

The chemical behavior of most toxicants has been extensively studied and is reported in the literature. Compatibilities and solubilities can be readily determined and measured experimentally. With all this available background information, gross errors are usually avoidable. However, for really effective and economical formulations which will give reliable results under all sorts of adverse conditions, we must resort to the art of blending, an art which is still in the realm of trial and error.

An example of unpredictable results is found in the recent work by Mayhew and Hyatt (8), who studied the variation in certain surface-active properties of the homologous series of condensation products of nonyl phenol with increasing mole ratios of ethylene oxide. They established that, in a 45% toxaphene concentrate in kerosene, a 6-mole ethylene oxide nonyl phenol gave especially good emulsification, whereas, in a 25% DDT concentrate in xylene, a 9.5-mole material gave the best results. These results are not surprising, but merely show that each formulation requires its own specific hydrophilic-hydrophobic ratio in its emulsifier. However, a reaction product of nonyl phenol with 6 moles of ethylene oxide represents a mixture with a wide distribution of different mole ratio compounds, the 6-mole material being merely the expression of an average molecular weight.

Mayhew and Hyatt found that by molecular distillation they could obtain rather narrow cuts, each of which represented essentially pure compounds instead of mixtures. Some of these distilled fractions showed greatly improved functions over the corresponding average molecular weight materials, when tested, for example, for wetting properties by the Draves-Clarkson test. But when the distilled 6-mole fraction was used in the toxaphene formulation and the distilled 9.5-mole fraction in the DDT formulation, it was found that in both cases the emulsifying properties were almost entirely lost.

To find this striking lack of correlation between emulsification and other surface-active properties may at first come as an unpleasant experience. But it is soon learned that this lack of correlation of properties is invariably the rule rather than an exception. Furthermore, even within one field of application, there is a great specificity in function, which is illustrated by the fact that an emulsifier that gives excellent performance in one formulation may often fail completely in a slightly different toxicant-solvent system.

Testing Emulsifying Properties

An additional, and most important, part of formulating is the testing of the concentrate's emulsifying properties. Several methods are commonly employed. These test methods may serve a threefold purpose—to guide the formulator in developing the formulation, to standardize the finished formulation, and to correlate the laboratory findings with actual field use conditions. For the first purpose, the method should be simple, since, in the development of a single formulation, it may be necessary to prepare and test several hundred emulsions. For the second purpose, the test method should be both simple and precise, so it can be readily duplicated in different laboratories. The third requirement can only be approached, at best, and none of the available laboratory methods is entirely satisfactory.

The more important characteristics to be determined for each formulation are ease or spontaneity of emulsification, emulsion stability, and ability to re-emulsify after separation has occurred.

In this laboratory, the ease of emulsification is evaluated by visual observations of the cloud formed when a definite amount of concentrate (the exact amount depends on the rate of dilution desired) is released from a Mohr pipet, the tip of which is held 2 inches above the surface of the water, into a definite volume of water of standardized hardness, contained in a 100-ml. glass-stoppered graduate, both concentrate and water being kept at 25° C. Different operators are fairly well able to duplicate results, but there are no quantitative measure-

ments which could express these results in simple numerical values. The conditions of the test can be accentuated by using a narrow tube 3 or 4 feet long. Here the appearance of the emulsion cloud can be followed as it travels all the way down the tube. While small differences become more apparent under these exaggerated conditions, so many variables like viscosity, specific gravity, and turbulent flow can affect the results that it becomes difficult to find a close relationship between the behavior in narrow tubes and in an actual spray tank.

Emulsion stability is usually determined visually by observing the rate of creaming. Various test methods are described in a number of government specifications, as to both the formation of the emulsion and the conditions of observing creaming rates. The emulsions may be formed by shaking, stirring (manual or mechanical), or inverting glass-stoppered cylinders a prescribed number of times. The creaming rates are usually observed either in graduated cylinders or in Nessler tubes. Griffin and Behrens (4) have devised a special apparatus for observing emulsions, which greatly facilitates the comparison of a large number of emulsions under standardized illumination. Other means of measuring emulsion stability have been suggested, such as determining the rate of change of the emulsion's opacity by optical measurements, or of its density by hydrometer readings (9).

At best, all these tests are short-cut methods, having a relationship with the concentration of toxicant present at various layers of the emulsion in the spray tank, a relationship which, however, could be established exactly only by chemical or biological analysis. But as long as the laboratory methods cannot possibly duplicate all the conditions that are encountered in actual field use, the test methods might as well be simple, rapid, and reproducible. Several groups of investigators at agricultural experiment stations have done a large amount of emulsion testing in connection with actual spraying of small test plots. They have drawn up special score sheets for entering creaming rates and other visual observations, which can serve as a fairly reliable forecast of the probable performance of the respective concentrates in the field.

Re-emulsifiability is usually determined and rated by applying the methods of forming the fresh emulsion, such as inverting a glass cylinder or Nessler tube after the emulsion has settled out on standing for a certain length of time (usually 24 hours) and by measuring the resulting emulsion stability. In an ideal emulsion, the rate of creaming should be sufficiently slow that after 24 hours no visible separation has occurred. However, in some formulations this would require a rather high use level of surface-

active agents and in many applications such highly stable emulsions may be undesirable. It is therefore important to have emulsions which will settle out on standing in such a manner that they can readily be re-emulsified with a minimum of agitation. In the early days of DDT when this kind of agricultural emulsion was first investigated, it was believed that the visual appearance of the separated cream layer would give an indication of its re-emulsifiability. At that stage of emulsion technology, the appearance of free oil was considered the danger signal that the emulsion was broken and would re-emulsify only with great difficulty, if at all. This is now no longer the case.

Figure 1 shows the kind of separation obtained (after 24 hours' standing) from a 25% emulsifiable DDT concentrate in a high boiling aromatic petroleum solvent which has been formulated with one of the recently developed non-ionic anionic emulsifier blends at a 3% use level. The figure shows the almost clear oil layer, indicating complete phase separation.

Figure 2 shows the same emulsion after only one complete inversion—a rich, creamy looking homogeneous emulsion of a low creaming rate which will show no visible separation for several hours, but when separation finally does occur, it will again be in the form of free oil. This, of course, is an exaggerated case, and to demonstrate this effect careful selection of both the aromatic solvent and the hardness of the water was necessary. However, this demonstration is instructive in that the presence of some free oil in the cream layer need not necessarily cause concern, as long as the re-emulsification remains unimpaired. On the other hand, emulsions may frequently separate, on standing,

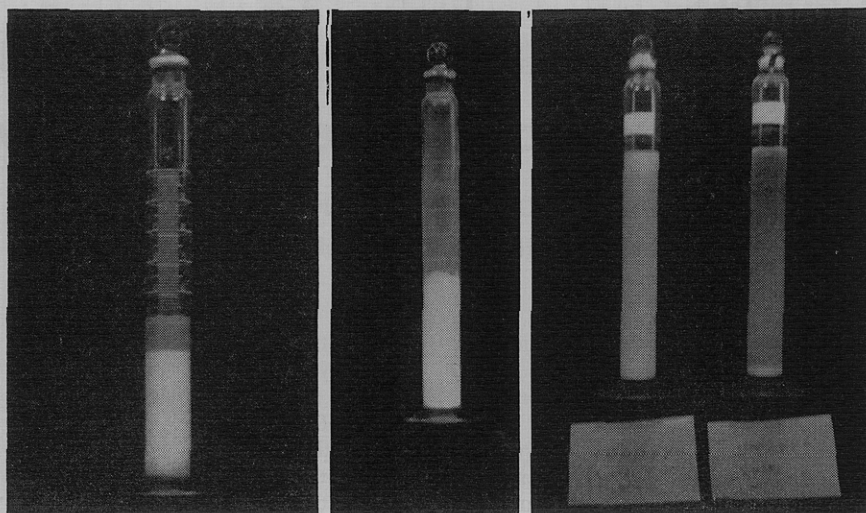
into heavy cream layers with no trace of free oil, but which no amount of normal agitation will reconstitute into a workable emulsion.

Water Used

Another factor which greatly influences the properties of an emulsion is the nature of the water being used. When a new formulation is developed, or an accepted formulation is tested in the laboratory, only in rare cases does the laboratory have information with respect to the kind of local water supply available for spraying the concentrate. For this reason, it is common practice to use a number of standard waters of definite hardness in laboratory testing. Well-known examples can be found in some of the military and federal specifications for emulsifiable concentrates which describe the exact composition of hard water in terms of grams of calcium chloride and magnesium chloride per liter. The total hardness of these waters is in the range of 290 to 340 p.p.m. expressed as calcium carbonate; this can be considered as fairly representative of natural waters over a wide area of the country.

These synthetic hard waters are very useful as a standard of reference, but for a reliable test method to predict the behavior of emulsifiable concentrates in various hard and soft water areas they are not sufficient. Factors other than total hardness enter into the picture—for example, the ratio of calcium to magnesium salts, or the presence of sodium or potassium salts which, while they do not at all contribute to the hardness of the water, exert a strong ionic salt effect on the emulsification. An example of this is the two 24-hour-old emulsions shown in Figure 3. Both are made from the same 6-pound toxaphene concentrate in two synthetically prepared

Figure 1. Separation from a DDT concentrate
 Figure 2. Separation from a 24-hour-old emulsion of toxaphene
 Figure 3. Left. 1000 p.p.m. CaCl_2 and MgSO_4 . Right. 1000 p.p.m. CaCl_2



hard waters with a hardness of exactly 1000 p.p.m. expressed as calcium carbonate. A striking difference is apparent. The one on the right is in water which contains only calcium chloride and shows a heavy cream layer on the bottom. The emulsion on the left is in water containing both calcium chloride and magnesium sulfate in a molar ratio of 3 to 2, and shows far superior stability.

This also is an exaggerated case; no natural water would contain only a single mineral constituent. However, it does show the limitations to be expected from reliance solely on a series of synthetic waters. For this reason it has been found necessary to collect a large number of natural water samples, from all over the country, which are stored in polyethylene lined bottles. Obviously, a collection such as this cannot be considered representative of the over-all water supply, as some of these samples are from single wells or swamp waters which were supplied because they gave rise to some difficulty in spraying. These water samples are analyzed and the effect of their composition on emulsification is carefully studied. In time, sufficient data should be accumulated to permit the compensation in formulation for most of the unusual or difficult water conditions that may be encountered.

Aging Qualities

The final step in the formulation of concentrates, in so far as laboratory testing is concerned, is a study of aging qualities. Unsatisfactory aging may manifest itself in a variety of forms, from minor defects like discoloration and loss of clarity, which merely affect the appearance of the concentrates, to the more serious functional deficiencies, such as separation in layers, crystallization of the toxicant, or even total loss of emulsification. In addition, there is always the possibility of a reduction in biological potency of the toxicant, due to a decomposition which may not be apparent in an

examination of the concentrate's physical properties. In many cases, when there is insufficient time to observe the effect of normal aging of a concentrate, it is necessary to use accelerated aging tests at elevated temperatures. Unfortunately, the results obtained under these conditions are not too reliable, and at best are only approximations. Because the effect of temperature on stability not only is different for each toxicant but also depends on the concentration of the toxicant in each formulation, it becomes almost impossible to find any exact correlation between the results of accelerated aging tests and the aging qualities under normal storage conditions. Some toxicants (such as toxaphene, *6*), when subjected to elevated temperatures even for only a very short time, seem to suffer a slight though autocatalytic decomposition which will greatly shorten stability on subsequent storage, even at ordinary temperatures.

When all the actual formulating work is done, there still remains a number of problems in which the laboratory can supply information or guidance on the proper use and handling of concentrates. These will include, for instance, corrosion studies on various metal surfaces and testing of resistant coating materials for their suitability as container linings. Special attention should be given to formulations which will be marketed in small containers such as 1-gallon cans, where the use of liners is not economically feasible.

Furthermore, there is the problem of the compatibility of the concentrate with other common agricultural materials, in either liquid or powder form, with which it may come in contact. For instance, liquid insecticide concentrates are often mixed with fungicides which are usually in the form of wettable powders or dusts. Some of these materials, especially certain types of Bordeaux mixtures, may well interfere with the normal emulsification of the insecticide

concentrate and cause rapid settling or even flocculation. Knowledge of these possible limitations beforehand will avoid trouble and poor results in the field.

Conclusions

Although the problems are numerous and often complex, the art of formulation has now sufficiently advanced so that the new synthetic pesticides can be applied with a high degree of efficiency, safety, and economy.

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PESTICIDES FORMULATION

Influence of Formulation on Effectiveness

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PROMINENT AMONG THE FACTORS affecting the performance of pesticides is the manner in which they are formulated for commercial use. The principal proprietary pesticide formulations are the wettable powders, emulsifiable concentrates, emulsions, solutions,

and dusts. The present investigation deals only with the first two, primarily in relation to four acaricides: Aramite, Geigy-338, Sulphenone, and parathion. Many other pesticides will be investigated in the course of a research project, of which the present paper should be con-

sidered as no more than a progress report. It is expected that all the aforementioned formulations will eventually be investigated with regard to the physical factors that influence their pesticidal effectiveness.

A wettable powder is a dry mixture of