Progress in Liquid Pesticide

Blended anionic-nonionic emulsifiers have made it possible to advance liquid pesticide formulation toward improved function and greater economy

THE PAST 14 years have witnessed phenomenal and continued growth in the use of organic pesticides in agriculture. This growth has been due largely to two factors: first, a clearer understanding of the biological principles underlying the often complex action of a growing list of organic pesticides, and second, steady progress in the technology of their formulation and application.

Progress in Formulation Technology

These technological advances have been in two directions: toward improved function under all kinds of conditions, and toward greater economy in achieving these desired functions at greatly reduced levels of emulsifying agents.

Two U. S. Department of Agriculture bulletins, published 10 years apart, provide an example of what has been accomplished in this respect. Publication No. 606 (*9*), issued in August 1946, describes a 25% DDT emulsifiable concentrate as containing 10% emulsifier, and comments that this was a tremendous improvement over the original formula which had contained 20%. In contrast, a bulletin on elm disease sprays, which the U. S. Forest Service released in April 1956 (*8*), lists a formula which contains 32.4% DDT and as little as 2.2% emulsifier.

Anionic-Nonionic Blends

This progress has been made possible by the introduction of specific types of blended anionic-nonionic emulsifiers.

The first blends had been made with various salts of refined natural petroleum sulfonates which greatly improved the dispersibility and versatility of the resulting formulations. When pure alkyl aryl sulfonic acids became commercially available, use of their calcium salts led to remarkable improvements, especially in toxaphene formulations. Certain ratios of calcium sulfonates and nonionic components would impart very low interfacial tension to the oil-water interface, causing spontaneous emulsification of the concentrate.

However, because of the insolubility of the calcium salts of 2,4-dichlorophenoxy acetic and 2,4,5-trichlorophenoxy acetic acids, considerable trouble has been experienced with some 2,4-D and 2,4,5-T ester formulations. The technical esters often contain appreciable amounts of free acid; in addition, some free acid may be formed by hydrolysis on standing, particularly when heavy metals and moisture are present. Even small amounts of the insoluble calcium salts look like a copious and therefore objectionable gelatinous sludge. Hence it is now accepted practice to use calcium-free emulsifiers in 2,4-D and 2,4,5-T formulations. The calcium sulfonates may be replaced with blends of selected polyamine salts of alkyl aryl sulfonic acids, which, in combination with certain nonionic surfactants, will produce very effective emulsifier systems without danger of sludge formation.

Velsicol Chemical Corp.

Figure 1: Equipment used to broadcast liquid heptachlor-fertilizer mixture and disk it into the soil for control of soil insects over several seasons

Methods of Evaluation

As these new blended emulsifiers, when properly formulated, provide a really spectacular degree of self-emulsification, B. I. Sparr and C. V. Bowen (*7*) have devised an apparatus and have described a method of evaluating the spontaneity of emulsification of heavier-than-water emulsifiable concentrates. An adaptation of this method has already been made one of the performance specifications in export bids for 60% emulsifiable toxaphene concentrates.

Measurements of emulsion stability, which are not necessarily related to spontaneity of emulsification, have been reported in the literature for a long time. W. C. Griffin and R. W. Behrens (*1*, *3*), and D. A. Pearce (*6*) have described special equipment for evaluating and comparing emulsion stabilities.

Matched Pairs of Special Emulsifiers

As demands for standards of performance grow more stringent, it becomes correspondingly important to allow for the variations in solvents and technical grades of pesticides, which greatly affect the emulsion characteristics of the formulations. These differences can usually be overcome by adjustments among the various emulsifier components, once a given type of blend has been established.

The manufacturers of emulsifiers know by experience what to expect in the usual variations of certain toxicants. Therefore they have been able to divide the complete emulsifier

Formulations

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Figure 2: Equipment combines seeding with application of fertilizer and pesticide. Mixture is placed below and to one side of seed, and covered by packer wheel.

blends into two or more fractions; in each fraction the internal balance has been shifted by a carefully calculated amount. This enables the formulators to combine them in simple ratios so as to obtain the desired performance in each formulation. When appreciable variations are encountered in solvents or toxicants, the same emulsion characteristics can be achieved with the same level of total emulsifier simply by a change in the ratios of the two blended fractions.

No universal emulsifier has yet been found, nor does such an emulsifier appear likely in the near future. Therefore, it has become the accepted practice in the industry to attempt to use special pairs of matched emulsifiers. This system provides greater flexibility because it enables the formulator to prepare a multitude of different formulations merely by changing the ratio of the two matched emulsifier blends. This same procedure also permits him to adapt his formulations to meet unusual water conditions or extremely high or low rates of toxicant dilution.

Effect of Formulation on Phytotoxicity

The effect of proper formulation on the success or failure of a spraying program in general, and on the introduction of new pesticides in particular, has been clearly recognized. E. D. Whitman (*10*) reported that in the early field trials with CIPC [isopropyl-N-(3 chlorophenyl) carbamate], some farmers experienced serious trouble because the toxicant in the formulation settled too rapidly to the bottom of the spray tank; some areas received too heavy a dose, leading to considerable stunting of cotton.

M. J. Janis (*5*) showed the importance of proper formulation in greenhouse tests on potted green bean plants. DDT was dissolved in a highly aromatic solvent which by itself was so phytotoxic that, uncompounded, it could even be used as a herbicide. When enough emulsifier was added to ensure a reasonably stable and uniform emulsion, no burning of plant tissue resulted. But when the level of emulsifier was reduced to the degree that coarse and very unstable emulsions were formed, considerable burning of plant tissue was observed.

Problems of Solubility: Guthion, IPC, Phosdrin

The rapid rate at which new and entirely dissimilar types of chemical compounds are being introduced as pesticide materials poses challenging problems to the formulation chemist. For instance, there are important considerations of solubilities. It is not so many years since the industry was concerned either with toxicants such as chlordan or toxaphene which were readily soluble in most organic solvents, or with compounds such as DDT, BHC, aldrin, or dieldrin which were still appreciably soluble in aromatic solvents. But many of the new materials, such as Guthion (*O,O*-dimethyl S-[4-oxo-benzotriazine-3-methyl] phosphorodithioate) or IPC (isopropyl phenyl carbamate), are crystalline solids of very limited solubility in aromatic solvents. While their solubility is much greater in highly polar solvents, such as low-molecular weight glycol ethers or dimethyl sulfoxide, the water solubility of these solvents prohibits their use in emulsifiable concentrates. On addition to water, the solvent goes into the aqueous phase, resulting in immediate precipitation of the toxicant. Liquid formulations of these pesticides therefore require a very careful blend of several solvents, allowing for many additional factors besides solubility, such as emulsion characteristics, phytotoxicity, cost, and availability. Usually they contain no more than 2 lb. of active ingredient per gallon of concentrate. For certain compounds, such as Sevin (*N*-methyl-1-naphthyl carbamate), which are very sparingly soluble even in blends of polar solvents, the preferred formulations are wettable powders or liquid dispersions of finely-ground solids.

By contrast, some of the newer phosphate insecticides are completely water-soluble; for instance, Phosdrin (*O,O*-dimethyl 1-carbomethoxy-1-propen-2-yl phosphate) might be applied simply as an aqueous solution if it were not for the hydrolysis of the active ingredient on several months' standing. Phosdrin is therefore formulated in xylene or similar aromatic solvents at concentrations of either 2 or 4 lb. of active ingredient per gallon; in this type of formulation the emulsifying agent's main function is to emulsify the solvent, as the toxicant itself mixes quite readily with the water.

Crag Fly Repellent, CIPC

Many other interesting and often unusual relationships between solvent and toxicant enter into emulsion technology. Several toxicants exhibit certain properties of surface-activity due to their molecular structure. Crag fly repellent (butoxy-polypropylene glycol) provides a striking illustration of formulations which combine a high degree of flash-dispersion, particularly in very hard waters, with a rather poor emulsion stability. It appears that the molecular structure of butoxy-polypropylene glycol tends toward water-in-oil emulsions, which, under certain conditions, may upset the balance of the emulsion system and may even result in phase inversion.

The emulsification of CIPC presents similar phenomena which, however, are aggravated by the crystalline nature of CIPC. After an emulsion of CIPC has been formed, tiny crystals are gradually precipitated on the oil-water interface of the oil droplets; this results in a continuous change of interfacial tension, and dramatically reduces emulsion stability unless the balance of components in the emulsifier has been adjusted to allow for this gradual change. For these reasons it has been found necessary to develop specific emulsifiers for formulations of certain toxicants such as Crag fly repellent or CIPC.

Pentachlorophenol

Another toxicant with which the limitations of conventional emulsifiers become apparent is pentachlorophenol. In part, this is due to the poor solubility of PCP in aromatic petroleum solvents. But in seeking a suitable solvent blend, the formulator must also beware of the strong tendency of PCP toward supercooling. Prolonged storage of samples of PCP formulations without apparent difficulty, at very low temperatures, gives no assurance that the PCP in production lots may not suddenly form a precipitate. It is often advisable to cool the concentrate to a point at which the PCP begins to crystallize and then, by gradual warming, establish the temperature at which the formulation will again be a clear solution. An even more difficult problem is raised by chemical incompatibility of PCP with the polyethoxy group of many nonionic surfactants which are essential components of most of the current available emulsifiers. It is now possible to prepare satisfactory PCP formulations using special complex sulfonates as the emulsifying agents.

Combined Liquid Pesticide-Fertilizer Solution Applications

Recent developments in processes of manufacturing phosphoric acid have greatly influenced the methods and practices of the fertilizer industry. Wet-process acid had contained large amounts of iron and alumina impurities which precipitated on neutralization with ammonia. This, of course, precluded the use of liquid ammonium phosphate solutions; instead, mixed fertilizers were applied in a dry form. Availability of cheap electric furnace grade phosphoric acid has brought a rapid increase in the use of liquid mixed fertilizer solutions, particularly in the North Central and Pacific states.

Table I shows the consumption of liquid mixed fertilizers, on a regional basis, in the year ended June 30, 1957.

Figure 3: Equipment used in recently completed field trials to apply formulations of Nemagon along with fertilizer solutions

Shell Chemical Corp.

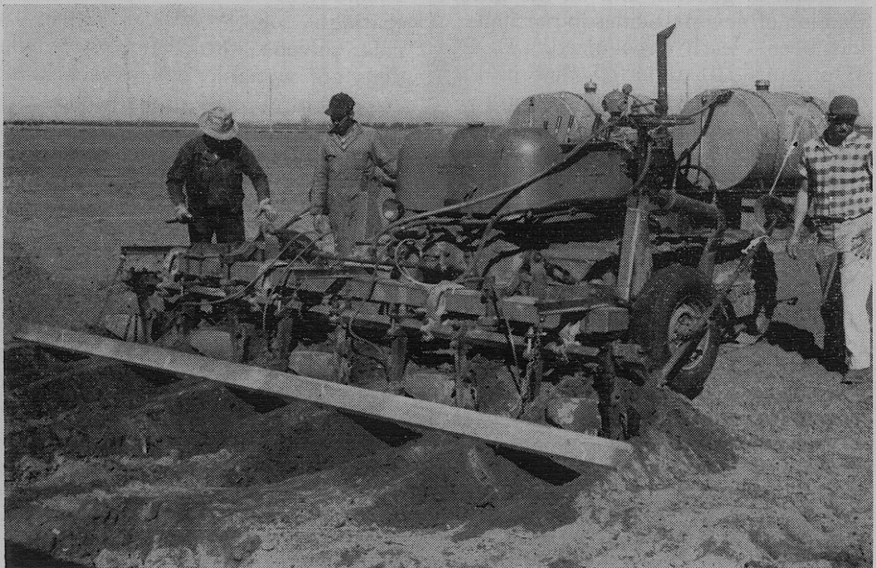

Table I: Consumption of Liquid Mixed Fertilizers During 195–657

	TONS
New England	200
Middle Atlantic	4,200
South Atlantic	2,200
East North Central	105,000
West North Central	46,000
East South Central	1,800
West South Central	11,000
Mountain	500
Pacific	74,000
CONTINENTAL U. S.	244,900

The data were supplied by K. D. Jacob of USDA.

Increased consumption of fertilizer solutions has presented the formulation chemist with the novel problem of working out a system in which liquid fertilizers could be applied with pesticide emulsions in one combined application. Pesticides had been mixed with fertilizers in the dry form for several years. However, this raised numerous difficulties; many fertilizer manufacturers lacked the proper mixing equipment to ensure uniform distribution of small quantities of pesticides throughout a large bulk of fertilizer material. In addition, the incorporation of pesticides into the fertilizer necessitated both an extensive safety program for the handling of toxic materials, and registration of the finished material under the Pesticide Act.

A further disadvantage of dry mixes lies in their fixed composition. At the time of manufacture it is often impossible to predict what kind of pest infestation will be encountered in the field at the time the fertilizer is to be applied. A higher dosage of pesticide may be required, or an entirely different toxicant may be indicated from that incorporated in the dry mix. There are also problems of caking and deterioration of toxicant on prolonged storage. All these difficulties could be overcome through a simple and effective method for mixing liquid fertilizer solutions with liquid pesticide formulations right in the field, and at the time of actual application.

The first systems in which the new methods were tried were all nitrogen solutions, containing only ammonia, ammonium nitrate, and urea. It was possible, with some modifications in their compositions, to adapt a number of existing emulsifiers for this application. However, with the growing demand for concentrated mixed fertilizer solutions containing phosphorus, nitrogen, and sometimes potash, it was found that conventional and existing emulsifiers were no longer adequate. Since it is well known that salts are very efficient emulsion breakers, it could be expected that emulsifiable toxicant concentrates would completely fail to emulsify in the presence of high concentrations of mono- and polyvalent electrolytes.

However, we discovered that entirely different systems of surfactants, strongly anionic in character (and not particularly effective in ordinary waters), have the remarkable property of emulsifying organic solvents in concentrated salt solutions. These new emulsifying agents would now, it appeared, make it possible to apply pesticides with liquid fertilizers in one simple combined operation. But another difficulty loomed: the range and variation of commercial liquid fertilizers are almost limitless. Table II shows only a very small sample of the fertilizers now in use. It can be seen that even the N-P_2O_5-K_2O analysis does not sufficiently identify a particular fertilizer solution. For instance, in the two 7-7-7 fertilizer solutions, part of the nitrogen may be derived either from urea or from ammonium nitrate; this variation in composition not only results in a difference in crystallization temperature of almost 40° F., but it also affects the degree of saturation of the solution, which in turn influences its emulsification characteristics.

For these reasons it proved necessary to resort again to a system of matched pairs of emulsifiers.

Specific Applications

Combined applications of liquid fertilizers with pesticides to control infestations of many different soil insects, such as wire worms, cut worms, white grubs, and root worms, have now been successfully used on a large scale for more than three seasons. The insecticides most widely employed have been formulations of aldrin, dieldrin, and heptachlor. Fig. 1 shows the type of equipment used to broadcast the liquid heptachlor-fertilizer mixture, which is then disked into the soil. This method usually provides control of many soil insects for more than one season.

Fig. 2 shows an ingenious method of combining the planting of seeds with the application of fertilizer and pesticide. The heptachlor-fertilizer mixture is applied below and to one side of the seed, and covered by the packer wheel. This method eliminates one trip through the fields, and is an exceptionally effective method of placing starter fertilizer; for soil insecticides, however, the first method yields better results.

Recent studies on improved methods of soil fumigation have led to new pesticides, such as Nemagon (1,2-dibromo-3-chloropropane), which combine effective control of nematodes with greatly reduced toxicity to many plants. Fig. 3 shows the type of equipment used in extensive field trials, just completed, in which Nemagon formulations were applied with liquid fertilizer solutions.

Another new development, still largely in the experimental stage, is the combined application of liquid fertilizer solutions with formulations of 2,4-D and 2,4,5-T esters in the upgrading of vast areas of grazing lands.

These are but examples of the many new techniques of spray applications made possible by the availability of these new emulsifiers. Because of their outstanding tolerance to concentrated salt solutions, they have fitted well into the various programs of combining pesticides with liquid fertilizers; however, this is by no means the limit of their usefulness.

Ammate Formulations

A very interesting and, in a manner, a very closely related problem, for instance, has been encountered in the formulation of Ammate (ammonium sulfamate), a highly water-soluble brush and weed killer. It had been found that in certain applications superior control could be obtained if the aqueous Ammate solutions were combined with organic solvents such as kerosene or fuel oil. But the salting-out effect of the sulfamate salt on the kerosene in the presence of conventional emulsifiers had precluded this application on a commercial basis for a long time. Now it has become possible to incorporate a blend of these new emulsifiers (in a somewhat modified form) into the kerosene, with the result that concentrated Ammate-kerosene combinations have been used successfully on a fairly large scale.

Table II: Composition of Typical Liquid Fertilizers

ANALYSIS	32-0-0 (%)	9-9-9 (%)	8-24-0 (%)	8-8-8 (%)	10-20-0 (%)	10-20-0 (%)	7-7-7 (%)	7-7-7 (%)	5-10-10 (%)
Aqueous ammonia (29% NH_3)	...	12.5	33.3	11.1	27.8	27.8	9.7	9.7	13.9
Phosphoric acid (54.5% P_2O_5)	...	16.7	44.5	14.8	37.1	37.1	13.0	13.0	18.5
Urea	35.4	13.3	...	11.8	7.4	...	10.4	...	3.7
Ammonium nitrate	44.3	...	...	...	...	10.0	...	14.0	...
Potassium chloride	...	14.5	...	12.9	...	...	11.3	11.3	16.1
Water	20.3	43.0	22.2	49.4	27.7	25.1	55.6	52.0	47.8
Crystallization temp. (°F.)	32	13	23	0	0	1	1	40	22

Invert Emulsions

There has been considerable interest recently in new types of 2,4-D and 2,4,5-T formulations in which the toxicants are applied as water-in-oil emulsions. Both the free acids and several of their esters are being used, mainly as aircraft sprays. There is some evidence that the danger of drift is reduced in these applications. However, handling is critical, since water-in-oil emulsions have a strong tendency to become, under prolonged agitation, too viscous and unmanageable for spraying. The emulsifiers which were developed for these systems therefore had to be able to control the viscosity characteristics of these emulsions within carefully defined limits.

Taken as a whole, the technology of formulations has kept pace with the demands of a vital and growing industry. New toxicants are constantly being developed, often with very unusual physical and chemical properties. New methods of application are being suggested, often based on seemingly incompatible systems. It is here that the formulation chemist finds the never-ending challenge of employing all the limitless possibilities of skill and imagination—to pave the way toward the realization of new ideas. At the same time he must be a firm guardian of unfailing quality and performance.

A portion of this paper was presented at the 131st National Meeting of the American Chemical Society, Miami, Florida, April 10, 1957.

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