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COMMERCIAL HERBICIDES

Present Methods of Formulation

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Herbicides in wide use today include 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-chloro-o-toloxyacetic acid (MCP), dinitro-o-sec-butylphenol (DNOSBP), and pentachlorophenol. This paper discusses some of the methods used to formulate these chemicals into usable commercial products, as well as problems relating to the choice of amines as solubilizers for 2,4-D and 2,4,5-T formulations. Many types of emulsifiable oil solutions of 2,4-D and 2,4,5-T esters are in commercial use in formulations containing 1 to 4 pounds of the acid equivalent per gallon.

In PROVIDING usable commercial formulations of herbicides, the prime objectives are to put the particular herbicidal chemical into a form handy for the user and his equipment and to supply it in the most effective form, as cheaply as possible.

A formulation is necessary with most herbicides because of the physical nature of the chemical. Some chemicals are water-insoluble, some are oil-insoluble, others are solid lumps. Frequently in their original form they are practically useless to the consumer. For example, a water solution of a chemical simplifies its application when dosages as low as 4 ounces per acre are involved, for it is nearly impossible to distribute 4 ounces of a solid over an acre in a uniform manner. Because herbicides of the plant growth regulator type are effective in such small amounts, their proper formulating is essential to their most effective and economical use.

This paper discusses some of the practices encountered in the formulation of herbicides such as 2,4-D, 2,4,5-T, pentachlorophenol, and the dinitro compounds.

Water-soluble salts of 2,4-dichlorophenoxyacetic acid are currently enjoying wide usage in the United States and elsewhere. Such forms of 2,4-D include the sodium, ammonium, and amine salts. The first two forms find little usage today whereas the amine salts are widely used.

Among the amines that are being used in commercial quantities in 2,4-D herbicides the following can be listed: triethanolamine, diethanolamine, 2-propanol amine, alkanolamine mixtures, dimethylamine, trimethylamine, triethylamine, and isopropylamine.

Current large scale practice with the amine salts of 2,4-D consists of formulating these salts as a water solution containing 4 pounds of 2,4-D acid equivalent per gallon. Lesser amounts are formulated at lower or higher quantities of 2,4-D acid per gallon. Where less than about 2 pounds of 2,4-D acid per gallon is used, it is generally necessary to use an antifreeze in the formulation in addition to the water.

For purposes of discussion a typical amine formulation may be considered to have the following general formula:

2,4-D acid	4 pounds per gallon
Amine	....
Sequestering agent	....
Water	To make 1 gallon

Some properties of certain of the amines useful in 2,4-D formulation work are listed in Table I.

As these amine salts of 2,4-D have nearly equal weed-killing properties and all can be used to provide formulations having good storage properties,

Table I. Amines Useful with 2,4-D

Amine (Tech. Grade)	Lb. Amine per Lb. 2,4-D	Flash Point of Amine, °F.	Boiling Point of Amine at 760 Mm., °C.	Equivalent Wt.
Triethanolamine	0.64	355	360	140–145
Diethanolamine	0.48	280	268	104–108
Triethylamine	0.46	20 (0° C.)	89.5	101 anh.
Isopropylamine	0.27	20	31.9	59 anh.
Dimethylamine	0.21	42 (25% soln.)	7.2	45 anh.

it is possible to give attention to some of the other problems incident to the manufacture of a commercial 2,4-D amine formulation.

Cost of Chemicals

In the actual manufacture of formulations for sale, a prime consideration is the cost of the chemicals used. It is apparent from Table I that certain of the alkyl amines have an attractive position due to their low equivalent weights. Dimethylamine and triethylamine are very useful as economical solubilizers for 2,4-D, if such objectionable features as low flash point, toxicity to humans, and volatility can be tolerated in the equipment available. For example, if explosion-proof wiring and well ventilated areas are not available in the formulation plant, the alkyl amines can present a distinct hazard when used. The alkanol amines, on the other hand, would be much less hazardous under such conditions and thus their extra cost might be justified.

Sequestering Agents

Although the major problem facing the herbicide manufacturer in the preparation of an amine 2,4-D concentrate may center around the choice of the amine, there exists yet another serious problem if the formulation is to be used in hard water. Insoluble calcium and magnesium salts of 2,4-D are formed when the water-soluble formulation is diluted in hard waters at certain concentrations. The salts thus formed generally cause no trouble at dilutions of, say, 1 or 2 pounds of 2,4-D acid per 100 gallons of water, for at that concentration the salts are sufficiently soluble or dispersed and screen and nozzle clogging does not occur. However, when the same formulation is used in low-volume spray equipment at concentrations around 4 pounds of 2,4-D acid per 25 gallons of hard water, the calcium and magnesium salts of 2,4-D are very troublesome.

This problem is met by the use of such sequestering agents as ethylenediaminetetraacetic acid and citric acid. Methylcellulose as described in the Dosser patent (*7*) and other trade-named agents also find use here. It is necessary to use enough sequestering agent to complex the calcium and magnesium present in the spray dilution water. This requires a study of the waters of the region where the formulation is to be sold, so that adequate hard water protection can be build into the formulation. Obviously, there are practical limits as to how much sequestering agent can be included in an amine 2,4-D formulation. Generally, commercial formulations are designed to perform well in water of 1000 p.p.m. hardness containing 1 pound of 2,4-D acid in from 2.5 to 10 gallons of water.

2,4,5-T amine formulations are somewhat more difficult to prepare and concentrates of satisfactory storage quality containing 4 pounds of acid equivalent per gallon cannot be prepared with all the amines listed above. Triethylamine and trimethylamine, however, can be successfully used. Furthermore, the sequestering problem with 2,4,5-T amine solutions is considerably more difficult because of the marked insolubility of the calcium and magnesium salts. Amine solutions of 2,4,5-T have not found wide usage.

Most chemists are familiar with the fact that esters of the chlorophenoxyacetic acids exhibit greater weed-killing properties than the water-soluble salts. Because of these properties, the esters have found wide use in herbicidal formulations dating from very early use of 2,4-D.

Although many types of ester formulations have been used, the largest use has centered around the oil-water emulsifiable solutions of the ester; a considerable tonnage of dilute ester dusts is used in the Northwest and in Canada.

The emulsifiable oil solutions discussed here are of the simplest type possible, and no attempt is made to describe the many variations. The general formula then for an ester formulation includes ester of 2,4-D or 2,4,5-T, emulsifier, and solvent.

Literally dozens of different esters of 2,4-D and 2,4,5-T have been prepared, formulated, and tested in the past six years. Esters of 2,4-D that have found commercial use are the methyl, ethyl, isopropyl, *n*-butyl, and mixed amyl, polyethylene glycol monoesters, butoxyethanol, and propylene glycol butyl ether esters. With 2,4,5-T the methyl, isopropyl, pentyl, butoxyethanol, and propylene glycol butyl ether esters have found commercial use.

These esters have all been used in commercial formulations containing from 1 to 4 pounds of 2,4-D or 2,4,5-T acid equivalent per gallon.

Solubilities of Esters

In formulating these esters of 2,4-D and 2,4,5-T it is first of all necessary to know something of their solubility in commercially available solvents. Listed in Table II are the solubilities of some esters of 2,4-D and 2,4,5-T in various solvents at 20° F. after 24 hours' storage at a concentration of 50% by weight.

Obviously, 20° F. is not the lowest storage temperature that will be encountered by a herbicidal formulation in commercial practice, but the test is sufficiently rigorous to point up some of the physical differences between the esters. The formulation chemist, then, can take advantage of the increased solubility of the alkyl esters of higher molecular weight in petroleum solvents to provide more concentrated formulations exhibiting good cold-weather storage properties.

Furthermore, the differences in the petroleum solubility of the esters can be utilized to aid in bettering the emulsifiability of the finished formulation by taking advantage of the tolerance of some of the esters for aliphatics in the solvent system, thus permitting the chem-

Table II. Solubilities of Various Esters of 2,4-D and 2,4,5-T

2,4-D Esters	Kerosene	Stoddard Solvent	Xylene	Methylated Naphthalene
Methyl	I	I	I	I
Isopropyl	I	I	S	S?
n-Butyl	S	S	S	S
Mixed amyl	S	S	S	S
Propylene glycol butyl ether	S	S	S	S
2,4,5-T esters				
Methyl	I	I	I	I
Isopropyl	I	I	I	I
Propylene glycol butyl ether	S?	S?	S	S

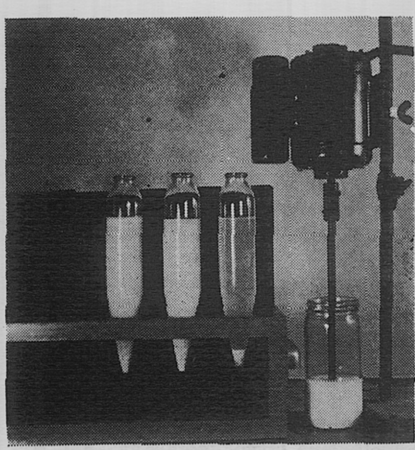


Figure 1. Settling tubes

ist to adjust the specific gravity to a value closer to 1. This can be done, for example, with the propylene glycol butyl ether esters of 2,4-D and 2,4,5-T.

Solvents useful in herbicidal formulations can be chosen from a wide variety of trade-named solvents that are commercially available. They must first of all be good solvents for the particular esters being used. They must be uniform in quality, readily available, and low in cost. Solvents useful in formulating emulsifiable ester concentrates with the lower alkyl esters of 2,4-D have the characteristics listed in Table III.

Table III. Physical Characteristics of a 2,4-D Ester Solvent

Mixed aniline point, ° F.	82–52
Kauri-butanol value	79–98
Aromatics, %	80–100
Sp. gr. at 68° F.	0.895–0.860
Flash point, ° F. (cc.)	164–81
Boiling range, ° F.	274–386/290–495

For reasons of shipping classification, solvents of flash point lower than 81° F. are not included. Thus, formulations made from the above solvents would have flash points above the 80° F. red-label classification.

Evaluating Emulsifiers

The emulsifiers used in the 2,4-D and 2,4,5-T herbicides present a very complex situation. Many emulsifiers are available. Some are used alone in the formulation; others are used in conjunction with other emulsifiers. Most of the useful emulsifiers will be found among the nonionics, although certain blends of anionic with nonionic emulsifiers find wide use today. These latter blends are especially striking in their initial dispersion when used in waters containing calcium and magnesium ions.

The first step in evaluating emulsifiers consists of establishing as a standard a herbicidal formulation that is of proved merit—i.e., one on which there are field data regarding its actual performance in commercial sprayers.

Next it is necessary to establish a uniform testing procedure for critically evaluating other emulsions in reference to the standard.

Finally, this performance must be capable of numerical or graphical presentation, so that critical comparisons can be made.

Procedure. A simple procedure then is to take a standard brand herbicide that has been on the market for some time and has demonstrated good performance in a wide variety of equipment and evaluate it in the following manner.

Observe the initial dispersion (ease of emulsification) in hard and soft water by pipetting 1 ml. into 100 ml. of water.

Prepare an emulsion by adding 4 ml. of the formulation to 400 ml. of water (use any water of interest) and agitate under controlled conditions.

Immediately transfer 100 ml. of the emulsion thus formed to a 100-ml. cone-shaped centrifuge tube and record the milliliters of cream settling at 10-minute intervals for 2 hours.

Keep the emulsion undisturbed for 24 hours and observe milliliters of cream settled at that time. Plot per cent of cream settled against time.

In such a manner it is possible quickly and cheaply to determine how an emulsifier is performing. Variations in emulsifier content can be rapidly checked and the results are very meaningful to the formulation chemist, for they refer back to a known formulation.

Figure 1 illustrates the ASTM settling tubes used in this test and shows the sort of information that can be obtained.

Figure 2 illustrates how the effect of such factors as per cent emulsifier in the formulation and the effect of hard water can be evaluated. The performance of different emulsifiers can also be easily evaluated in this manner.

Esters of 2,4-D and 2,4,5-T are used as oil concentrates in certain applications, and this sort of formulation is achieved by use of the information presented under the discussion on solvents.

Dusts

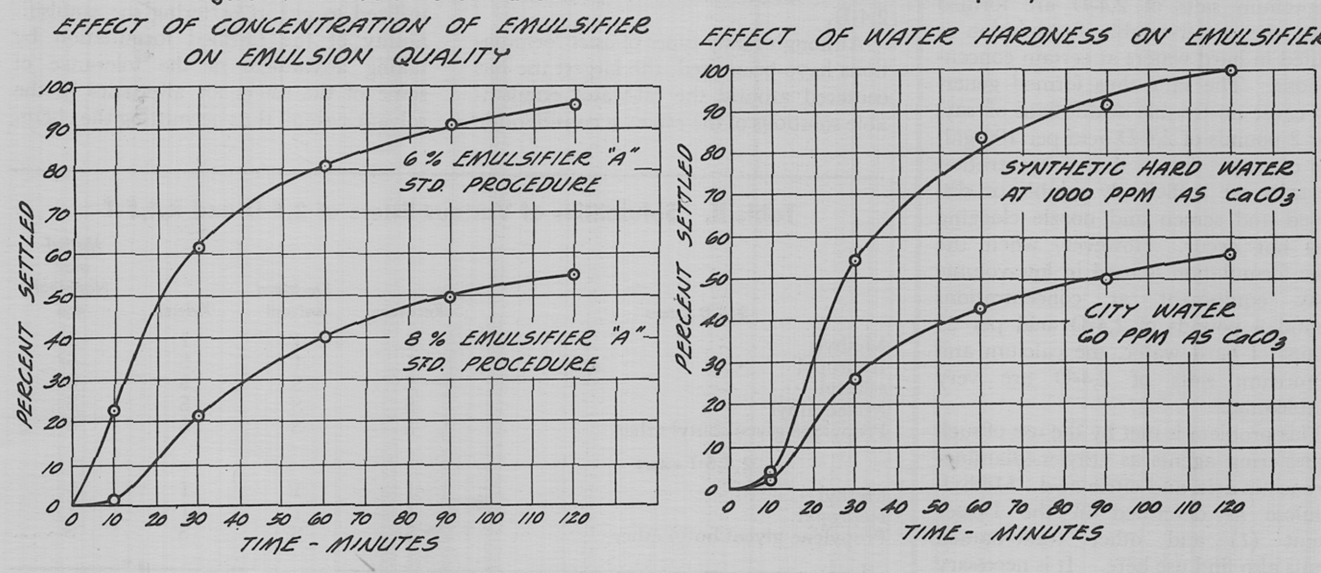
Another type of formulation that has found a good deal of use is the 2,4-D dust, which usually contains 5% of 2,4-D acid equivalent as an ester. A 2,4-D dust can be made from a previously prepared dust concentrate, diluted to provide the finished dust. A second method involves the direct impregnation of the dust diluent with the ester in liquid form. Both forms have been used successfully, although the latter form presents some problems regarding homogeneity.

In preparing dust concentrates from the isopropyl ester of 2,4-D, for example, a clay such as an attapulgite or a diatomaceous earth can be used as the diluent. The dust diluent itself can be a locally available talc or a pyrophyllite.

MCP and DNOSPB

Herbicides containing 4-chloro-*o*-tol-

Figure 2. Effects of concentration of emulsifier and water hardness on quality of emulsion



oxyacetic acid (MCP), are used today in the form of the sodium salt or an amine salt. In general, the information provided on amine salt formulations of 2,4-D holds true for 4-chloro-*o*-toloxyacetic acid and the current practice is much the same as that discussed under 2,4-D amines.

Dinitro herbicides, those containing compounds similar to the dinitro-*o-sec*-butylphenol (DNOSBP), are formulated both as amine solutions and as emulsifiable oil solutions.

The amine concentrate solutions of dinitro-*o-sec*-butyl phenol are pretty much restricted to alkanolamine salts, owing to the relative insolubility of the ammonium and alkyl amine salts. The less soluble ammonium dinitro-*o-sec*-butyl phenol can be used in the lower concentration selective-type formulation, while the alkanolamine salts need to be used in the higher concentration pre-emergent type formulation.

In formulations of salts of dinitro-*o-sec*-butyl phenol and related compounds it is necessary to think in terms of hard water protection where usage is in low volume equipment, again because of the insolubility of calcium and magnesium salts of the phenol at these concentrations.

Pentachlorophenol formulations are used in weed control generally in the form of oil solutions. Emulsifiable formulations can also be prepared. Solvents useful with pentachlorophenol are similar to those useful with 2,4-D esters, except that some of the heavier aromatic oils of dark color can be used.

Formulation Problems

The problems of the formulation chemist are many and varied and have only briefly been touched upon. A few of the things that the chemist needs to know about the intended use of the product before a formulation is devised are:

1. How will it be used—i.e., what amount per acre?
2. What are the physical characteristics of the chemical, including solubilities, toxicology, etc?
3. What are the corrosion problems connected with the use of the chemical?
4. How much money can be afforded in the formulation?
5. Where will the formulation be used?

Given the above information, it is possible to do a good job of formulating a herbicide. Trouble comes, for example, when it is thought that a chemical will be applied at say 1 pound in 100 gallons of water per acre and then equipment is developed to the point where people are applying the same chemical at rates of 1 pound in 5 gallons of water per acre. Such was the case with the amine salts of 2,4-D. Almost overnight a good product became useless as users began to apply it at rates for which it had not been designed. Now the formulation chemist finds that he must continually keep an eye on the developments in equipment and techniques used in the application of his products. Only by so doing can he be sure that his product is performing at peak efficiency.

Application equipment is important to the formulator in yet another way, in that any product put on the market must be tested so that undue wear or corrosion to the application equipment will become apparent and the adequacy of protective measures evaluated.

Such testing generally starts in the laboratory with carefully controlled tests on individual metals at the time field work begins. If a corrosion problem exists, steps are then taken to remedy it. Subsequent field testing in standard application equipment corroborates the laboratory findings. Considerable time and effort are put forth to ensure that the herbicides do not harm the application equipment.

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HERBICIDES

Residues in Soil

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There is little direct evidence of a hazard associated with residues of any particular herbicide, but ample indication of the need for intensive studies of herbicides in soil. Critical factors are the effect on soil microorganisms and soil properties and removal of herbicides from soil. 2,4-D is relatively nontoxic to most soil organisms at concentrations ordinarily used for weed control. Certain other herbicides appear to be very inhibitory to microbial activity. The significance of inhibition of microorganisms for growth of subsequent crops has not been established. Herbicides or effects of herbicides are removed from soil by leaching, retention by the soil colloids, decomposition, and volatilization. Aqueous solubility affects leaching, but possible differential fixation of formulations and the carrier used may also have an influence. Chemical changes following application of a herbicide to soil complicate a comparison of formulations of different solubilities. Soil microorganisms decompose many herbicides; soil moisture, soil temperature, and other factors most conducive to microbial activity are conducive to herbicide decomposition. Volatility may be an important factor in the removal of a herbicide from soil.