THE SIGNIFICANCE OF FORMULATION AND ITS RELATIONSHIP TO SELECTIVE HERBICIDE EFFICIENCY

By S. W. PRESTON and B. J. THOMSON,
Timbrol Ltd., Sydney, Australia

WE propose in this paper to describe and explain briefly some features of the complex mixtures which constitute the various herbicide formulation types. Many of the inorganic chemicals (for example, sodium arsenite, NaClO_3 , NaCl , borates, etc.) and some organic chemicals can actually be used for effective weed control as normally manufactured. Others, and mainly the organic class of chemicals, require formulation involving special blending with one or more adjuvants to make them suitable for general use. There are two main and four less important types. Before dealing with these different types it might be just as well at this stage to attempt to define the ideal herbicide formulation. The ideal herbicide formulation should be highly effective, low in cost for desired effect, easy to use, non-hazardous, and stable to storage under all conditions. Needless to say, the ideal formulation has never been formed! A more complete list of the desirable properties of a formulation appear in Table 1.

TABLE 1—DESIRABLE PROPERTIES OF A FORMULATION

1. **Highly Effective**
 - (a) Field tested
 - (b) Departmentally approved or registered
2. **Low Cost**
 - (a) High active ingredient concentration
3. **Easy-to-use**
 - (a) Instantaneous dispersion or solution
 - (b) Stable in hard and soft water
 - (c) Spray nozzles not blocked by normal spray concentration
 - (d) Convenient dilution rate
 - (e) Non-corrosive to equipment
 - (f) Clear labelling of directions for mixing and using
 - (g) No special application equipment required
4. **Non-hazardous**
 - (a) Non-inflammable
 - (b) Non-poisonous to humans or stock
5. **Stable to Storage**
 - (a) No settling or separation in containers at high or low temperatures
 - (b) Non-corrosive to containers

In deciding upon the formulation type, it is necessary to have an understanding of the physical properties of the base chemical including its solubilities in various solvents, the proposed end use, and the formulation cost which can be tolerated.

The majority of organic herbicides can be prepared as either water soluble concentrates or water emulsifiable concentrates. The remainder fall into the categories of wettable or suspendable powders and pastes, oil soluble concentrates, dusts, and fumigants. Table 2 shows these formulation types and their usual components.

TABLE 2—FORMULATION TYPES

Name	Usual Components	Examples
1. Water soluble concentrates	Base chemical with or without adjuvants such as wetters, sequestering agents, or synergists	(a) Sodium salts of 2,4-D and PCP, TCA, Dalapon, NIX, Ammate
(a) Powders		(b) Amine salts of 2,4-D and MCP, sodium salt of PCP, Endothal, MH
(b) Liquids		(c) Sodium salts of DNOC, PCP, and 2,4-D
(c) Pastes and slurries		2,4-D and 2,4,5-T esters, PCP, coal tar, and petroleum oils
2. Emulsifiable concentrates	Base chemical, solvent, co-solvent, and emulsifier(s)	2,4-D and 2,4,5-T esters, PCP, coal tar, and petroleum oils
3. Oil soluble concentrates	Base chemical, solvent, and wetter	CMU, DCMU, IPC, and CIPC, 2,4-D acid
4. Wettable or dispersible powders or pastes	Base chemical, filler, suspending agent, and wetting agent	CaCN ₂ , sodium salt of 2,4-D
5. Dusts	Base chemical and filler	Chlorpicrin, Me-Br, DD
6. Fumigants	Base chemical	

We will deal with each of the above formulation types in turn and discuss their various alternative components and their significance with respect to herbicide efficiency and selectivity where this is applicable.

1. WATER SOLUBLE CONCENTRATES

Water soluble concentrates usually consist of homogeneous mixtures of the base chemical or its derivative with a wetting agent or sequestering agent. They can be in the form of (a) free flowing, quick dissolving powders, (b) clear mobile liquids, or (c) pastes or slurries.

(a) Quite often the base chemical, as manufactured, is readily water soluble, stable to storage in the dry form, and, in fact, generally conforms to the list of favourable properties in Table 1. In this case it requires no real formulation and is marketed as such in the highly concentrated solid form. Included in this group are TCA, Dalapon, sodium salt of 2,4-D, and PCP, etc. Wetting agents are sometimes incorporated with those inherently difficult to wet. For example, the sodium salt of 2,4-D

can be made flash dissolving if incorporated with wetting agents. Care must be taken to keep the amount of added wetter to a minimum, otherwise some loss of selectivity may result. Wetting agents are added to the Dalapon proprietary formulation (approximately 4 per cent. anionic wetter) to enhance uniform wetting of grass foliage by the dilute spray solution. An unformulated sodium salt of 2,2-dichloropropionic acid is also available to experimenters. The manufacturers recommend (1) the alkyl aryl sodium sulphonates for use with Dalapon. Herbicidal compositions frequently include components other than the chief active agent for a specific function. An interesting example of the use of additives is the application of the antimicrobial properties of borax, whereby 2,4-D and 2,4,5-T are enabled to be used as soil sterilants (4). 2,4-D alone in moist fertile loam is completely destroyed in 3 to 6 weeks.

(b) An important class of the water soluble concentrates are the liquid formulations which include derivatives of 2,4-D, MCP, and DNBP. Both 2,4-D acid and MCP acid are white crystalline solids of relatively low water solubility, and, unless specially formulated, as such are of little value herbicidally. They can be converted into useful weedkilling chemicals by reacting them with alkalis such as ammonia, caustic soda, caustic potash, diethanolamine, triethanolamine, dimethylamine, triethylamine, etc. Given satisfactory formulation properties, the final choice is largely dependent on the availability and cost of alkali for neutralising. The other factors to be considered are solubility, inflammability, toxicity, herbicidal efficiency, etc. The solubilities of the various salts vary widely at near freezing temperatures, and this is of importance with respect to the low temperature stability of the highly concentrated solutions. The use of more costly formulating equipment and certain health and fire hazards could, for example, offset the cost of a cheaper alkylamine such as dimethylamine and favour the use of triethanolamine. Although the number of hormone salts which can be made is theoretically very great, the 2,4-D triethanolamine or dimethylamine salt solutions, the mixed sodium-ammonium and triethanolamine salts of MCP, and the alkanolamine and the ammonium salts of DNBP are those most generally incorporated in commercial formulations. The question arises then as to the relative herbicidal activity of these different derivatives. It has been shown (2) in the case of 2,4-D that the alkylamine and alkanolamine salts are very similar herbicidally. There is some evidence available to show that the former are slightly less selective. The alkylamine and alkanolamine derivatives of MCP probably behave similarly. The superior activity of amine salts and ammonium salts (or mixtures of ammonium sulphate and the sodium salt of DNOC) over and above that of the sodium salt of DNOC itself is well known. Crafts and Reiber (3) have proposed that the toxic action of both forms of DNOC proceeds via a hydrolysis of the phenate ion forming the DNOC molecule which is preferentially absorbed by the plant. In the case of the more active DNOC derivatives this hydrolysis-absorption process can proceed to completion. In comparisons between the alkali metal salts of 2,4-D and the ammonium or amine salts (substituted ammonias) it is usual to find that the latter types are more active herbicidally. It is reasonable to assume that a similar absorption process applies to the various salts of 2,4-D and of DNOC.

A feature which can be far more important and which can override the slight differences of derivative type is the effect of added wetting agents in aqueous concentrates. In recent studies on some aspects of entry of 2,4-D into leaves Weintraub and others (3) state that only 7 per cent. as much 2,4-D (aqueous solution) was needed to produce a standard degree of response as in the absence of surfactant, that is, a 14-fold enhancement. Optima concentrations of surfactant were of the order of 0.1 per cent. Of the surfactants tested anionic and non-ionics were

equally effective, while the cationic compounds gave considerably less enhancement. Unfortunately, there is no related reference available to show how this marked influence of wetters affects the actual death of weeds. There is further evidence to show that increase in efficiency of 2,4-D by added surfactants is not solely a function of the depression of surface tension. Without elaborating on the difference in herbicidal activity between amine salts and esters, it might be mentioned that claims have been made in the U.S.A. that, even when applied to the foliage of woody species, amine salts containing non-ionic wetting agents are equal in performance to ester emulsifiable concentrates containing an equivalent amount of 2,4-D or 2,4,5-T acid (6).

There are obvious complications arising out of the incorporation of wetting agents in liquid concentrates which are used at different dilutions and with waters of varying hardness. Thus, 4oz. of the amine salt of 2,4-D applied in 10 gallons/acre can be fatal to both weeds; for example, young saffron thistle (*Carthamus lanatus*) and linseed, whereas in over 40 gallons/acre selective weeding can be achieved with minimum crop damage. If, however, an excess of wetting agent is included in the latter spray, severe crop damage can still result. The formulator generally adjusts the concentration of wetter to ensure that the herbicidal activity is optimal, while selectivity is not unduly impaired over most of the normal rates of dilution. Attempts are being made by the Australian Standards Association to establish suitable standards for the surface activity of herbicides.

The phenomenon involving the precipitation of insoluble Ca, Mg, and Fe salts of 2,4-D when highly concentrated spray solutions are prepared from amine salt concentrates and hard water also must be cared for by the formulator. Sufficient of a sequestering agent such as ethylenediamine tetra-acetic acid or citric acid is added to amine salt concentrates to prevent precipitation, and as far as is known has no direct effect on the herbicidal activity. Some of the available surfactants behave in the dual role of delaying the precipitation of insoluble salts of 2,4-D and MCP and of improving the wetting properties.

(c) The water soluble paste or slurry type of formulations are usually manufactured when the base chemical solubility in cheap solvents is very low or are not in the form of readily water soluble derivatives. Sodium DNOC and 2,4-D sodium salt are sold commercially in this form in Australia. Apart from the physical form in which they are present similar considerations with respect to effect of formulation upon efficiency, cost, and ease of use apply to all classes of water soluble compounds.

2. EMULSIFIABLE CONCENTRATES

The insoluble hormone acids described before can be reacted with alcohols to form another type of derivative called esters. These are generally water immiscible and oil soluble and before they can be used with a water carrier or diluent, they must be blended with solvents and emulsifiers to form emulsifiable concentrates. The choice of alcohol with which to esterify the hormone acid is very great, but for reasons of cost, availability, volatility, solvent solubility, etc., the number of alcohols actually used is relatively few. The corresponding esters include the alkyl derivatives such as ethyl, isopropyl, butyl, octyl, and nonyl, and those containing hydrophilic substituents such as butoxyethanol, polyethylene glycol, and polypropylene glycol butyl ether esters. Generally speaking, the alkyl esters formulated under similar conditions will give similar herbicidal activity per unit acid equivalent. Certain of the other groups of esters such as 2,4-D polyethylene glycol esters having partial water and oil solubility and a better tendency to translocate, have been

shown, on some species, to be more effective than esters with no hydrophilic substituents and lower tendency to be compatible with the aqueous mesophyll and phloem. 2,4,5-T polyethylene glycol ester formulations used on gorse and blackberry, however, have not compared as favourably as butyl ester formulations applied at similar acid equivalent concentrations (7). Reasons for species specificity such as this to different derivatives of the same base chemicals are not at all well understood.

The choice of solvent for the preparation of emulsifiable concentrate is likewise given careful consideration. It is generally agreed that translocated herbicides such as 2,4-D and MCP should not be used in conjunction with contact herbicides such as aromatic oils which can kill the cells and tissues and so prevent the absorption of the former type. Solvents with minimum aromatic content are therefore usually employed for hormone formulation. However, a certain percentage of dearer aromatic solvents is often incorporated as a co-solvent to keep emulsifier and base chemical homogeneous at low temperatures. Where additional oils are added to spray solutions in an attempt to increase chemical uptake through waxy leaves, these should be restricted to the cheaper and lower aromatic content type such as diesel distillate (approximately 20 per cent. aromatics) or lighting kerosene (6 per cent.). It has been postulated (8) that accumulation of aromatic fractions at the periphery of emulsified oils could cause excessive contact injury.

The physical properties of oil-in-water emulsions play an important part in the effective use of emulsified herbicides. The properties of a ready to use emulsion depend essentially on the choice of emulsifier or emulsifier blends incorporated in the formulation. For example, the formulator chooses emulsifiers which give ease and spontaneity of emulsification, good emulsion stability, and ease of dispersion in both hard and soft water. Most of the useful emulsifiers for 2,4-D and 2,4,5-T will be found among the group of emulsifiers known as non-ionics or among blends of these with anionics. Recently attention has been given to the use of cationic emulsifiers for preparing herbicide sprays. These surfactants have been useful for assisting the dyeing of synthetic fibres where they cause the oil phase (dye) of an emulsion to wet and strip out on to the fibre preferentially. This special property of cationics has not been found so far to enhance the activity of 2,4,5-T esters in a limited brush control trial in N.S.W., nor has it been shown to be of any great advantage for improving formulations used against some hard to kill subaquatic weeds in Victoria. Nevertheless, it is a potentially interesting tool which may prove to be of value for certain weed problems. One way to evaluate the worth of emulsifiers or formulations is to compare such physical properties as initial flash dispersion and rate of separation (creaming) in standard equipment with a formulation arbitrarily adopted as a standard because of its proven good field performance. It is also necessary to consider emulsifier cost, availability, flash point, and solubility in cheap industrial solvents when developing new emulsifiable formulations.

With regard to emulsion stability and its effect on herbicidal activity there is an open field for investigation which is considered to be of particular importance when high spray volumes are essential as in scrub control. It has often been stated that highly stable emulsions will not break in time before the majority of the liquid retained on the leaf surface has run off. On the other hand, fast-breaking emulsions will require constant tank agitation. Whether a fast-breaking emulsion gives superior herbicidal activity will depend more on whether the interfacial tension relations favour the oil or water phase wetting the leaf. If oil separation from an emulsion is to the top of the water, any run off from a leaf surface will be rich in active ingredient and the herbicide activity

may be less. Conversely, when an emulsion breaks in such a way that any oil phase moving towards the leaf surface will wet it, then increase in herbicidal activity can be expected. The surface tension measurement of an emulsion gives a good indication as to whether the leaf surface will be wet adequately by it without excess run off. A surface tension of 30 to 35 dynes per cm. is held to give good field performance (9).

3. OIL SOLUBLE CONCENTRATES

These consist of simple solutions of base chemicals or derivative in non-polar solvents. For example, 2,4-D and 2,4,5-T esters can be diluted with cheap solvents such as diesel distillate and kerosene and applied by low volume land equipment or aircraft to weeds and brush species. The formulation of these requires an understanding of the end use and consideration must be given to such factors as the choice of ester class, volatility, and viscosity of the carrier solvent, together with the desirability or otherwise of contact herbicidal activity. The incorporation of special wetters for increasing penetration and spreading has been recommended by some surfactant suppliers, but little data are available to substantiate these claims.

4. WETTABLE OR DISPERSIBLE POWDERS AND PASTES

These are not used extensively as formulations for herbicides. This type of herbicide formulation is of value where the base chemical is particularly insoluble in cheap solvents. CMU is used exclusively as a wettable powder formulation for this reason. CIPC and IPC are sometimes manufactured as wettable powders and, as such, have the advantages of a highly concentrated product.

It is interesting to record here that a micronised 2,4-D-sulphur mixture containing a wetting agent is giving extraordinarily good results with ribbonweed (*Vallisneria spiralis*) a difficult to kill subaquatic weed of irrigation systems in Northern Victoria (10). It is claimed that sulphur is the only material of many screened which imparts sufficient adhesion of the 2,4-D to the smooth leaves to enable absorption to proceed. These mixtures show promise for other than aquatic species weed control.

5. DUSTS

Dusts also fall into the category of the less common type of herbicide formulations, as they are subject to serious loss by wind and are generally dependent on rain following application for effectiveness. 2,4-D has been formulated as dusts with inert fillers and also with fertilisers, insecticides, and lime. As a further example, calcium cyanamide is applied to cotton as a dust formulation.

6. FUMIGANTS

Weed control by preventive measures is carried out by the use of fumigants which act as seed sterilants. These chemicals are usually volatile liquids or gases and are not formulated in the true sense of the word.

In conclusion, we would like to mention that many of the characteristics of the various formulation types have been determined only as a result of detailed experimentation in the field and in the laboratory. To achieve the optimum benefit from the effort involved in developing an effective herbicide the co-operation between manufacturer, formulator, and government departmental personnel should continue along the closest possible lines. Each plays an important and related part in the proper development of a useful herbicide.

BIBLIOGRAPHY

1. Dalapon Bulletin Number 2. The Dow Chemical Company, Midland, Michigan. 1953.
2. "Comparative Studies of Certain Amine Salts of 2,4-D". C. A. Schexnayder. Third Proceedings of the Southern Weed Conference, p. 4, 1950.
3. "Studies on the Activation of Herbicides". A. S. Crafts and H. G. Reiber. Hilgardia, 16, No. 10, p. 487, 1945.
4. Australian Patent Applications, 4731/55.
5. "Studies of Entry of 2,4-D into Leaves". R. L. Weintraub, J. N. Yeatman, J. W. Brown, J. A. Throne, J. D. Skoss, J. R. Conover. Proceedings of the Eighth Annual Meeting North-eastern Weed Control Conference, p. 5.
6. Technical Pamphlet on Formulation of 2,4-D and 2,4,5-T Amine Salts. Rohm and Haas Company, Philadelphia, U.S.A.
7. "Comparison of the Polyethylene Glycol Esters of the Phenoxyacetic Acid Derivatives". P. S. Ferens. Proceedings of the 7th New Zealand Weed Control Conference, p. 11, 1954.
8. "Theories on the Herbicidal Action of Petroleum Herbicides". S. L. Dallyn and R. D. Sweet. Proceedings of the Fifth Annual Meeting of the North-eastern Weed Control Conference, p. 13, 1951.
9. "Herbicide Specifications and Laboratory Evaluation Procedures". J. W. Suggett. Proceedings of the Ninth North eastern Weed Control Conference, p. 453, 1955.
10. "Weed Control in Irrigation Channels and Drains". W. P. Dunk. Supplement to Technical Bulletin No. 8, State Rivers and Water Supply Commission, Victoria, 1955.

SOME GENERAL REFERENCES

1. "2,4-D Mechanisms of Action", R. L. Weintraub, Journal of Agriculture and Food Chemistry, 1, N. 3, p. 250, 1953.
2. "Commercial Herbicides—Present Method of Formulation", J. A. Kelly, Journal of Agricultural and Food Chemistry, 1, No. 3, p. 254, 1953.
3. "Pesticide Formulation—Liquid Concentrate Problems, Edgar Selz, Journal of Agricultural and Food Chemistry, 1, No. 5, p. 381, 1953.
4. "Pesticide Formulation—Influence of Formulation on Effectiveness", W. Ebeling and R. J. Pence, Journal of Agricultural and Food Chemistry, 1, No. 5, p. 386, 1953.
5. "Emulsion Testing—A Basis for Tests for Emulsifiable Concentrates of Agricultural Chemicals", R. W. Behrens and W. C. Griffin, Journal of Agricultural and Food Chemistry, 1, No. 11, p. 720, 1953.
6. "Difference in Activity between 2,4-D Acetic Acid and other Auxins, and its Significance in Herbicidal Action", J. Van Overbeek, R. Blondeaux, and V. Horne, Plant Physiology, 26, No. 4, p. 687-696, 1951.

DISCUSSION

Q.—Do sugars and boron compounds increase translocation?

A.—Sugars, boron compounds, and trace elements are all claimed to increase herbicidal activity, but my company has done no work with these substances.

Comment: We have tried phosphoric acid, urea, and several other compounds as additives. We found that to get any effect, we had to use substances such as oil to increase the penetration or the degree of solubility.

A.—The most important feature is the relationship of the wetting between the weedkiller and the plant surface, not the addition of other compounds.

Q.—Is nitrogen (as in urea compounds) supposed to improve penetration through the plant surface?

Comment: My firm has done a lot of work with urea in this connection and the weakness is that you have to apply the urea say a week before the weedkiller. No one is going to spray twice.

Comment: If the weedkiller was in a form such as 2,4-D sulphate, which is supposed to break down in the soil before it becomes phytotoxic, it may be possible to apply weedkiller and urea together.