The concepts and problems of formulating phenoxy acid type herbicide for spot spray application using controlled droplet application (C.D.A.)

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SUMMARY

Controlled Droplet Application (C.D.A.) is a technique whereby low and ultra-low volume of pesticides may be applied as droplets of near uniform size. This technique has been used extensively in crop spraying but has been little used for spot spraying weeds with herbicides. Further development of this technique for spot spraying requires new herbicide formulations suitable for application using C.D.A. equipment.

Formulations of 2,4-D amine and ester and 2,4,5-T ester ranging in concentrations from 2 to 20% a.i. have been prepared and are now undergoing storage stability and field testing.

It is necessary to include a marking agent into C.D.A. formulations for spot spraying. Titanium dioxide has been found to be most suitable when included at a level of 10% w/v. To prevent excessive settling and to aid resuspension a fumed silica is incorporated into the formulations at a level of 0.5% w/v using a high shear mixer. A further requirement for its adequate dispersion in 2,4-D amine aqueous formulations is the addition of a non-ionic wetting agent.

To reduce vapour and spray drift it is desirable that low volatile active ingredients and carriers are used in the formulations. Consequently, when formulating esters of 2,4-D and 2,4,5-T low volatile iso-octyl esters were used as the active ingredients and deodorized kerosene as the carrier. The active ingredient in the 2,4-D dimethyl amine formulations is non-volatile and it has been formulated in aqueous solution. However, depending on the droplet size being used, an alternative formulation utilizing a non-volatile oil soluble amine such as the N-oleyl-1,3-propylene diamine salt of 2,4-D in a non-volatile solvent may be more suitable for C.D.A. formulations.

INTRODUCTION

C.D.A. is a method whereby low volumes of pesticides (5 to 30 ℓ/ha) may be applied to plants in droplets with a narrow and predictable variation in size. In the past the control of weeds with herbicides using C.D.A. has been mainly restricted to row crops. In many situations in Australia weed control is carried out by spot spraying individual plants or clumps of plants using high volumes with a constant concentration of herbicide in solution. As high volume spot spray application volumes range from 1000 to 3000 ℓ/ha, it is envisaged that the development of a low volume C.D.A. technique will lead to significant savings in application costs (Combellack, 1978).

The range of hand-held C.D.A. equipment, some of which requires minor modifications to design, that can be used for the spot application of herbicides to weeds has been described (Combellack and Shaw, 1977).

With C.D.A. the production of predictable and uniform droplet sizes enables a more accurate assessment of drift hazard than for high volume equipment which produce a wide range of droplet sizes, thus the application of chemicals can be made closer to susceptible crops than is currently recommended.

The general principles affecting droplet production and the behaviour of such droplets moving to and impacting upon the target have been reviewed (Bals, 1973; Combellack and Shaw, 1977, and Combellack, 1978). Combellack (1978) suggested that the ideal situation is "the production of uniform droplets using a non-volatile chemical in a non-evaporative carrier, projected under conditions of low wind, high relative humidity and low temperature". Thus when producing C.D.A. formulations cognizance of volatility of the active ingredient and carrier are necessary if spray drift is to be minimized, whilst the influence of viscosity on flow rates is important in determining drop size (Bals, 1969; Combellack and Shaw, 1977) and spray coverage (Maas and de Lange, 1970).

The interaction of droplet size and distribution on biological efficacy is important and it has been concluded (Behrens, 1957) that an optimum drop size and distribution may exist for each species for a particular herbicidal formulation. However the practical limitations to droplet size and distribution which do occur include equipment design, the physical properties of the formulation, meteorological and microclimatic conditions and other factors which affect the movement to and impaction of the droplets onto the target.

If C.D.A. is to become an acceptable method for low volume spot applications of herbicides, formulations must be available which are suitable for use with the equipment. All of the above factors must be taken into account. However because low volumes of application make it difficult to see which plants or parts of plants have been sprayed it is necessary to incorporate a marking agent which is instantly visible on the plant's surface. Ease of manufacture, suitability for use in the field, toxicity, cost and shelf life are other aspects which must be considered when devising a C.D.A. formulation.

Since the major proportion of spot spraying which is conducted by the Department of Crown Lands and Survey is for noxious weed control using the phenoxy acid type herbicides, 2,4,5-T ester, 2,4-D ester and 2,4-D amine, the initial work has been aimed at formulating these materials.

FORMULATIONS

(a) Active ingredients

Formulations of 2,4-D amine for low volume applications with hand held C.D.A. equipment have been prepared at concentrations of up to 20% a.i. using a proprietary 50% formulation of the dimethylamine salt of 2,4-D as the source of the active ingredient. Water, which has been utilized as the carrier with all amine formulations, presents problems when high levels of evaporation of the water carrier cause a reduction in size of the droplets sufficient for them to become airborne with a consequent increase in drift hazard. This hazard could be reduced by using the N-oleyl-1,3-propylene diamine salt of 2,4-D in a non-volatile oil. These formulations will be evaluated in the future.

As the ester formulations of 2,4-D and 2,4,5-T are often more effective than the amines for control of many weeds they are widely used. The ethyl ester of 2,4-D and the butyl ester of 2,4,5-T are both highly volatile and formulations of these materials are used for weed control at safe distances from susceptible crops. The use of high volatile esters as the active ingredient for C.D.A. formulations was considered undesirable because increased levels of damage to non-target species may occur due to high levels of vapour drift resulting from the volatilization of the active ingredient from the highly concentrated droplets.

Commercially available low volatile formulations of 2,4-D and 2,4,5-T ester utilize the iso-octyl and butoxyethanol esters of these materials. These esters are oil soluble and can therefore be prepared in low volatile carriers. As only the iso-octyl esters were readily available as the unformulated material these were used in the preparation of the C.D.A. trial formulations.

(b) Marking agents for C.D.A. spot spray formulations

The desirable characteristics possessed by a marking agent in a C.D.A. formulation include:

(a) brilliance on contact with a broad range of plants of different colour and with different surface characteristics

(b) chemical compatability with the ingredients of the formulation

(c) physical stability

(d) low cost

(e) user acceptability, and

(f) environmental safety.

A range of organic dyes was tested and all were found to be unsuitable because the level of visibility on the plant surface was low even at high concentrations (1% w/v). User resistance would also be encountered because the removal of these dyes from the skin and clothing was found to be difficult.

The marking properties of a number of inorganic materials including talc, kaolin, montmorillonite, quicklime, gypsum, ground aluminium and titanium dioxide (TiO_2) when suspended in deodorized kerosene and water were tested. Ground aluminium, when applied to plants, did not exhibit adequate marking properties. With the exception of TiO_2, all of the other materials required a high degree of evaporation of the carrier from the droplets after impaction on the plant for adequate visibility. In contrast the brilliant reflectant properties of TiO_2 made the droplets instantly visible on a wide range of plants. The optimum concentration of TiO_2 was found to be 10% w/v. Relative ease of removal from contaminated skin, clothing and equipment, rainfastness on the plant surface and chemical inertness were other desirable characteristics.

Coated and uncoated grades of TiO_2, refined using either the chloride or sulphide processes were tested. On the basis of ease of suspension in oil and aqueous carriers, degree of flocculation and cost, Laporte Runa ARH-20 grade, which is an uncoated material refined using the sulphide process, was found to be most suitable.

Upon storage, settling of TiO_2 leads to increasing difficulties in resuspension. The incorporation of a fumed silica suspending agent at a level of 0.5% w/v using a high shear mixer overcomes this problem without adversely affecting formulation viscosity. To increase the dispersibility of TiO_2 in aqueous 2,4-D amine formulations it was necessary to add a non-ionic wetting agent ("Nonidet WK"). The levels of surfactant required increased from 0.5% to 2.0% w/v as the amount of active ingredient increased from 2% w/v to 20% w/v. Storage tests for 6 months have shown that a small amount of flocculation had occurred which indicates that this problem has not been completely overcome with the amine formulations. Flocculation had not occurred with ester formulations.

(c) <u>The carrier</u>

The properties of solvents used for low volume application of pesticides using C.D.A. have been reviewed by Maas (1971) and Wrigley (1973). Maas (1971) summarized the properties of an ideal solvent as:

(a) low volatility

(b) high dissolving power for the pesticide

(c) non phytotoxic

(d) low viscosity, and

(e) compatibility with the pesticide.

Low cost, ready availability and safety to the user must also be taken into account.

The ability of the active ingredient to dissolve in the carrier can be readily ascertained. Phytotoxicity may effect uptake or translocation mechanisms of the herbicide by the plant and reduce its effectiveness (Behrens, 1973).

The evaporation rate of the carrier under prevailing climatic conditions is a critical factor if environmental risk due to drift is to be minimized and optimum droplet size at the target is to be achieved.

Very few solvents will adequately fulfil all the above criteria and therefore some compromises must be made (Maas, 1971). Of the solvents which have been tested for use in spot spraying of iso-octyl ester formulations of 2,4,5-T and 2,4-D, deodorized kerosene has been found to be more suitable than a range of other solvents tested which included isoparaffinic oils, "process oils"; heavy aromatic naphtha, low odour paraffin and "Solvesso" solvents.

The disadvantages associated with using water as a carrier for 2,4-D amine preparations have already been discussed and these preparations should only be applied under conditions giving rise to droplets of greater than 200 μ diameter.

(d) Formulation testing

Before a formulation can be considered to be suitable for market release it is necessary to know the likely shelf life of the product and whether it is effective in the field. Much of the relevant information can be obtained by conducting accelerated storage stability tests as described by Niessen (1975). Tests underway on present C.D.A. formulations include investigations into the chemical compatibility of the ingredients with the package and the influences of light, temperature, acidity, alkalinity, oxidation and humidity on stability. The most important changes which are likely to occur in formulations for C.D.A. are degradation of the active ingredient and undesirable changes in physical properties such as viscosity and emulsion or suspension stability.

Field testing to determine the biological efficacy of the formulations against a range of weeds has been conducted (Combellack and Harris, 1978 a and b). When they are available the results of stability and field tests will enable recommendations to be made for the use of this technique and registration of the formulations to be obtained.

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