Formulation And Use Of Invert Emulsions And Other Herbicides[1]

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Though there are many herbicides used in agriculture today, 2,4-dichlorophenoxy acetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) are still the most versatile and widely used for weed and brush control. In order to devote more time to a discussion of formulation, only these two compounds will be mentioned in this paper. It should be understood that most of the herbicides available today can also be formulated in the manner described here for 2,4-D and 2,4,5-T.

These two compounds as they are made in the laboratory are white crystalline powders insoluble in water. If they were packaged and sent to the consumer in this form, it would be virtually impossible to apply them to plants effectively. To be useful, they must first be put into soluble form; they must be formulated as esters, emulsifiable acids or amines.

The two main objectives of formulating are to put the herbicide in the best possible form for the end use for which it is intended, and to improve the performance of the herbicide in controlling plants by increasing its penetration, translocation or its accumulation within the plant.

One of the most common methods of putting 2,4-D and 2,4,5-T into usable form is that of esterification. In this process, 2,4-D or 2,4,5-T is combined with an alcohol and this chemical reaction produces what is called an ester. An ester is not just a mixture of 2,4,5-T acid and alcohol. It is an entirely new compound.

Most usable esters, like the basic 2,4-D and 2,4,5-T acids, are not soluble in water. They can, however, be made oil soluble by various means. By dissolving the ester herbicide in oil and then adding components that will make it possible to mix this ester-oil combination with water, a formulation that can be applied readily in the field with water as the carrier can be produced. The components that make possible the mixing of the ester-oil combination with water are known as emulsifiers. They produce the white milky appearance when a properly formulated weed or brushkiller is added to water.

Esters may be referred to as either "high volatile" or "low volatile" depending on the alcohol from which they are made. High volatile esters are those from alcohols that have a comparatively high degree of biological volatility, such as methyl, butyl, ethyl, pentyl and isopropyl alcohols. The ester generally takes it name from the alcohol from which it was made. Thus the above alcohols would produce the methyl, butyl, ethyl, pentyl and isoporpyl esters of 2,4-D or 2,4,5-T. Allen (2) found that "low carbon straight-chain alkyl esters have greater phytotoxic volatility than the high carbon straight-chain esters, and the phytotoxic volatility decreases with the increase in the number of carbon molecules". Examples of esters having relatively low biological volatility are butoxy ethanol, propylene glycol butyl ether and isooctyl.

Because of the danger of damaging desirable plants with the vapors of high volatile esters, most of the ester weed killers used today are of the low volatile type. Volatility, however, is not the only criterion used in selecting an ester for a weed killer formulation. Field performance of the ester on the specific weed species to be controlled must be good, equalling or surpassing those already in use. Also, it must lend itself to commercial production. Some highly active low volatile esters have had to be discarded because of formulation difficulties.

The selection of the best ester to use with due consideration being given to its field performance and cost is fundamental, but the making of a good weed killer also demands good formulation. Differences in the reported performance of various esters in more likely due to formulation quality than to differences inherent in the esters themselves.

Crafts (5); C. L. Hammer and associates (11); L. S. Audus (4); J. L. Weintraub, J. H. Reinhart, and R. A. Scherff (26) and others show that apparently maximum penetration and translocation of 2,4-D and 2,4,5-T occurs at pH levels below 5 (4,5,11,26). The presence of free acid in emulsifiable form in an ester brushkiller formulation results in a lowering of the pH. The pH of an ester containing no free acid would be approximately 7, while one containing from 5 to 10 percent free acid would be in the pH range of 3 to 5. We thus expect to get much better penetration and translocation from the acid ester than from the neutral ester. This should be especially true in aerial application where volumes of only 3 to 5 gallons of solution per acre are applied and the pH of the final solution is more easily influenced than where high volumes of 300 to 400 gallons are sprayed from the ground. This theory has not yet been tested fully in the field, and doing so might produce some interesting results.

In addition to the proper ester and its blending with free acid to produce a solution pH in the optimum range of 3 to 5, another factor—the addition of oil—is necessary in formulating ester weed killers and is believed beneficial in leaf cuticle penetration (18). Crafts (5) states that ". . . oil, soaking into the cuticle, tends to saturate it with respect to its lipophyllic (oil-holding) capacity and so to free the 2,4-D ester from movement into the phloem in the aqueous phase," although this has not yet been completely substantiated in field testing.

Where foliage applications are to be made, the main problem involved with oil is the selection of the proper amount of oil to cause saturation of the cuticle without severe damage to the living cells in the plant foliage. This is true of oil in the formulation itself and of additional oil that might be added as a carrier in the field. Phytotoxicity of the oil can be very important when crop selectivity is an objective in weed control. Formulating chemists should always be consulted before non-phytotoxic oils are added in the field. The particular weed killer ester being used may not be soluble in the non-phytotoxic oil and a poor field mix may result.

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[1] Paper presented at the Eleventh Annual Nebraska Aerial Applicators Short Course. February 8 and 9, 1962, and by John E. Gallagher at the Hyacinth Control Society, June 18 to 21, 1967.

There is evidence today indicating that esters, though important in penetration, may not function in the translocation and accumulation of 2,4-D and 2,4,5-T in plants. Crafts (8) and Rodgers (19) have both conducted research indicating that esters may be hydrolyzed upon entering plant foliage and remain in the leaf, while in the case of woody plants the acid moves downward in the plant phloem.

The exact form in which 2,4-D and 2,4,5-T move in plants is not definitely known, but it is thought that they move as acids in the aqueous phase of the plant (6,7,8,25).

Attempting to make practical use of this fact, water soluble amine formulations made by dissolving 2,4-D or 2,4,5-T acid in a solution of amine and water were prepared. However, although ground applications at high volumes have been successful, aerial applications of these amines at low volumes have often given erratic results (15, 20). This could be due to the impervious nature of the cuticle to water soluble sprays at the time of application, or it could be due to rapid evaporation in high temperatures. Hardness of water can also affect the penetration of amine sprays. Unless an amine formulation is properly sequestered for use in hard water, a white precipitate which is usually the insoluble calcium salt of the herbicide will be formed. This precipitate plugs spray nozzles and is very difficult for foliage to absorb.

Adding penetrants, wetting agents and surfactants to water soluble amines has helped improve the penetration of amine foliage sprays. Another approach has led to the development of oil-soluble amines. Here the amine of 2,4-D or 2,4,5-T is in an oil phase which is emulsified in water. It is theorized that the amine in the oil phase will overcome the cuticle barrier and still move in the water phase of the plant once the cuticle is passed. Oil-soluble amines are frequently insoluble in water and it may be that they are converted to acid or a water soluble amine within the plant before translocation.

Whether or not there is a ready return to the water phase has not yet been proven. The fact that kills with foliage application of the oil-soluble amines have been equal to, or moderately superior to water-borne amines, particularly late in the season or during dry weather, indicates that this could be the case (13, 15). From field results to date, compared to low volatile esters, the real advantage that the oil soluble amine would offer is one of decreased volatility. A good basic study of the fate of 2,4,5-T oil soluble amine once within a plant is needed today.

Mention should be made at this time of the work being conducted by Starr (22,23) and others on the use of the emulsifiable acid formula of 2,4,5-T through mistblowers. Unlike the chemical reaction that produces an ester or the solubilizing process that produces an amine, the emulsifiable acid is prepared by emulsifying, or suspending, the free acid of 2,4-D or 2,4,5-T in water. The possible beneficial effect of the presence of small amounts of this free acid on the pH of an ester formulation has already been mentioned. It should be emphasized at this point that free acid in emulsifiable form is also a very good herbicide formulation by itself as Crafts (5) and others have found. Starr (22) has reported results with the emulsifiable acid of 2,4,5-T applied in water through a portable mist blower to be superior to both low volatile esters and amines on sweet gum, hickory, post and black jack oak. Further evidence of the effectiveness of emulsifiable acid formulas can be seen in the increased use of the emulsifiable acid of 2,4-D for weed control in Texas and California.

Development of the low volatile ester, the amine, and the emulsifiable acid formulas of 2,4-D and 2,4,5-T greatly reduced the danger of volatility injury. At the same time that work was being done on the problem of volatility, studies were initiated on formulations to reduce the problem of drift. At this point we should understand the difference between volatility and drift. Volatility is the almost unmeasurable movement of a vapor from the point of application as evidenced by formative effects on plants. This movement can occur after application in hot weather. Drift is the movement of fine droplets of spray away from the spray area at the time of application. As a result of these early studies the low drift invert emulsion formulas were developed (3,14,15,16).

Invert emulsions are thick, white, water-in-oil emulsions. In this type of emulsion the oil containing the herbicide is in a continuous external phase around the water droplets. In conventional oil-in-water emulsions the oil and herbicide are in discontinuous oil phase dispersed throughout the water. Invert emulsions are used as carriers for such herbicides as 2,4-D and 2,4,5-T. They are not herbicides in themselves.

Besides controlling drift, it was thought the highly viscous emulsion would increase penetration as a result of greater build-up on plant foliage. The fact that the herbicide is in the external oil-phase would then bring it into close contact with plant foliage for a relatively long time. This proved to be generally true, but it seems to be a distinct disadvantage when inverts are applied to stems and foliage of brush or weeds at high volumes of 400 gallons or more per acre. (3). Within a matter of hours, the entire aerial portion of the plant is browned out from the build-up of thick, white emulsion on the leaves and stems. A second year evaluation of our woody plant test plots revealed that aerial portions of the original plants were killed, but heavy resprouting from the root collar zone occurred on nearly all woody plant species (3,14). This was apparently because the viscous invert emulsion stayed were it was applied and did not run down the stem under the ground litter the way a conventional emulsion would have. It was assumed that no translocation of the herbicide into the roots had occurred and that this was probably due to the rapid injury of the aerial portion of the plant.

Subsequent greenhouse studies on mesquite (*Prosopis* spp.) by Hull (12) indicate that better translocation of 2,4,5-T as an ester in an invert emulsion carrier, compared to an ester in oil occurs if light applications to individual leaves are made. This increased translocation of the invert carrier was also observed by Rediske (21) on greenhouse grown alder (*Alnus rubra*). This information led to aerial application of the invert emulsion of 2,4,5-T at volumes ranging from 5 to 30 gallons per acre. Results generally show that, when these low volumes are properly applied so that even coverage is obtained, the invert emulsion is a effective as a conventional emulsion with the advantage of reduced drift (9,10,14,16,22). However, application by air is more critical because the swath is quite definite with little drift or swirl to cause overlap.

At the present time, the greatest potential of the invert emulsion seems to be for aerial application on utility rights-of-way (16). Applied through a helicopter mounted centrifugal sprayer flying at speeds not to exceed 30 mph, much of the drift from aerial applications of conventional emulsions on these rights-of-way has been eliminated.

Though extensively tried, the centrifugal sprayer has not yet proved satisfactory for dispensing invert emulsions from fixed wing aircraft. Higher flying speeds than those used in helicopter flying have resulted in more shear of the invert droplets. This in turn has caused more fine particles in the pattern and more drift.

Several tests have been run applying the invert emulsion from standard boom and nozzle equipment on fixed wing aircraft. The problem here is that the viscous premixed invert emulsion must be thinned with oil in order to pump it through the booms found on most fixed wing aircraft today. As an invert emulsion is thinned, it approaches the viscosity of a standard oil-in-water emulsion and begins to lose its low drift characteristic. For this reason, premixed invert emulsions are not recommended for application through conventional boom equipment on either fixed wing air craft or helicopters at this time.

Akesson and Yates (1) are currently working on modifications of existing spray equipment on fixed wing aircraft in an attempt to get thick pre-mixed inverts through a boom and nozzle system. Should this work be successful, it would greatly reduce the hazards from herbicidal drift in the areas where fixed wing aircraft operate.

Nearly all of the work to date with invert emulsions has been done on weeds or brush growing on non-cropped areas. Little is known about the use of the invert emulsion in cropped lands. One could imagine that the rapid penetration of oil and herbicide characteristic of the external oil phase of this formulation might cause excessive injury to crop foilage even with low volume aerial applications. Much more work is needed before the invert emusion formula of 2,4-D could be recommended for weed control in crops.

During the past twenty years great progress has been made in increasing the safety and improving the application of herbicides by air. There is much yet to be learned. Progress has been made in controlling volatility and drift by introduction of the low volatile esters, the amines, and the invert emulsion. Scientists have learned much about the absorption, translocation and activity of 2,4-D and 2,4,5-T. Chemists have taken this knowledge and used it to make more effective formulations, and applicators are now contributing greatly in the practical application of these formulas in the field.

The continuation of this fine cooperation effort on the part of each of these groups offers the best chance for solving some of the problems in formulating and applying herbicides that face us today. Undoubtedly a number of you have specific problems on which you think the chemical industry should be working. We would be very glad to hear of them.

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