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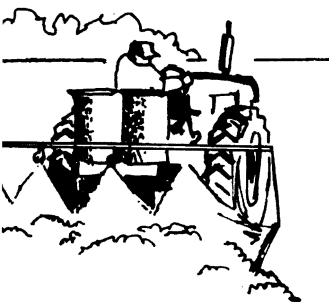
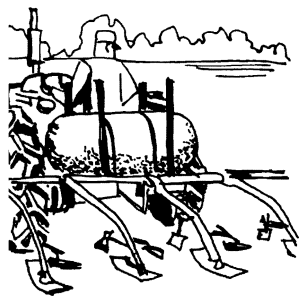
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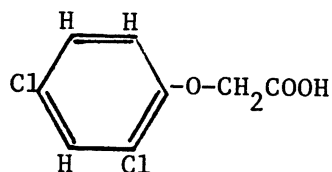
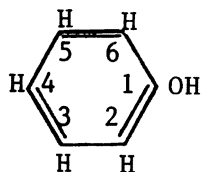
CHEMISTRY AND FORMULATIONS OF 2,4-D

by

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2,4-D is our most common weed control material, but many people do not know that there are many different kinds of 2,4-D. All formulations have the same basic weed killing ingredient but are formulated in various ways for specific purposes. The many formulations can be divided into major groups which will be discussed separately. These are: a) acid, b) salts, c) amines, d) esters (high and low volatile), and e) oil-soluble amines. In addition to 2,4-D, there are several other closely related compounds which are considered as derivatives of phenol and hence the name phenoxy herbicides. These include 2,4,5-T, silvex, MCPA, 2,4-DB, and others. Comparing the molecular structure of 2,4-D with that of phenol, you can better visualize how the chemical name is developed.



The phenol ring is numbered for convenience as shown. Each angle of the ring represents a carbon atom. By observing the two molecules you can see that chlorine atoms have been substituted on the ring at the 2 and 4 position and a 2 carbon unit (acetic acid) has been added. 2,4,5-T is identical with 2,4-D with the exception of an additional chlorine atom substituted at the 5 position of the ring.

The growth regulatory and weed control potentials of 2,4-D were discovered in the early 1940's. Early information on the use of 2,4-D was classified during the war period.

Although a tremendous amount of research has been conducted with 2,4-D, it is still not clear how 2,4-D kills plants or why it is selective for broadleaf plants. Studies have shown that many plant processes are affected by 2,4-D. Respiration, food utilization, cell division and cell enlargement are all increased following application. Recent work would indicate that it has a more basic action which is an effect on the nucleic acids of the cells. The nucleic acids contain the information for directing cell processes and to disrupt this system can cause many side effects. The common expression that 2,4-D causes a plant to grow itself to death may be as near the truth as any present scientific explanation.

The 2,4-D applied to a plant leaf must gain entry to be effective. Once inside it may be moved through the plant. This movement is called translocation and is responsible for the root kill of many deep rooted plants. Movement occurs in the living tissue which carries food throughout the plant (phloem). When excessive rates of 2,4-D are applied or other materials added to give a contact burn, living tissue is destroyed and translocation into the root system is reduced or prevented. Thus addition of oil to a foliar spray of 2,4-D and/or 2,4,5-T will hasten top kill but excessive re-growth may occur.

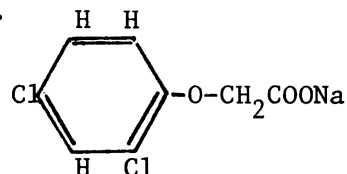
2,4-D is also used as a preemergence herbicide. Again its action is primarily selective for broadleaf weeds. Under ideal conditions some control of emerging grasses may be realized. Duration of 2,4-D in the soil is short and usually does not exceed 4 weeks. Loss from the soil is primarily by the action of soil microorganisms.

FORMULATIONS OF 2,4-D:

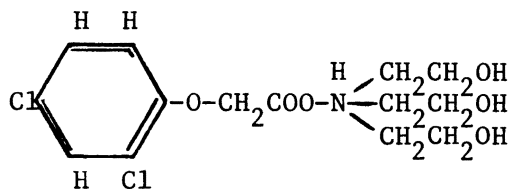
Acid: The pure acid of 2,4-D has very low water solubility but may be dissolved in various solvents or suspension agents that can mix with water. AmChem's Weedone 638 is an example of an acid formulation of 2,4-D.

Salts: Various salt formulations of 2,4-D are on the market. These appear as white powders that dissolve in water.

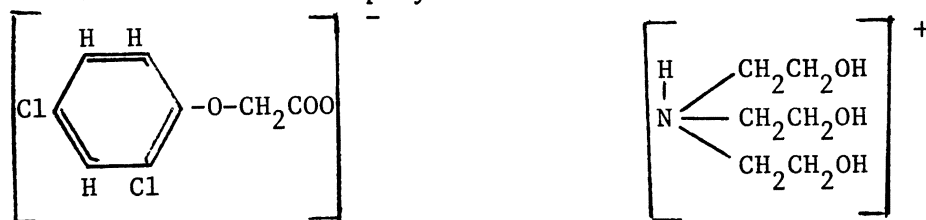
Shown is the sodium salt, but others include the potassium, lithium, and ammonium salts.



Amines: The amines and esters are by far the more popular formulations. The amines are more accurately known as amine salts since they combine an amine grouping with one of the above salts. Amines are ammonia (NH₃) derivatives with hydrogen atoms replaced by alcohol groupings. Methanol (CH₃OH) and ethanol (CH₃CH₂OH) are common substitutions. A common commercial formulation is the triethanolamine salt of 2,4-D.



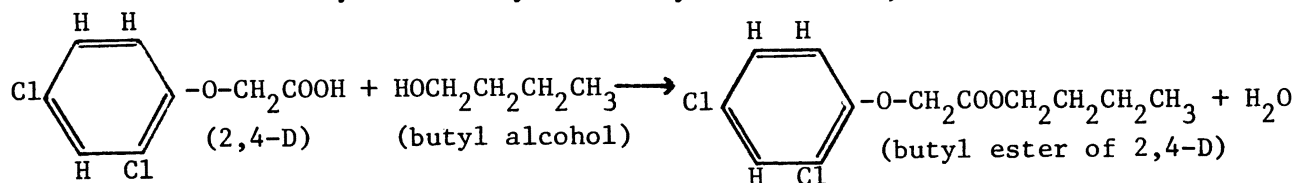
The amine salts are quite soluble in water and form true solutions when added to a spray tank. The amine salts as well as the salt formulations dissociate in the spray tank as follows:



Thus if other salts (calcium and magnesium in hard water, or others in liquid fertilizer) are present, reactions may occur which will result in insoluble precipitates. Such precipitates can clog sprayers and are extremely difficult to remove.

Amine salts and salts are nonvolatile and do not evaporate after reaching the plant or soil surface. Thus where high temperatures (excess of 80°F.) are expected or when applications in close proximity to actively growing sensitive plants, the amines should be used in preference to ester formulations. A disadvantage of the amines is their water solubility which allows them to be washed from the plant surface by rain. As a rule the majority of the applied 2,4-D which is going to enter the plant will have done so in the first 6 hours. Thus if an amine salt formulation remains on the plant for at least 6 hours prior to rain no serious loss of effectiveness should occur.

Esters: An ester is formed by combining an alcohol with an acid. The resulting ester receives its name from the alcohol used. Thus 2,4-D acid combined with butyl alcohol yields butyl ester of 2,4-D as shown below.



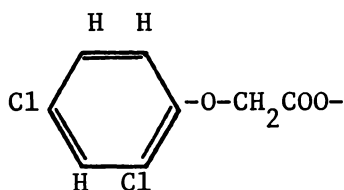
Esters are soluble in organic solvents and nearly insoluble in water. Commercial ester formulations are dissolved in oil carriers with an emulsifier. When added to water in the spray tank they form emulsions of tiny oil droplets (containing 2,4-D) dispersed in water. Such a dispersion creates a milky appearance rather than the clear (but colored) solution which results when an amine salt is added.

When esters are sprayed on a plant surface the water evaporates and leaves a thin film of oil containing 2,4-D. As esters are oil soluble rather than water soluble, they do not wash off as readily during rain. Esters are also considered to have greater killing power than amines on certain plants. (On some woody species the amines may be superior to esters.) This is thought to be partially due the presence of the oil

carrier which permits increased penetration of esters. Leaf surfaces are covered by a waxy substance called cutin. The oils containing 2,4-D can conceivably dissolve their way into or through the waxy layer. An example of this is with wild garlic where we recommend specifically the ester formulation. This plant has a particularly waxy leaf surface and results with amine formulations are much less effective.

Volatility of esters: Many individuals do not understand the difference between volatility and spray drift. Volatility is the evaporation of the 2,4-D ester molecules from the plant or soil surface after application. Spray drift is the physical movement of tiny spray droplets at the time of application. Spray drift is dependent upon wind velocity, droplet size, and distance to ground. Droplet size is primarily controlled by pressure, nozzle size, and nozzle design, and nature of material being applied. Most cases of injury are from spray drift and not due to volatile vapor drift. ALL FORMULATIONS CAN RESULT IN SPRAY DRIFT WHEN MISUSED.

Ester formulations vary widely in their degree of volatility. Volatility of 2,4-D esters is primarily controlled by the length of the carbon chain that composes the alcohol portion of the 2,4-D ester molecule. Four of the common ester formulations in decreasing order of volatility are:



- a) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH} \\ | \\ \text{CH}_3 \end{array}$ (isopropyl)
- b) $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (butyl)
- c) $\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (butoxyethanol)
- d) $\begin{array}{c} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH-CH}_3 \\ | \\ \text{CH}_3 \end{array}$ (isooctyl)

When the alcohol portion exceeds 4 carbons in length, the ester is considered to be low volatile. Thus the isopropyl and butyl esters are sold merely as "ester" while the butoxyethanol and isooctyl esters are sold as "low volatile esters". The high volatile esters have been out-lawed in many states and are not recommended for any purpose in Virginia. At temperatures in excess of 100°F. volatilization of the low volatile formulations becomes significant. As leaf or soil temperatures exceed air temperatures, we suggest that low volatile esters not be used when air temperatures exceed 80°F.

Oil-Soluble Amines

From the above discussion you can see that esters may be superior to amines because they do not readily wash from the plant surface and because of their possible increased penetration. The amines, however, are superior to the esters by virtue of nonvolatility. Oil-soluble amines were formulated to combine the benefits of both into a single formulation. Dacamine (Diamond-Shamrock) and Emulsamine (AmChem) are examples of oil-soluble amine

formulations of 2,4-D. The disadvantages of the oil-soluble amine formulations are their higher cost and syrupy consistency which makes it difficult to pour them from containers at cool temperatures. Also the drift potential of oil-soluble amines may be greater than that of water soluble amines or esters because of the greater amount of emulsifier present in the formulation.

ALL FORMULATIONS OF 2,4-D POSE POTENTIAL DRIFT PROBLEMS AND INJURY CAN ONLY BE AVOIDED BY PROPER APPLICATION.

Trade and brand names are used only for the purpose of information and the Virginia Cooperative Extension Service does not guarantee nor warrant the standard of the product, nor does it imply approval of the product to the exclusion of others which may also be suitable.

Keys to Proper Use of Pesticides

1. Read the label on each pesticide container before each use. Follow instructions to the letter; heed all cautions and warnings, and note precautions about residues.
2. Keep pesticides in the containers in which you bought them. Put them where children or animals cannot get to them, preferably under lock and away from food, feed, seed, or other material that may become harmful if contaminated.
3. Dispose of empty containers in the manner specified on the label. If disposal instructions are not printed on the label, burn the containers where smoke will not be a hazard, or bury them at least 18" deep in a place where water supplies will not be contaminated.

SEE YOUR DOCTOR IF SYMPTOMS OF ILLNESS OCCUR DURING OR AFTER USE OF PESTICIDES.