Selection of Fatty Acid Derivatives

Surfactant Formulations for the Control of Plant Meristems

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The selective action of fatty acid derivatives as chemical pruning agents and tobacco sucker control agents depends on the class and amount of surfactant used to emulsify them. Effective emulsions killed the most active meristematic tissues without damaging the remaining parts of the plant. Emulsion systems were selected through a four-step procedure: Evaluate surfactants as emulsifiers of fatty acid derivatives; apply efficient emulsifiers as aqueous sprays to select nontoxic ones; apply emulsions containing surfactant and fatty acid derivatives (1-to-1 ratio) to determine extent of tissue kill and axillary bud regrowth; and evaluate various ratios of fatty acid derivative to surfactant to find the most effective emulsions. Effective methyl decanoate and 1-decanol emulsions were prepared with polyoxyethylene(20) sorbitan monolaurate and polyoxyethylene(20) sorbitan monooleate, respectively. Terminal buds were killed, and lateral shoots developed normally on chrysanthemum plants treated with emulsions containing the ester or the alcohol at a 1-to-1 ratio with the surfactants. Terminal buds or axillary buds of decapitated tobacco plants were killed by emulsions containing 2 parts of alcohol to 1 part of surfactant or 3 parts of ester to 1 part of surfactant. The various fatty acid derivatives have specific hydrophile-lipophile balance (HLB) requirements for the formation of stable emulsions. Particular plant species, or even cultivars, appear also to have specific HLB requirements for efficient utilization of the emulsions.

Previous reports showed (Cathey *et al.*, 1966; Steffens *et al.*, 1967; Tso, 1964) that the fatty acid methyl esters and alcohols with chain lengths of C_8 to C_{12} were highly active in selectively killing or inhibiting axillary bud growth of tobacco and terminal bud growth of a wide variety of plants. These chemicals have thus been called chemical pruning agents or tobacco sucker control agents. However, without the proper type and amount of surfactant, the esters and alcohols exhibit nonselective kill of tissue.

Jansen *et al.* (1961) and Jansen (1964) have shown that surfactant type and amount markedly affect the activity of herbicides. In the absence of herbicides, a number of surfactants showed inherent phytotoxicity at relatively high levels and some stimulated growth at low concentrations. There were some indications of synergism between some of the active herbicides and surfactants when properly selected and formulated.

Surfactants can act as emulsifiers, wetting agents, solubilizers, detergents, suspending agents, etc., when included in sprays for agricultural uses. Smith and Foy (1966) reported that C^{14}-labeled polyoxyethylene (20) sorbitan monolaurate (Tween 20) was very poorly translocated in plants, if at all. The selective kill of meristematic tissue by fatty alcohol and ester emulsions is related to the ability of the alcohols and esters *per se* or the alcohol—or ester—surfactant system (possibly in combination with water) to penetrate young plant tissue. Studies with C^{14}–labeled methyl laurate emulsions have shown that once penetration has occurred, the ester, *per se,* is not translocated but is restricted to the general area of application (Tso *et al.*, 1966).

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This paper reports findings on the interaction of surfactant systems with the fatty acid esters and fatty alcohols as chemical pruning agents and tobacco sucker control agents.

MATERIALS AND METHODS

Test Plants. *Nicotiana tabacum* L. cv. Xanthi-nc, Connecticut Broadleaf, and Hicks and *Chrysanthemum morifolium* Ramat. cv. Improved Indianapolis yellow plants were greenhouse-cultured as previously described (Cathey and Steffens, 1968; Steffens *et al.*, 1967). The plants were treated with aqueous sprays which contained fatty alcohols or fatty acid esters, the alcohols or esters plus surfactant, or surfactant alone.

Tobacco Tests. Tests on tobacco plants were conducted in two ways. With Xanthi, the terminal buds were not removed before treatment to determine the effectiveness of the spray for inhibiting terminal bud growth. Connecticut Broadleaf and Hicks plants were treated after removal of the terminal bud to determine the effectiveness of the spray for inhibiting the growth of axillary buds. About 5 ml. of spray solution were applied to each Xanthi plant and 20 ml. of spray were applied to each Connecticut Broadleaf or Hicks plant with air pressure sprayers as previously described (Steffens *et al.*, 1967). The spray covered portions of the upper leaves and drained down along the stem of the plant and thus also came in contact with the small axillary buds.

Tobacco plants were harvested 14 days after treatment. Results of tests are expressed as per cent reduction in weight of suckers from topped plants and per cent reduction in top growth of untopped plants. Weights of suckers or top growth of treated plants were compared with suckers or tops from untreated controls.

Chrysanthemum Tests. The sprays were applied with an ordinary throat atomizer. The entire top of the plant, including terminal bud and surrounding leaves of various stages of maturity, was sprayed until the foliage glistened but not until runoff. Lateral growth was harvested and weighed 21 days after treatment. The objective was to kill the terminal meristem, thus allowing the axillary shoots to develop. Results are expressed as a percentage of the growth of manually pruned plants. Lateral buds from the upper portion of the stem were counted.

Spray Solutions. The fatty acid esters and fatty alcohols used in these experiments are insoluble in water. Therefore, stable emulsions must be prepared with the aid of surfactants. The selection of surfactant type and amount to form stable emulsions of these chemicals is described below. Fairly stable water suspensions can also be prepared with the fatty acid derivatives and alcohols by use of high-frequency sound with no added surfactants. Many surfactants and surfactant combinations diluted with water were applied to plants to determine if the surfactants themselves were phytotoxic.

The following fatty acid esters were tested: methyl hexanoate (C_6), methyl octanoate (C_8), methyl decanoate (C_{10}), methyl dodecanoate (C_{12}), methyl tetradecanoate (C_{14}), and methyl hexadecanoate (C_{16}). The tests with1-decanol represent the results obtained with the fatty alcohols.

Selection of Surfactants. Since there is such a multiplicity of available surfactants, we initiated our search using the hydrophile-lipophile balance (HLB) system (Behrens, 1964; Griffin, 1965). The HLB value is an expression of the relative simultaneous attraction of an emulsifier for water or oil. The HLB of an emulsifier is an indication of its behavior characteristics but not of emulsifier efficiency. Both the best HLB and the best chemical class of emulsifier must be found.

Emulsion Preparation. All emulsions were prepared in the following manner: The fatty ester or alcohol was thoroughly mixed or blended with equal weights (or less) of surfactant. Water was added until the mixture thickened or formed a gel. Water was slowly added to the required volume while stirring to form a colloidal emulsion which was opalescent and stable. It is imperative that the ester or alcohol be thoroughly blended with the surfactant before any water is added. Other procedures almost always result in emulsions with poor stability.

RESULTS

By screening surfactants with different HLB's, it was determined that, for emulsion stability, an HLB of about 13 was best for methyl decanoate and an HLB of about 15 was suitable for 1-decanol when the ratio of ester or alcohol to surfactant was 3 to 1. Several hundred surfactants and surfactant blends were tested for their ability to form stable methyl decanoate emulsions. A smaller number were tested with 1-decanol. The emulsions were prepared as described, uniformly mixed after preparation, and allowed to stand a standard period of time. To determine relative stability, the fatty layer or "cream" which separated out at the top of the tube was measured. Of the many surfactants tested, relatively few produced stable methyl decanoate and 1-decanol emulsions.

Figure 1. Improved Indianapolis Yellow chrysanthemum sprayed with preparations of 0.16*M* methyl decanoate

Left to right. Sonified suspension, terminal bud killed, leaf damage; emulsified with phosphate surfactant, terminal and lateral buds killed, leaf damage; an ethoxylated alcohol, terminal bud stunted, leaf damage; and an ethoxylated sorbitan fatty ester [polyoxyethylene(20) sorbitan monolaurate], terminal bud killed, later buds developing normally. Photographed 21 days after treatment

Once surfactants were found which formed stable emulsions with the esters and alcohols, the surfactants alone in water were applied to test plants. Many surfactants at levels necessary to form stable emulsions (1% or more) with the esters and alcohols themselves damage foliage and stem tissue of plants. A large number of surfactants which formed stable emulsions with the esters and alcohols were unsuitable for this reason.

The stable emulsions, with ester and alcohol concentrations in a range known to be effective for chemically pruning chrysanthemum and controlling sucker growth of tobacco, were applied to test plants. In the case of chrysanthemum, the useful emulsions selectively killed the stem apex without damaging the side growing points, foliage, and stem tissue (Figure 1). It is also required that the side shoots on chemically pinched chrysanthemum plants develop as rapidly and in the same number as on hand-pinched plants. The methyl decanoate–surfactant systems meeting the requirements for chemically pinching chrysanthemums are indicated in Table I. The surfactants listed are not all-inclusive, but illustrate the surfactant families found useful for preparing emulsions for chemically pinching chrysanthemums.

For tobacco, the emulsions considered promising killed both the terminal and axillary buds of Xanthi plants or the axillary buds of decapitated Connecticut Broadleaf or Hicks plants without causing leaf injury or distortion. Some of the 1-decanol–surfactant systems fulfilling these requirements are indicated in Table II. Again the surfactants listed illustrate the surfactant types which have shown promise in the author's tests. The surfactants used to make emulsions of the fatty acid derivatives which caused no visible injury as shown in Tables I and II, had no visible effects on plants when

Table I. Effect of Surfactant Type or Class for Emulsifying Methyl Decanoate to Chemically Prune Improved Indianapolis Yellow Chrysanthemum

Spray was 0.16*M* methyl decanoate with 3% surfactant

Representative Surfactant			Weight of	
Class, type, and trade name	Chemical description[a]	Source[b]	Lateral Shoots,[c] %	Leaf Injury[d]
Nonionic surfactants				
Phenol type				
Tergitol 12-P-12	Polyoxyethylene(12) dodecylphenol	5	103	—
Tergitol NPX	Polyoxyethylene(10) nonylphenol	5	44	+
Fatty ester type				
Tween 20	Polyoxyethylene(20) sorbitan monolaurate	1	102	0
Tween 21	Polyoxyethylene(4) sorbitan monolaurate	1	67	—
Tween 80	Polyoxyethylene(20) sorbitan monooleate	1	87	0
Other types				
ACL-429	Ethoxylated imidazoline	1	102	0
G 1288	Polyoxyethylene fatty glyceride	1	119	0
G 1300	Polyoxyethylene fatty glyceride	1	79	0
Triton B-1956	Modified phthalic glycerol alkyl resin	4	139	+
Anionic surfactants				
Gafac PE 510	Free acids of complex organic phosphate esters	2	110	+++
Gafac PE 510	Free acids of complex organic phosphate esters	2	114	+++
Santomerse #85	Sodium dodecyl benzene sulfonate	3	129	+
Petronate K	Higher alkyarylsulfonates	6	59	++++

[a] Figures in parenthesis designate mole ratios of ethylene oxide per hydrophobe.
[b] 1 = Atlas Chemical Industries, Wilmington, Del.; 2 = General Aniline and Film Corp., 140 West 51st St., New York, N.Y.; 3 = Monsanto Chemical Co., 800 North Lindbergh Blvd., St. Louis, Mo.; 4 = Rohm & Haas Co., Washington Square, Philadelphia, Pa.; 5 = Union Carbide Chemical Co., 270 Park Ave., New York, N.Y.; 6 = Witco Chemical Co., 277 Park Ave., New York, N.Y.
[c] Weight of lateral shoots from manually pruned plants = 100% after 21 days.
[d] Injury; 0 = none to ++++ = severe.

Table II. Effect of Surfactant Type or Class for Emulsifying 1-Decanol to Control Terminal Bud Growth on Xanthi Tobacco

Spray was 0.16*M* 1-decanol with 3% surfactant

Representative Surfactant			Terminal	
Class, type, and trade name	Chemical description[a]	Source[b]	Bud Control,[c] %	Leaf Injury[d]
Nonionic surfactants				
Alcohol type				
Brij 58	Polyoxyethylene(20) cetyl ether	1	92	+
Brij 78	Polyoxyethylene(20) stearyl ether	1	95	+
Brij 98	Polyoxyethylene(20) oleyl ether	1	69	+
Fatty ester type				
Tween 40	Polyoxyethylene(20) sorbitan monopalmitate	1	91	0
Tween 60	Polyoxyethylene(20) sorbitan monostearate	1	99	0
Tween 80	Polyoxyethylene(20) sorbitan monooleate	1	92	0
Other types				
ACL-429	Ethoxylated imidazoline	1	100	+
Anionic surfactants				
Gafac PE 510	Free acids of complex organic phosphate esters	2	100	+++

[a] Figures in parenthesis designate mole ratios of ethylene oxide per hydrophobe.
[b] See footnote[b], Table I.
[c] Per cent by which treatment reduced weight of top growth compared to untreated control after 14 days.
[d] Injury; 0 = none to +++ = severe.

they were applied alone as aqueous sprays at concentrations up to 3%.

At relatively high concentrations, methyl esters, shorter or longer than C_{10}, also control tobacco sucker growth. As shown in previous publications, on a molar basis, the C_{10} methyl ester is the most effective; the C_8 is usually less active; and esters longer than C_{10} can cause marked leaf injury. When the methyl esters with even-number carbon chain lengths of C_8 to C_{16} were applied to greenhouse-grown tobacco at the relatively high concentration of 5% with 1% surfactant (polyoxyethylene sorbitan monolaurate), all esters killed the axillary buds (Figure 2, left). The injury level increased progressively from a low of 2 (very slight) with the C_8 ester to 10 (severe) with the C_{16} ester. When these esters were applied without surfactant (sonified), their effectiveness markedly decreased and they tended to act nonselectively and erratically (Figure 2, right). The leaf injury caused by all the esters without surfactants was high (severe to very severe). These results

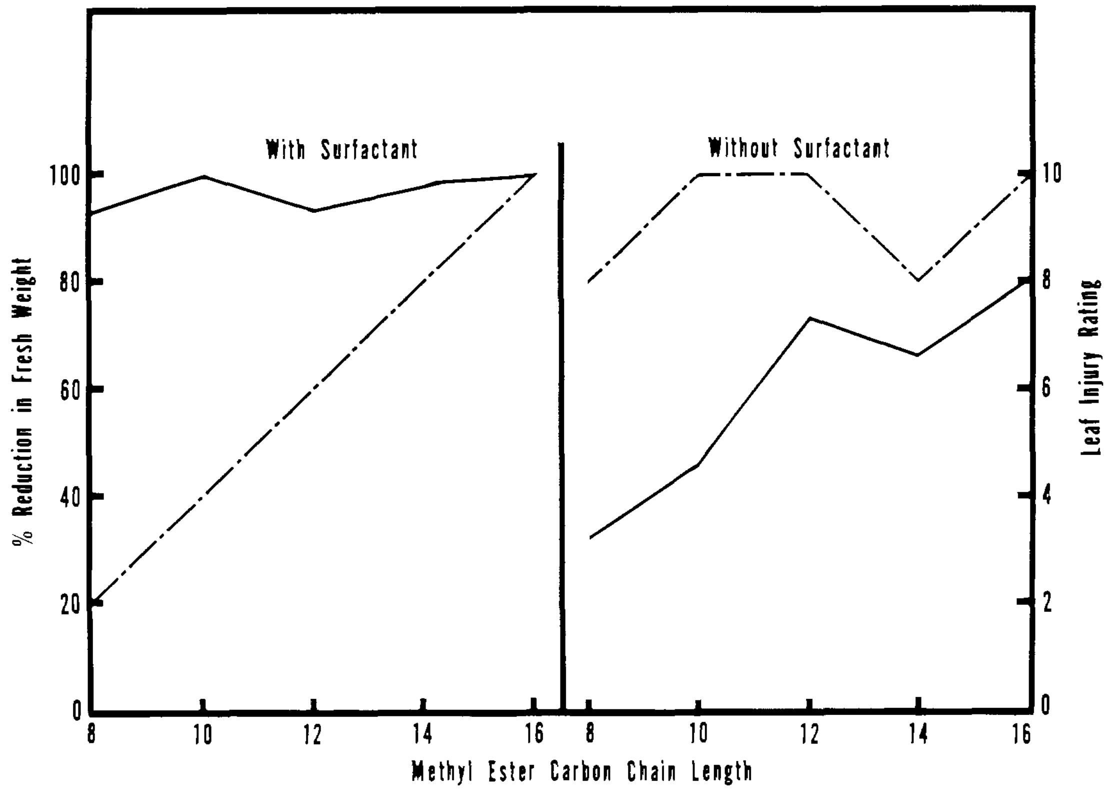

Figure 2. Effect of fatty acid methyl esters with and without surfactant

——— Terminal bud growth (% reduction in fresh weight)
– — – Leaf injury (0 none, 10 severe) of tobacco

Topped plants treated with 5% fatty acid methyl esters: *Left,* spray solution included 1% polyoxyethylene sorbitan monolaurate type surfactant; *right,* methyl esters dispersed by sonification just before spray applied. Results 14 days after treatment

illustrate the role of surfactants in improving selectivity and reducing leaf injury.

The ratio of surfactant to alcohol or ester also plays an important role in determining the over-all effectiveness of the spray emulsions. This was illustrated by applying to Xanthi tobacco plants sprays which had varying amounts of polyoxyethylene(20) sorbitan monooleate but a constant amount of 1-decanol. The 1-decanol concentration was relatively high (3%), to demonstrate the effect of surfactants in reducing leaf injury caused by the alcohol. Figure 3 shows that the effectiveness of the emulsion is reduced and leaf injury is increased as the amount of surfactant is reduced in the spray solution. Figure 4 illustrates the type and extent of leaf injury caused by lowering the surfactant level. The data show that 2 parts of 1-decanol to 1 part of polyoxyethylene(20) sorbitan monooleate inhibited terminal and axillary bud growth on Xanthi plants with only minor amounts of leaf injury.

For a given nonionic hydrophobe, the addition of increasing amounts of ethylene oxide renders the resulting surfactant increasingly more hydrophilic (higher HLB's). Within a given chemical type, however, surfactants of a high and low HLB may be proportionally blended to provide any HLB within the range, equivalent to intermediate degrees of ethoxylation of the hydrophobe. Experience in emulsion technology has shown that individual solute-solvent systems have specific required HLB's for optimum emulsification. In this work this principle was expanded to determine the required HLB for chemical pinching of Improved Indianapolis Yellow chrysanthemum. In preparing HLB series for three surfactant chemical types, the most effective HLB for pinching chrysanthemum with the methyl decanoate emulsions ranged between 16 and 17 (Figure 5). The emulsions containing surfactants with HLB's lower than 16 and higher than 17 were less effective. The particular relationship shown in Figure 5 may hold true only for the specific set of circumstances encountered in these tests—the ratio of fatty ester to surfactant, emulsion concentration, surfactant type, and plant species or even cultivar. Similar tests were tried with tobacco without success. To be effective on tobacco, the emulsion must kill the axillary buds so that regrowth does not occur rapidly. The concentrations of fatty esters or alcohol required for this may have masked the more subtle effect of HLB differences.

DISCUSSION

The role of the surfactant type and amount as discussed in this paper goes beyond the concepts generally used by workers studying plant-growth regulators. Many

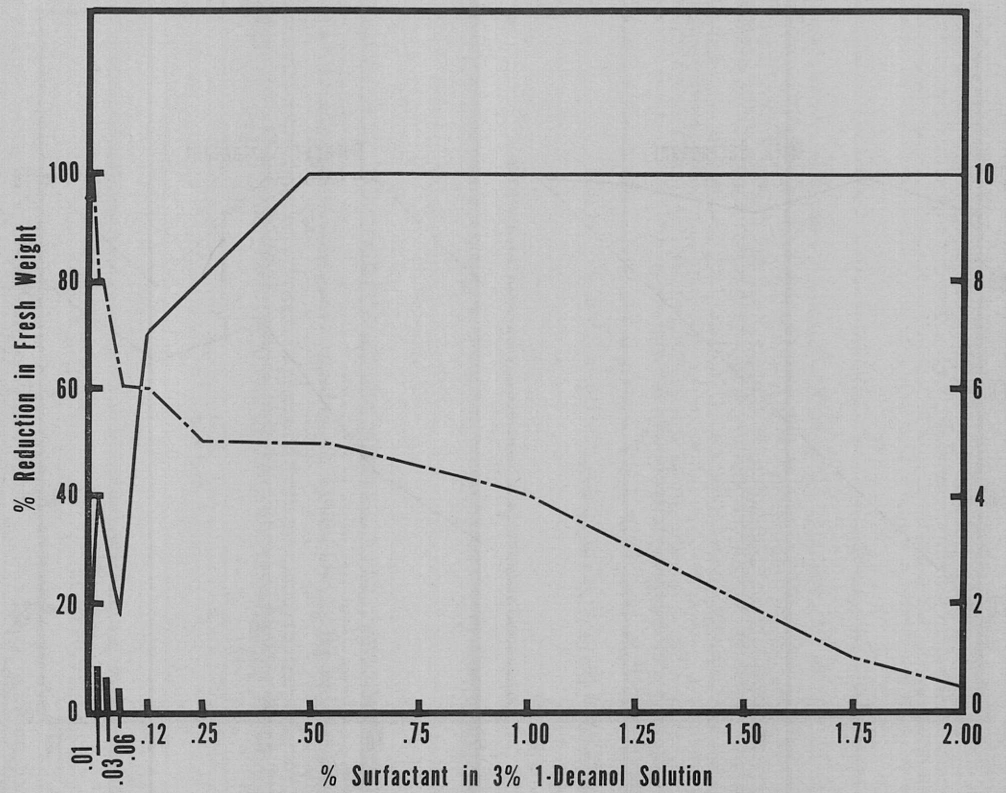

Figure 3. Effect of 0.16*M* 1-decanol containing various levels of polyoxyethylene(20) sorbitan monooleate surfactant

——— Terminal bud growth (% reduction in fresh weight)
– — – Leaf injury (0 none, 10 severe) of Xanthi tobacco 14 days after treatment

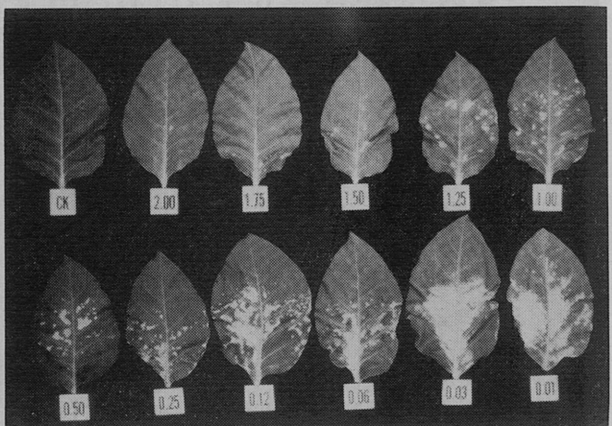

Figure 4. Injury to Xanthi tobacco leaves from plants treated with 0.16*M* 1-decanol containing various levels (per cent) of polyoxyethylene(20) sorbitan monooleate surfactant

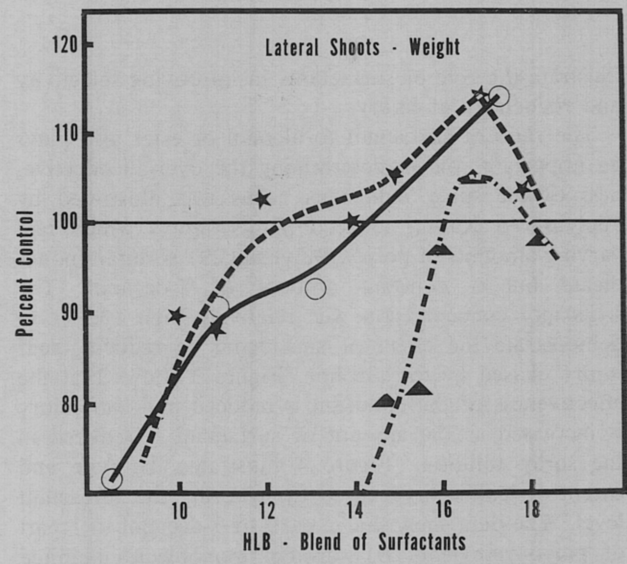

Figure 5. Effect of 0.16*M* methyl decanoate emulsified with surfactants (3%) having different hydrophilic-lipophilic balance (HLB) on lateral shoot weight of Improved Indianapolis Yellow chrysanthemum

Lateral shoots harvested 3 weeks after treatment. Manually pruned plants equal 100%
○ Sorbitan monolaurate and polyoxyethylene sorbitan monolaurate blends
* Sorbitan monolaurate and polyoxyethylene sorbitan monooleate blends
▲ Polyoxyethylene fatty glyceride blends

plant-growth regulators are soluble in water; a wetting agent at a rate of 0.05 to 0.1% is added to aid in spraying. The traditional descriptions of active and additive compounds do not apply in the presentation.

The system described is based on the blending of the two chemicals, the formation of micelles, and their dispersion in water. The emulsions thus formed penetrate only the youngest and most active meristematic tissues and apparently remain on or near the surfaces of the more mature tissues without damaging them. The extent of plant tissue kill depends upon many factors. Some of these, as to the type of leaf, its degree of succulence, and the ease with which it can be wet, set up the requirements for the type and amount of surfactant which must be used to utilize the fatty acid derivatives effectively as pruning or sucker control agents. When surfactants are not included in the final spray solutions, nonselective tissue kill occurs, which results in low effectiveness and marked leaf injury.

Thus far, only empirical observations can be made in the laboratory on the type and stability of the emulsions. Many different surfactants from various classes were effective emulsifiers of the fatty acid derivatives. Many of the surfactants which were effective emulsifiers when applied as aqueous sprays at rates of 1 to 3% damaged the more mature parts of the plants and thus were excluded from further testing. Other surfactants, even in the same class as phytotoxic ones, were effective emulsifiers of the fatty acid derivatives and produced restricted and selective killing of tissues without damaging the remaining parts of the plants. The final decision on the selection of an effective emulsion must be made from testing various ratios of the fatty acid derivatives and the surfactants on plants. Hydrophile-lipophile balance (HLB) of a given surfactant type is important in selecting the most stable emulsion, but the HLB requirement of a particular plant species, or even cultivar, may also be important in determining the efficiency of the applied emulsion.

The most effective emulsions as pruning or suckering agents were different for the chrysanthemum and tobacco plants. In previous papers the authors showed that the structural requirements for the action of the fatty acid derivatives were similar for the various species of plants tested. The role of the surfactant then becomes a way of inducing the fatty acid derivatives to produce a specific effect on a specific plant species. Varying degrees of leaf damage on the mature leaves of the various species tested were also observed; other species can exhibit severe leaf damage when treated with emulsions that were effective on chrysanthemum and tobacco. Other surfactants from different classes, even ones which were discarded as being toxic to chrysanthemum or tobacco leaves, may be effective emulsifiers of fatty acid derivatives and produce safe and selective chemical pruning or sucker control agents on other plants.

Techniques are needed to determine for a specific species of plant the classes and kinds of surfactants which will aid in the uptake and selective action of the applied chemicals. This approach is already being used to increase the effectiveness and selectivity of herbicides, insecticides, and to a lesser extent, fungicides and bactericides. It should also be used to increase the usefulness of applied growth regulators.

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