Fats and Oils in Agriculture

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ABSTRACT AND SUMMARY

Fats, oils, and their derivatives are reviewed, in their roles as emulsifiers and surfactants and as pesticide derivatives, and in their activity per se. As emulsifiers and surfactants they offer a wide range of hydrophile-lipophile balance (HLB) values to assist formulators in developing saleable products. Their lipoid solubilities aid in evaporation retardation, plant penetration, and absorption. Often they greatly improve the performance of the active ingredients. Nitrogen derivatives such as amines and quaternaries, fatty alcohols, acid esters, and other agricultural chemicals are reviewed. Examples are cited on the effect of the length of the carbon chain and their number in such herbicides as 2,4-D and dalapon, as well as the biological properties of various aliphatic groups in insect larvicides, plant growth regulators, and fungicides. The role vegetable oils can play in the looming energy shortages as petroleum oil substitutes is discussed. They offer a challenging future in agricultural applications.

INTRODUCTION

Fats and oils are valuable sources of renewable, versatile, biodegradable derivatives that have an important impact on agriculture. They are used as emulsifiers for oil-in-water and water-in-oil systems, as surfactants and wetting agents, as pesticide intermediates, and as agricultural aids per se.

EMULSIFIERS AND SURFACTANTS

The wide range of emulsifiers and surfactants can be classified as anionic, cationic, nonionic, and ampholytic (1) (Table I). Within these groups only a portion have been cleared by the Environmental Protection Agency for use in pesticidal applications. Most often blends of anionics and nonionics, and cationics and nonionics, or blends within the same group are used to best formulate a product or combination of products. Of particular importance is the hydrophilic-lipophilic balance, referred to as HLB value, of the emulsifier or surfactant structure.

As an example, a nonionic series of emulsifiers such as the ethylene glycol esters range from an HLB value of 1.5–almost totally fat soluble, to an HLB value of 19–almost totally water soluble (Fig. 1).

In general, compounds in the HLB range of 1 to 4 are only fat soluble. In the 4 to 7 range, the emulsifers are used to bring water-soluble products into an oil to form invert emulsions (mayonnaise-type). In the 7 to 9 range, toxicants are generally dispersed in water. The 8 to 20 range covers oil-in-water emulsions and in some cases, true solutions.

Up until the early 60s, the active pesticide ingredients such as chlordane, DDT, toxaphene, benzene hexachloride, and the phenoxy herbicides were relatively inexpensive. Formulators reluctant to increase the cost of the product found the anionics cheap and compatible with nonionics and the active ingredient; they became the emulsifiers of choice.

However, a number of the cheap toxicants have become implicated as being too persistent and are being banned as environmental pollutants. They are being replaced with less persistent but more expensive pesticides.

The trend today is to seek more efficient emulsifiers that will enhance the activity of the toxicant and thus lower the treatment costs per acre. The cationics once thought to be too expensive are now playing an increasing role in improving formulations. For example, Matteson and Taft (2) screened 87 adjuvants for their influence on the systemic activity of phorate {0,0-diethyl-S-[(ethylthio)-methyl] phosphorodithioate} and 4-dimethylamino-3,5-xylyl-N-methylcarbamate (Zectran®) added to nutrient solution in which cotton seedlings were growing. Boll weevils were confined for 48 hr on the plants. Only three adjuvants, all quaternary ammonium chlorides, enhanced the activity of Zectran from an average of 20.4% mortality to as high as 76.8%.

TABLE I

Classification of Emulsifiers and Surfactants[a]

- I. ANIONIC
  - [b]A. Carboxylic acids
    - 1. Carboxyl joined directly to hydrophobic group.
    - 2. Carboxyl joined through an intermediate linkage.
  - [b]B. Sulfuric esters (sulfates)
    - 1. Sulfate joined directly to hydrophobic group.
    - 2, Sulfate group joined through intermediate linkage.
  - C. Alkane sulfonic acids
    - 1. Sulfonic group directly linked to hydrophobic group.
    - 2. Sulfonic group joined through intermediate linkage.
  - D. Alkyl aromatic sulfonic acids
    - 1. Hydrophobic group joined directly to sulfonated aromatic nucleus.
    - 2. Hydrophobic group joined to sulfonated aromatic nucleus through intermediate linkage.
  - E. Miscellaneous anionic hydrophilic groups
    - 1. Phosphates and phosphoric acids.
    - [b]2. Persulfates, thiosulfates, etc.
    - [b]3. Sulfonamides.
    - [b]4. Sulfamic acids, etc.
- II. CATIONIC
  - A. Amine salts (primary, secondary, and tertiary)
    - 1. Amino group joined directly to hydrophobic group.
    - 2. Amino group joined through intermedaite linkage.
  - B. Quaternary ammonium compounds
    - 1. Nitrogen joined directly to hydrophilic group.
    - 2. Nitrogen joined through an intermediate group.
  - C. Other nitrogenous bases
    - 1. Nonquaternary bases (e.g., guanidine, thiouronium salts, etc.)
    - 2. Quaternary bases.
  - D. Nonnitrogenous bases
    - 1. Phosphonium compounds.
    - 2. Sulfonium compounds, etc.
- III. NONIONIC
  - A. Ester linkage to solubilizing groups
  - B. Ester linkage
  - C. Amide linkage
  - D. Miscellaneous linkages
  - E. Multiple linkages
- IV. AMPHOLYTIC
  - A. Amino and carboxy
    - 1. Nonquaternary
    - 2. Quaternary
  - B. Amino and sulfuric ester
    - 1. Nonquaternary
    - 2. Quaternary
  - C. Amino and alkane sulfonic acid
  - [b]D. Amino and aromatic sulfonic acid
  - E. Miscellaneous combinations of basic and acidic groups

[a] See reference (1).

[b] Nonfat or vegetable oil origin.

Anionics can affect absorption also. Sands and Bachelard (3) showed the effect of six surfactants and one solubilizer on the uptake of picloram by *Eucalyptus viminalis* and *E. polyanthemos* leaf discs. Two surfactants–lauryltrimethyl-

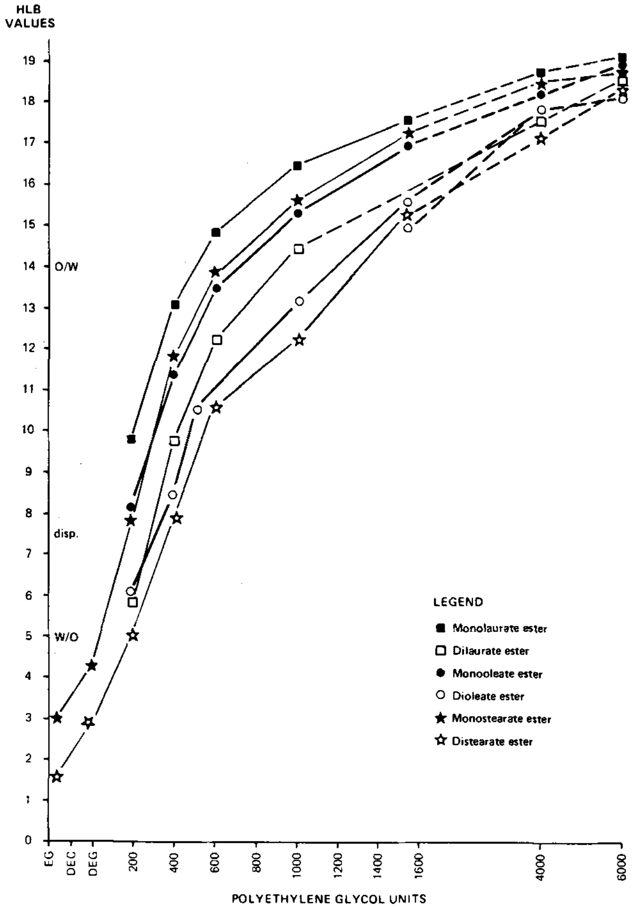

FIG. 1. Effect of addition of polyethyleneglycol (PEG) units on hydrophile-lipophile balance (HLB) value.

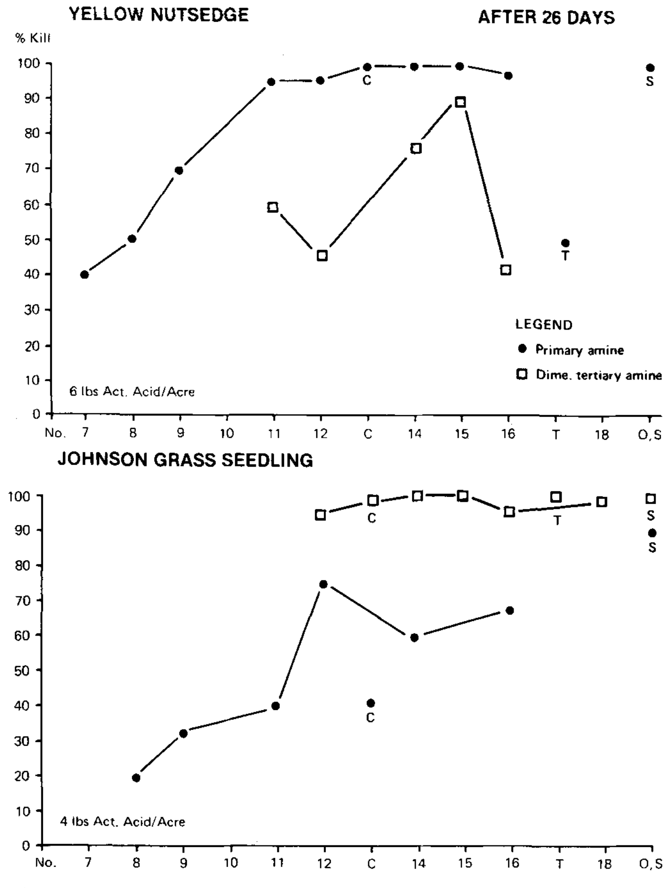

FIG. 2. Activity of dalapon amine salts after 26 days (greenhouse trials).

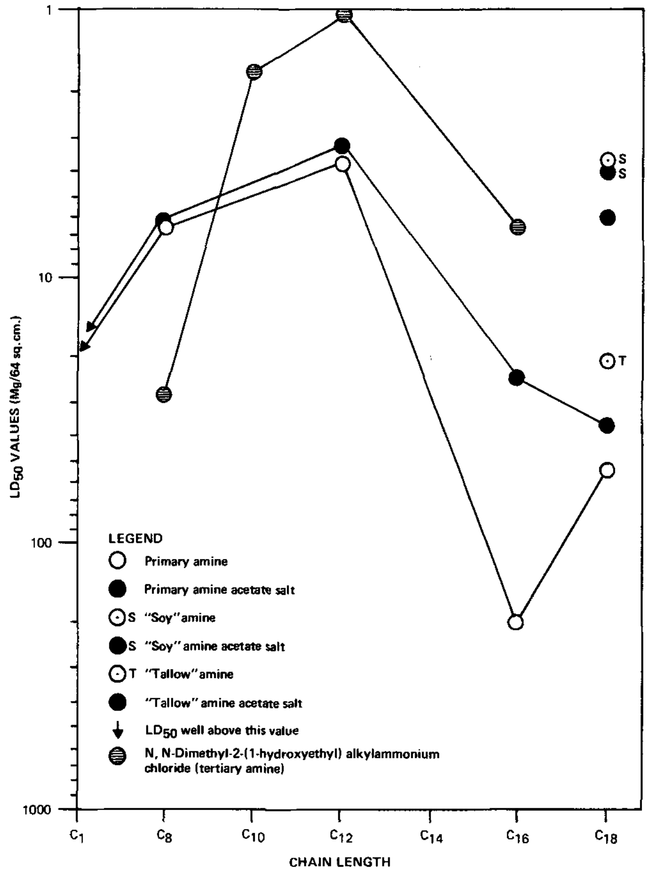

FIG. 3. Effect of varying chain lengths of aliphatic amines and their salts on the larvicidal activity of the compound.

ammonium chloride (Arquad® 12/50) and cocodimethylbenzylammonium chloride (Kemmat® QC-23)—were cationic; two—calcium dodecyl benzene sulfonate (Kemmat SC-15) and triethanolamine dodecyl benzene sulfonate (Decol® T/70)—were anionic; and two—nonylphenol condensate with 9 moles ethylene oxide per mole of phenol (Kemonic® 909) and monosorbitan lauryl ester with 20 moles of ethylene oxide (Tween® 20)—were nonionic. The solubilizer used was dimethyl sulfoxide (DMSO). The two anionics produced the greatest uptake of picloram by the leaf discs, closely followed by the quaternary, trimethyldodecylammonium chloride. Other examples of surfactant enhancement can be readily found in the literature.

Surfactants such as the long-chain fatty amine salts of fatty acids can form invert emulsions. These emulsions are unique in that the active pesticide can be in either the water or oil phase or both. This system is advantageous in preventing drift and reducing volatility.

PESTICIDE DERIVATIVES

The most important fatty derivatives in agricultural applications are those containing nitrogen. They fall in the categories of primary, secondary, tertiary and poly-amines; quaternary ammonium compounds; imidazolines; thioureas; and guanidines.

Several studies were made by Jansen (4) (USDA) that illustrate the importance of chain length, the number of long chain alkyl groups, the effect of ethoxylation, the solvent and even the dilution rate of application when the surfactant is attached to a herbicide such as 2,4-D. He used soybeans as an indicator plant and a sublethal dosage (0.1 lb/A) to illustrate the biological effects.

In aqueous sprays, the C_8 and C_{12} saturated primary amines were active but the C_{16} and C_{18} were inactive. In soy, oleoyl, and hydrogenated-tallow amines, only the H-tallow was inactive; the activity of soy and oleyl amines

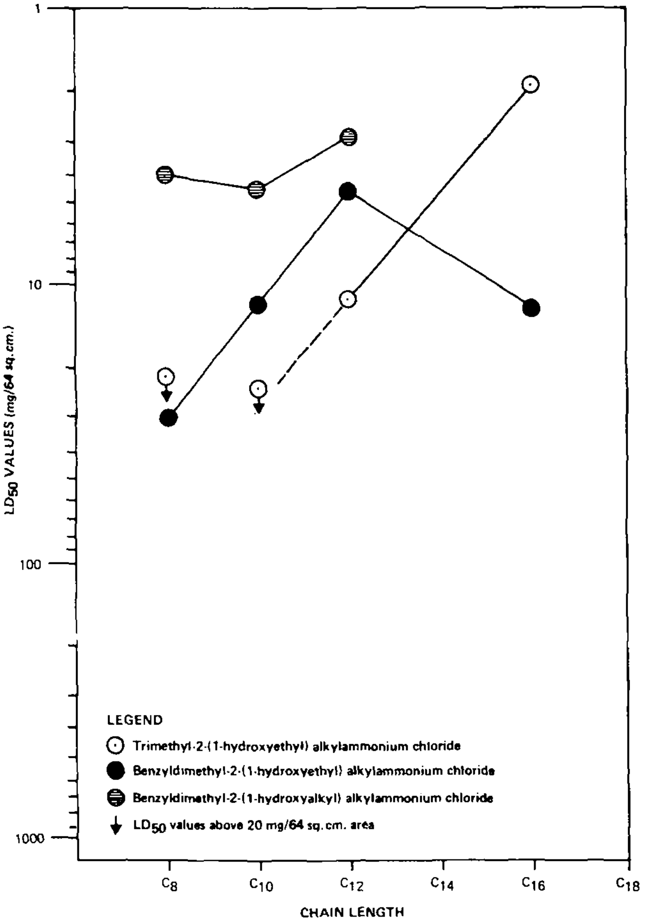

FIG. 4. Effect on biological activity with increasing length of the aliphatic group in quaternary ammonium compounds.

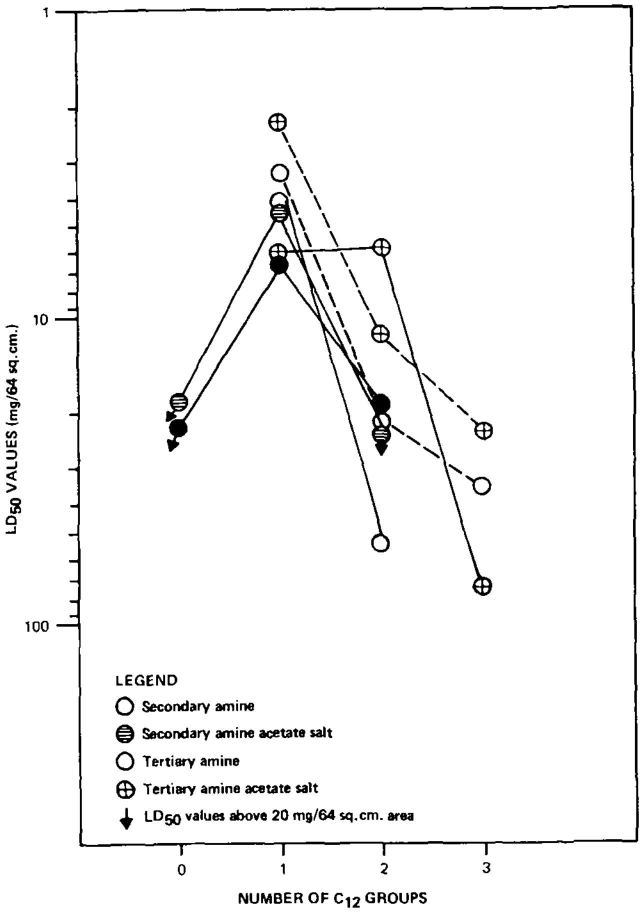

FIG. 5. Effect of increasing the number of higher aliphatic groups on the activity of amines and their salts.

was attributed to the presence of unsaturation.

In secondary and tertiary amines, the presence of two high molecular weight hydrocarbon substituents showed practically no activity; but with two low molecular weight moieties and one long aliphatic substituent, the compound was very active in an aqueous system.

Ethoxylation of either the long chain monoalkyl primary or long chain dialkyl secondary amines proved to be one of the most influential factors determining their activity in water. Progressive ethoxylation increased activity, most markedly in the case of the secondary amine. Jansen concluded that the structural features associated with the activity of surfactant-amine salts of 2,4-D in water are those commonly associated with the hydrophilic characteristics of the surfactants, the decreasing order of importance being the degree of ethoxylation and high degree of unsaturation in the aliphatic amine and the saturated hydrocarbon chains with fewer than 16 carbons per amine. The reverse is true, to a large extent, of the lipophilic surfactant characteristics in an oil medium.

In original studies not previously reported, we have investigated the effect of chain length of amine salts of dalapon (2,2-dichloropropionic acid) applied to yellow nutsedge and Johnsongrass seedlings in the greenhouse (Fig. 2). The results showed trends similar to those found by Jansen except in the case of yellow nutsedge, where the tertiary amine salts peaked at C$_{15}$. But against Johnsongrass, all derivatives showed high activity.

Tertiary amine salts of endothall acid (5) show unusually diverse biological activity. Dimethyl "coco" amine endothall is applied as an aquatic herbicide to control algae and noxious water weeds. The same compound in combination with tributylphosphorotrithioite (Folex®), a defoliant, very effectively accelerated desiccation and defoliation of cotton to improve harvest. The amine salt is also marketed as an effective harvest aid for alfalfa and clover seed, and as a potato vine killer. It has been tested in Hawaii and found to be an effective sugar cane ripener (6).

INSECTICIDAL ACTIVITY

The effect on insecticidal activity of chain length and number of aliphatic groups in free amines, their acetate salts, and quaternaries was also studied by the author with housefly larvae as the test species (Fig. 3). The insecticidal activity of the free amines and their salts peaked at C$_{12}$ alkyl with some increase in activity due to unsaturation. In the case of alkyl trimethylammonium chlorides, the peak activity was at C$_{16}$ and for the benzyl quaternary the peak was at C$_{12}$ alkyl (Fig. 4).

Increasing the number of alkyl groups from one to two or three greatly reduced the biological activity of secondary and tertiary amines; but for the case of alkylmethylammonium compounds, two long chain groups were most active (Fig.s 5 and 6) (7).

Similar studies on the effect of varying chain lengths and the number of aliphatic moieties on the biological activity were done on mosquito larvae (8,9), carpet beetle larvae (7), and houseflies. The most active larvicides were compounds containing 15 to 18 carbon atoms, particularly those with unsaturation. The fly repellent activity peaked around C$_{12}$ alkyl group (7).

PLANT GROWTH REGULATORS

The early tobacco sucker control practice consisted of topping tobacco at the midflower stage and either manually desuckering the plants at each leaf axil or using a sucker oil or a systemic agent such as maleic hydrazide. To avoid

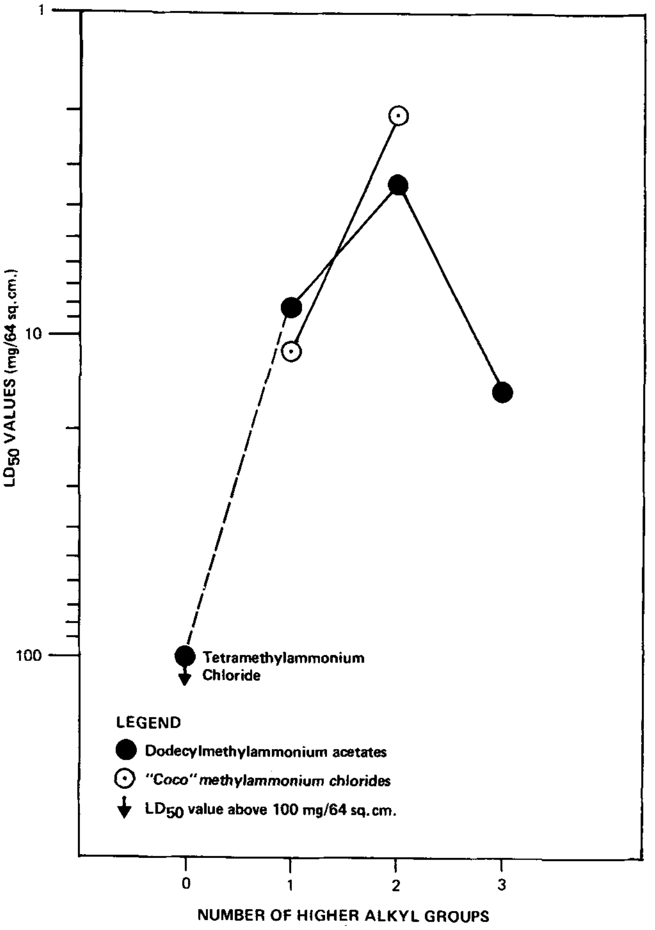

FIG. 6. Effect of increasing the number of higher aliphatic groups on the activity of quaternary ammonium compounds.

TABLE II

Chemical Pinching Agents and Tobacco Sucker Control Chemicals

	Effective % conc.
dimethyldodecylamine acetate	0.5-1.0
dimethyldodecylamine caprylate or caprate	0.75-1.25
methyl decanoate	2.5-5.0
decyl succinoate	1.5-2.0
alkyl (C_{8-11}) acetamides	0.75-1.0
decanol-octanol	2.0-5.0
undecanol	1.0-2.5

injury, the sucker oil had to be applied directly to the stalk where it ran down contacting the lateral buds and killing them.

Early in 1961, the author discovered the first effective water-soluble contact sucker control agent, dimethyldodecylamine acetate, that could be sprayed over the entire plant without leaf injury (10). This led to the discoveries by the USDA, the author, and a number of others that other fatty chemicals such as fatty alcohols (11), acetamides (12), ketones (13), esters of fatty acids (14), and fatty glycols (15) could also be used. One thing they all have in common is the fatty moiety (Table II). The selective action of these chemicals is due to the surfactant, the nature of the chemical, and epidermal structural differences between young and mature plant tissue. The same principles guide chemical pinching of other plants such as chrysanthemums and azaleas (16,17).

FUNGICIDES

Fatty chemicals have also been useful intermediates for plant fungicides. Two useful products illustrate the point. Dodecylamine acetate is used in the manufacture of dodine (dodecylguanidine acetate) and stearic acid in the production of glyodin (heptadecylimidazoline monoacetate). Mixtures of the two are reported to be synergistic (18).

Other fungicidal chemicals include 1-dodecyl-2-methyltetrahydropyrimidine (19,20), laurylisothiouronium chloride (21), and complexes and double salts of metals with long chain primary- and polyamines (22-25).

FUTURE OF FATS AND OILS

As petroleum products become short in supply or more expensive, the use of fats and oils and their derivatives increases, and they become more economical to use. For example, methyl oleate was developed to dry raisins on the vine and prunes on the tree (26). This chemical has drastically reduced the drying time and improved the quality of these products. The di-tallow quaternaries, useful in soil treatment to conserve soil moisture, can be used to reduce irrigation water requirements (27,28). The same is true with the use of fatty chemicals as plant antitranspirants (29). Further research to increase frost resistance in plants can reduce the need for smoke pots except in severe temperature drops (30).

As prices of vegetable oils come within the price range of petroleum products, they can compete as solvents or be used as cosolvents to conserve the use of petroleum products. Fatty nitrogen derivatives have been found to act as abscission agents in the harvest of citrus, to increase sugar in sugar cane and sugarbeets, and to act as insect sex lures, to name a few (31,32).

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