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RECOMMENDED SPECIFICATIONS FOR CITRUS SPRAY OILS IN FLORIDA[1]

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ABSTRACT

Petroleum oil has been widely used as a pesticide on Florida citrus for many years. Several million gallons of oils with varying properties are applied annually. While this use has been reasonably satisfactory, adverse effects on tree and fruit are common and frequently are of concern.

Research initiated in 1962 has disclosed the oil properties necessary for optimum performance as citrus tree sprays in Florida. The significance and methods of testing for these properties are discussed. Specifications are presented for 2 oil types; one designated FC 435-66 is for normal summer use and provides maximun pesticidal efficiency without excessive physiological effects on tree and fruit. The other, designated as FC 412-66, provides minimum physiological effect consistent with adequate pesticidal efficiency and is for use where a lighter, safer oil is needed.

More informative labeling of spray oils, including a disclosure of certain oil properties, is recommended.

INTRODUCTION

Emulsified oil has been one of the most widely used pesticides for the past 40 years and undoubtedly will retain this status for many years to come. Several million gallons of petroleum oil are sprayed on Florida citrus trees each year. All of this oil has been purchased without benefit of specifications to indicate that it was a suitable oil for Florida conditions. This was simply because no tests had been carried out in sufficient detail to pinpoint the desirable and undesirable characteristics of an oil. As a result, spray oils have varied widely in properties and the container labels have provided little information to describe the contents.

In 1962 a project was initiated at the Citrus Experiment Station to review the entire subject of spray oils, evaluate the oils currently offered as sprays for Florida citrus and attempt to define those properties associated with optimum performance. The results of research to this time are presented here as tentative specifications for Florida citrus spray oils. Suggestions for informative labeling also are given.

HISTORICAL BACKGROUND

One of the first uses of petroleum as an insecticide was by Hubbard who used kerosene emulsions on Florida citrus in the 1880's. These were supplanted by the light lubricating oils such as used by Yothers in 1911, which provided more insecticidal action than kerosene. The widespread use thereafter of the limited petroleum products of that day was accompanied by considerable tree damage, especially in California. Research in California in the 1920's led to the discovery that refining to an unsulfonated residue value above 85 greatly decreased the phytotoxic effects of spray oils from California crudes. Such oils were patented by Volck in April 1929. These patents affected the price and availability of refined spray oils for many years. In Florida where citrus is less susceptible to oil damage, less refined and cheaper oils were tried with reasonable success under optimum conditions. Nevertheless, damage to citrus trees and fruit, sometimes apparent but more often insidious, has and continues to result from improper use of oil spray. We believe much of this damage can be avoided.

Oil has many desirable attributes as a pesticide for citrus. It will control most kinds of scales and spider mites, and helps to control

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greasy spot disease. Used alone, emulsified oil is a reliable and economical pesticide that is safe to handle. It creates no residue problem, and does not lead to buildup of resistance by citrus pests. Oil also contributes to the effectiveness of other pesticides in a wide variety of admixtures. A review of the pesticidal properties of oil sprays has been prepared by Trammel (2). Trammel and Simanton (3) in a concurrent paper provide new information relating pesticidal performance to specific properties of oils.

Oil also has shown a number of undesirable characteristics as a tree spray. It has caused excessive leaf drop, a grade lowering fruit blemish known as oil blotch, a delay in degreening of maturing fruit and lower sugar content in maturing fruit. It is also suspected of predisposing trees to cold damage and reducing crop size the following year. A current article by Trammel and Simanton (4) presents new information relating phytotoxicity to certain properties of petroleum oil.

Complexities In The Use Of Oil Sprays

Despite half a century of experience with this common insecticide, correct use of spray oil still has a number of complexities.

First, the petroleum fraction used is a mixture of a hundred of more chemical entities, some of which are removed or altered by the wide variety of refining processes employed.

Second, it usually is necessary to apply the oil to the plant in the form of an emulsion. This preferably is an oil in water system, with the oil readily dispersible and then stable in the tank but quick breaking on contact with the plant. Emulsions can behave in a very erratic manner under field conditions, and sometimes leave an undesirable type of oil deposit.

Third, the ultimate deposit on the plant and in contact with the insect governs phytotoxicity and pesticidal efficiency, hence the manner of spray application can have considerable influence.

Each of the above complexities is an important factor in performance, even when the oil is applied alone. When mixed with other materials, the complexity is multiplied. In our recent work with spray oils, we have attempted to hold constant the emulsification system and the method of application to permit an evaluation of intrinsic properties of the petroleum oil *per se.*

Refining and Testing for Desirable Properties in Spray Oils

While spray oils can be made from many types of crude petroleum, those rich in paraffinic hydrocarbons produce the best oils and often require less refining. The selected crude oil is first distilled to separate the fraction containing the light lubricating oils. This fraction is then solvent extracted to remove sulfur compounds and other impurities as well as reactive hydrocarbons, including the aromatics. The next step is dewaxing following by further purification by contact with hydrogen gas, clay or by other methods. A final vacuum distillation refractionates the oil to precise boiling range. The success of these steps in meeting spray oil specifications is determined by tests, many of which have been standardized by the American Society for Testing and Materials (ASTM) (1). The tests pertinent to evaluation of spray oils are discussed here.

The *unsulfonated residue value* (UR) is determined by ASTM method D-483-63 and is a measure of degree of refinement. The oil is shaken several times while hot with 4 times its volume of a mixture of concentrated and fuming sulfuric acid. The percentage of oil not absorbed by the acid is the UR. A high UR indicates a high percentage of stable hydrocarbons, free of reactive impurities. It does not indicate the form of hydrocarbons. UR does not appear to be directly associated with insecticidal efficiency but it is a good indicator of overall quality and has an important relationship to the physiological effect of oil on the citrus tree.

In an experiment in which 'Hamlin' oranges were sprayed when 0.8 inch in diameter, in the size range most susceptible to oil blotch, we were unable to produce the blemish with highly refined oils (UR 92+) even with a full coverage spray at 1.5% oil concentration in 2 successive years. Fruit blotch did occur with the oil of low refinement (UR 86) and affected 55% of the fruits (Figure 1).

High UR oils tend to have less variable physiological effects on citrus than low UR oils because refining removes the more reactive aromatic compounds and the hydrocarbon composition is more consistent.

We recommend an unsulfonated residue value of 92 minimum.

Distillation temperatures of an oil are of paramount importance in relation to both in-

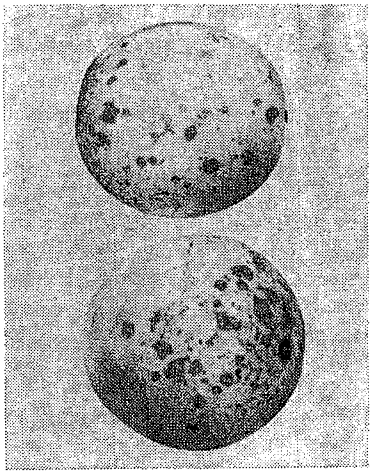

Figure 1.—Oil blotch on 'Hamlin' orange resulting from application of 1.5% of an 86 UR oil when fruit averaged 0.8 inch in diameter.

secticidal efficiency and phytotoxicity. We have found this relationship to exist over a wide range of hydrocarbon composition and to be largely independent of crude source, refinement, viscosity, gravity and other properties. In laboratory studies with specially prepared narrow cuts of paraffinic and napthenic spray oil fractions, Trammel (2) established that insecticidal efficiency against citrus red mite and Florida red scale increased as distillation temperature increased; but beyond a certain optimum range, efficiency decreased. Subsequent field trials confirmed the relationship (3),

Laboratory and field tests (2, 4) also established the relationship of distillation range to phytotoxicity.

Distillation temperatures of spray oils have customarily been determined and reported according to ASTM method D-447, which was adopted in 1941 especially for spray oils. It replaced ASTM method D-86, which is used for a wide variety of petroleum products. Both of these methods are conducted at atmospheric pressure. Distillation temperatures for spray oils at atmospheric pressure often exceed 700° F and with such heating thermal decomposition or "cracking" occurs; thus, a true characterization of the higher-boiling constituents is unobtainable. In 1961, ASTM method D-1160 was adopted as a standard vacuum distillation for petroleum products. In this method spray oils are distilled at 10 mm of Hg, and temperature does not reach the cracking point. We believe this method should replace D-447 for all distillation data on spray oils. Although temperature by D-1160 can be converted to atmospheric conditions, comparison with data by the other methods is unsound and misleading; therefore we recommend that D-1160 distillation temperatures at 10 mm Hg be expressed unconverted to avoid confusion.

The most highly insecticidal hydrocarbons have average molecular weights ranging from 300 to 370. By method D-1160 most of these distill in the range of 400° to 480° F. Thus, the most efficient oil should have a 50% distillation point near the center of this range with 10% and 90% points near 400° and 480° F, respectively. To go higher on the boiling range increases the phytotoxic effect without increasing insecticidal effect. A lower boiling range may provide increased plant safety but at some subsidence from maximum pesticidal effect. A relatively narrow distillation range (10% to 90% distilling within a spread of 80° F at 10 mm Hg) is specified to assure a high concentration of the desirable hydrocarbons in the oil. With a narrow range oil the 50% distillation temperature can be used as a reliable indicator of performance.

Gravity is usually reported as degrees API @ 60° F by ASTM method D-287, which employs a special hydrometer. Specific gravity measurement by ASTM method D-1298 is almost identical and in fact the ASTM-IP Petroleum Measurement Tables provide interconversion of gravity and density data by several methods.

High API gravity is associated with volatile fractions of petroleum, such as gasoline, and a low gravity with thick asphaltic oil; thus API gravity is in reverse order to specific gravity. With spray oils, a higher API gravity for a given distillation range indicates a higher proportion of paraffin-type compounds and fewer naphthenic and aromatic types. High paraffinicity has been found to be associated with better greasy spot control in oils otherwise comparable and tends to be associated with higher insecticidal efficiency. We recommend a gravity value of 31 minimum to assure a predominantly paraffinic composition regardless of crude source.

Viscosity is a measurement of resistance to flow and is usually reported as Saybolt Universal Seconds (SUS) at 100° F and sometimes at 210° F in addition. It can be measured directly by the Saybolt test ASTM D-88 or by the Kinematic test ASTM D-445 and then converted to SUS according to ASTM D-2161. Since viscosity has to do with shearing stress and bearing pressures it is important in evaluating the lubricating properties of oils. Unfortunately, viscosity value has been commonly used to indicate the heaviness of spray oil. The term is of little value in describing performance as a spray oil, and may be misleading unless interpreted in conjunction with hydrocarbon composition and gravity. Although satisfactory spray oils have viscosities in the range of 65 to 95 SUS at 100° F, we prefer not to use a viscosity figure in specifications for spray oils because more meaningful terms are available.

Pour point is that temperature, expressed in multiples of 5° F, above the temperature at which oil will not pour from a jar when tested by ASTM method D-97. A pour point value is applied to spray oils for two reasons: one is to evaluate flowability and solidification in cold weather as a guide to handling and formulation procedures; the other is to ascertain that the oil does not contain excessive paraffinic waxes which have low insecticidal value and thus dilute the more desirable hydrocarbons. Oils of high paraffinicity tend to have high pour points but the dewaxing treatment readily lowers pour point to a satisfactory level. We recommend a pour point of +20° F maximum.

Carbon ring analysis has been applied to spray oils to indicate the proportion of carbon atoms present in paraffinic structures, napthenic rings, and aromatic rings. A number of methods have been used but none has yet been adopted by ASTM. Highly paraffinic spray oils may contain 75% paraffinic carbon but well refined spray oils from naphthenic crudes will contain more than 45% paraffinic carbon. Naphthenic carbons generally run from 17 to 47%. These two types are desirable "saturates." Aromatic carbon may be present at 15% or higher in low UR oils but refining to 92 UR or higher removes the more reactive unsaturated aromatics. Not more than 6% of carbon of aromatic structure should be present in a high quality spray oil.

Because values for unsulfonated residue, gravity, distillation, and pour point assure a desirable composition, detailed hydrocarbon analysis is not required in spray oil specifications. A variety of other test data may be offered to characterize an oil, but to date they have not been established as indicators of spray oil performance.

Discussion and Conclusions

The many desirable attributes of petroleum as a citrus tree spray dictate that we should find ways to overcome the chief disadvantages, all of which concern phytotoxcity. The best way is to purchase the least phytotoxic oil with high insecticidal efficiency, then formulate it and apply it to best utilize these properties. Florida tests have led to derivation of 2 sets of spray oil specifications, one designated FC 435-66, and the other FC 412-66. The FC refers to Florida citrus, the 435 or 412 refers to the "heaviness" of the oil by a distillation test, and 66 refers to the year of publication. Oils meeting these specifications will have the following properties:

DESIGNATION	**FC 435-66**	**FC 412-66**
Distillation temperature at 10 mm Hg by ASTM D-1160, °F		
For 50% distilled	**435 ± 8**	**412 ± 8**
Temperature spread for 10% to 90% distilled	**Max 80**	**Max 80**
Unsulfonated residue (UR) by ASTM D-483, % by vol	**Min 92**	**Min 92**
Gravity by ASTM D-287, °API	**Min 31**	**Min 33**
Pour point by ASTM D-97, °F	**Max +20**	**Max +20**

Spray oil meeting FC 435-66 specifications has the highest insecticidal action consistent with tolerable physiological effect on tree and fruit in mid-summer. It is intended for application to citrus trees in Florida in the months of June and July at concentrations of 0.5% to 1.3% oil for the purposes and at the rates given in the Spray and Dust Schedule distributed by the Florida Citrus Commission. Oil meeting FC 412-66 specifications is a lighter oil and has the minimum physiological effect on tree and crop consistent with adequate insecticidal efficiency. It is preferred when applications must be made closer to harvest time or when tree growth is less vigorous due to weather or season.

Correct emulsification and proper application are very important, as always, for good results with oil.

Labels on spray oil containers have seldom given information about the quality or properties of the product. Buyers and users should insist that labels show the oil content of the product and all of the properties listed in the foregoing specifications. An alternative to listing properties would be a statement that the oil in the product meets the specifications for FC 435-66 or FC 412-66.

Adoption of these specifications will exclude those oils of low refinement that we have found capable of causing excessive leaf drop, fruit drop and fruit blemish. It will exclude those oils of too high and too wide boiling range which we have found capable of retarding fruit color and delaying fruit maturity. It will exclude those oils with limited insecticidal action which give poor control. Although much of the gallonage applied in 1966 meets the FC specifications, oils with the disadvantages cited are still being widely used on Florida citrus.

The recommended oils are not expected to cost the grower more on the average, and overall probably will cost him less. For example, if an oil of low insecticidal efficiency has been used in the past, it is possible to obtain control with 1.0% oil where 1.3% was required before. This could save as much as $1.05 per acre or permit a price differential of about 10 cents per gallon for oil. Where unsuitable oils have been used, it is possible for fruit solids to be increased by 0.25 pound per box which at 40 cents per pound is 10 cents. For a 6 box tree and 70 trees to the acre this is a saving of $42.00 per acre, which would justify a higher price for the 10 gallons of proper oil substituted. Use of the recommended oils will minimize delay in development of fruit color and sugar content which will favor early harvest dates and high packout.

Actually, the recommended oils will be inexpensive pesticides. In many cases they will cost no more per gallon than the unsuitable oil previously used. They probably will cost a few cents per gallon more than the cheap oils of low refinement now offered.

We believe the upgrading of citrus spray oils will lead to better pest control and less tree and crop damage with this widely favored pesticide, and thereby benefit the entire Florida citrus industry at little if any increase in cost.

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EVALUATION OF SUBSTITUTED URACIL HERBICIDES FOR USE IN CITRUS

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Abstract

Isocil (5-bromo-3-isopropyl-6-methyluracil) applied on Lakeland fine sand at 6.4 lb/A and bromacil (5-bromo-3-*sec* butyl-6-methyluracil) at 3.2 and 6.4 lb/A produced symptoms of mild toxicity in orange trees. Fair control of torpedograss (*Panicum repens* L.) and mild symptoms in trees resulted from 4 applications of bromacil on Pomello sand at 3 lb/A with 5- to 7-month intervals. Control of torpedograss was excellent, but toxicity symptoms were moderately severe after 3 applications at 6 lb/A.

Terbacil (5-chloro-3-*tert.* butyl-6-methyluracil) (formerly herbicide 732) and herbicide 733 (5-bromo-3-*tert.* butyl-6-methyluracil) controlled Bermudagrass (*Cynodon dactylon* (L.) Pers.) and annual weeds on Lakeland fine sand with only slight tree toxicity symptoms after 3 applications of 5 lb/A at 6-month intervals. A total of 6 or 9 lb/A of terbacil gave better control of annual weeds at the end of the season if applied in 2 or 3 sprays during a 4-month period rather than in a single spring application. Control of torpedograss on Felda soil was fair to good from terbacil or herbicide 733 in 3 applications at 4 lb/A with 4-month intervals. Treatments of 2 applications at 4 or 6 lb/A were less satisfactory. Control was better with 2 applications at 8 lb/A, but slight toxicity symptoms occurred in some trees.

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