Characterization of Petroleum Oils for the Control of Pests of Citrus

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About 1945, dosage-mortality correlations with serial narrow-cut fractions led to the concepts of the efficiency curve, critical molecular size, and optimal property values. Information indicates a threshold of molecular size at 460° F. at 10 mm. of Hg for interference with the physiological function of citrus. The value of selectivity became evident, and now refinery facilities can commercially produce narrow-range oils with a 10 to 90% distillation range of less than 60° F. at 10 mm. of Hg. Field trials show narrow-range oils are better. More improvement is possible with a smaller range. Better analytical methods are needed for distillation and for the distinction of differences in structural composition.

A brief review of various petroleum spray oil fractions and their effects on citrus trees and citrus pests seems helpful to an understanding of the characterization of petroleum oils currently deemed suitable for the control of citrus pests in California. The first trials in California of an oil in the light lubricating range for controlling citrus pests were made in 1900 (Wickson, 1901). The oils were distillates obtained directly from crude oil and used without further refining. Severe acute injury, so-called "burning," of foliage and fruit followed their application and was discouraging to their use. This practice continued until 1912, when failure to control California red scale, *Aonidiella aurantii* (Maskell), began to appear. The only alternative method at that time was fumigation with hydrogen cyanide. Careful investigation later proved (Quayle, 1938) that the suspicion of resistance was valid. This focused interest on research on oil for spraying citrus. Edeleanu described the process on the use of sulfur dioxide to remove aromatics in 1907 and the process was first applied commercially in France in 1911 (Gester, 1951). Information on the Edeleanu process probably influenced the preliminary work on oil for spraying citrus. Quayle (1915) stated that investigations at Riverside during 1914 (Gray and de Ong, 1926), provided the clue that the injury by petroleum oil to the citrus foliage was caused mostly by the part of the oil that was removed by acid treatment. These studies led to further development of foliage spray oils.

Determinations (de Ong *et al.*, 1927) made on raw distillate fractions in the spray-oil range in 1914 had values for unsulfonated residue as low as 51% and for gravity A.P.I. as low as 19.2. The direct relation of low unsulfonated residue to the injury to the citrus foliage and fruit was demonstrated conclusively.

Gester (1951) records that the Standard Oil Co. of California put a SO_2 extraction unit in operation in 1924. The general information indicates that a spray oil marketed in California in that year by W. H. Volck was refined by a sulfonation process. Patents on the sulfonation refining of spray oils were issued in 1929 to Volck (1929).

Other extraction solvents (Gester, 1951) were developed as substitutes for SO_2 for refining spray oils to a minimum unsulfonated residue (UR) of 92%. The development of hydrogenation refining introduced several advantages to processing that reduced unsaturation and made UR levels higher than 92% economically feasible. Riehl *et al.* (1964) reported that the efficiency of spray oils refined by hydrogenation against California red scale and citrus red mite eggs was as good as that of comparable oils refined by solvent extraction alone.

The quick breaking concept of dilute oil spray mixture described by de Ong *et al.* (1927) favored the economics of refined spray oils, because concentrations of 1.75% gave better control than the concentrations of 10 to 13% required with previous formulations. With these developments, the number of spray oils on the market increased rapidly, although there was considerable variation in pest control and effects on trees. Attempts to use the limited data on properties of the oils did not yield a meaningful pattern of the differences in field results.

Further investigation of these oils and possible ways to avoid undesirable effects on citrus trees was started by Smith (1932), who began studies in 1926 with various spray oils selected for differences in distillation range. He concluded that the performance and the effect on citrus trees were governed by degree of refinement—i.e., unsulfonated residue (Cox, 1943), distillation range, and quantity of oil deposited. This work provided the basis for standardization and led to the adoption in 1932 by the California Department of Agriculture of a classification with five grades of summer foliage spray oils (Erb, 1932; Marshall, 1932; Cox, 1942). The California specifications and distillation values at atmospheric pressure are listed in Table I. The advantages of distillation of spray oils at 10 mm. of Hg (American Society for Testing and Materials, 1966) were pointed out by Chapman *et al.* (1962). Distillation values of representative California grade spray oils are listed in

Table I. Selected Properties of California Grades of Foliage Spray Oils

	Min. UR, %	% Distil. 636° F. Atm. Press.	Distil. ° F. Atms. Press. 5%	90%	Vis. S.S.U. 100° F.
Kerosine	92	100	365	525	32
Mineral seal	91	95	497	650	46
Calif. grade	Specified		Observed		Av.
Light	90	64–79	555	685	55–65
Lt-med.	92	52–61	575	700	60–75
Medium	92	40–49	585	715	70–85
Hv-med.	92	28–37	595	715	80–95
Heavy	94	10–25	610	730	90–105

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Table II. The low-to-high spread for the distillation values was from different oils and is due to the range for per cent distilled at 636° F. in the California specifications for the various grades.

The variation in the performance of refined spray oils mentioned above led to experimental studies. Knight *et al.* (1929) reported that although saturated petroleum oils were not toxic to plants in the ordinary sense of the word, heavy oils (high distillation range temperatures) caused profound and long-continued metabolic disturbances. Yothers and McBride (1929) found in Florida that oil sprays reduced the total soluble solids of the juice of oranges. Although the adoption of specifications in California improved spray oils, the undesirable influence on juice quality still occurred. Detailed experiments by Sinclair *et al.* (1941) demonstrated that light-medium grade oil reduced total soluble solids. Practices useful in minimizing the adverse effects of oil spray in California were reported by Riehl *et al.* (1957).

The development of organic chemical insecticides since 1946 provided a wider variety of pest control materials to citrus growers. However, resistance of the citrus red mite, *Panonychus citri* (McGregor), to all the available organic chemical acaricides was recently reported (Jeppson, 1964). Resistance has not been found with spray oils; therefore, petroleum oil is an important pest control material.

The killing action of spray oil occurs by the physical interference of a barrier of oil to respiratory metabolism. This was demonstrated for California red scale by de Ong *et al.* (1927) and by Ebeling (1936), and for eggs of the oriental fruit moth, *Grapholitha molesta* (Busck), by Smith and Pearce (1948). Since mite eggs and scale, after settling, do not move about, the spray oil must be put in contact with them. The requirements of application coverage for spray oils are demanding but attainable (Carman, 1955; Riehl, 1961).

A very important contribution to research on spray oils was made by Chapman and Pearce of correlations of ovicidal mortality determinations with various physical properties of serial very narrow-cut fractions of saturated petroleum spray oil stocks (Pearce *et al.*, 1948). Eggs of several insects and mites were used. Spray trials were done in the laboratory using oil applications in dilute aqueous mixture and measured quantitatively by deposit determinations. The correlations showed the efficiency of the spray oil stock as curves approaching a hyperbolic shape with clearly indicated critical optimum values for the physical properties. The critical optimum showed the most useful level of hydrocarbon molecular size for the greatest selectivity against the pest. Specially prepared serial narrow-cut fractions with a range of approximately 10° F. of distinctly paraffinic and naphthenic compositions, made available by Pearce and Chapman (1952), and similar fractions of various types of composition made available by several petroleum companies, have been used at Riverside in the present work in laboratory experiments to obtain efficiency correlation curves against citrus red mite eggs and California red scale (Riehl and LaDue, 1952; Riehl *et al.*, 1953).

Reduction of the total soluble solids of the juice of oranges seems to be as sensitive an index as any of those used of the interference with tree function by oil spray. The investigations by Sinclair *et al.* (1941) showed that light-medium grade oil caused reduction of soluble solids. The effects of medium grade oil are more pronounced (Ebeling, 1950; Riehl *et al.*, 1954), so light-medium grade oil received preference for use on oranges in California. However, light-medium grade oil is not consistently effective against citrus red mite (Riehl *et al.*, 1958a). Light grade oil is ineffective for the control of mites and scale (Ebeling, 1950). On the other hand, an interest developed in the use of light grade oil in combination with toxicants as a means of retaining some features of oil spray and avoiding the effects of light-medium grade oil on the fruit. Experiments by Cressman (1955) indicated that light grade oil did not cause reduction of soluble solids. In Figure 1, a hand-fitted efficiency curve, taken from mortality results against citrus red mite eggs with several sets of serial narrow-cut fractions of highly paraffinic oils, is shown for a scale of 50% distillation temperature values at 10 mm. of Hg on the abscissa. The ranges of light, light-medium, and me-

Table II. Temperatures in ° F. for Distillation at 10 Mm. of Representative California Grades of Foliage Spray Oils

% Distilled	Light	Light Medium	Medium	Heavy
10				
Av.	326	337	348	374
Low	321	321	334	364
High	334	362	370	387
50				
Av.	368	390	395	418
Low	362	381	390	402
High	373	414	403	427
90				
Av.	434	463	468	483
Low	428	439	458	452
High	439	525	496	516
Range	108	126	120	109

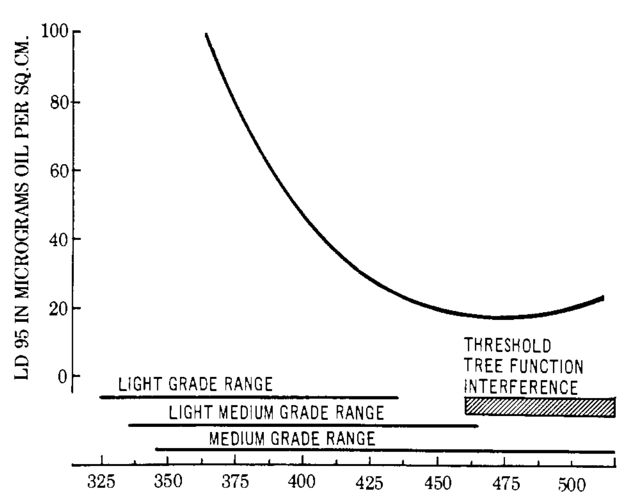

Figure 1. Hand-fitted efficiency curve for 50% distillation values at 10 mm. of Hg of several sets of serial narrow-cut fractions of highly paraffinic oils against citrus red mite eggs

dium grades are depicted on the same scale. The available evidence from effects on soluble solids suggests that the threshold for tree function interference begins above the range of light grade and within the range of light-medium grade. The best estimate from available current evidence indicates that the threshold begins at a level of about 460° F. at 10 mm. of Hg as shown by the band of diagonal lines in Figure 1. This temperature level is very close to the critical optimum for the efficiency curve of highly paraffinic oils against citrus red mite eggs. This suggests that selectivity could be used to define the distillation range of a spray oil in which the maximum for the 90% point of distillation is 460° F. at 10 mm. of Hg to provide high efficiency for control without causing interference with the physiological function of citrus trees.

Much better selectivity became available recently through developments in refinery equipment that made it possible to produce spray oils with a 10 to 90% distillation range at 10 mm. of Hg of 60° F. or less, about half or less than the range of previous spray oils, at costs within favorable economics to growers.

During the past three years, field experiments with navel and Valencia oranges and lemons were conducted in southern California with spray oil fractions made so that the range would be under the limit of 60° F. The properties of two of the experimental oils are listed in Table III. Distillation properties were the primary criterion for selection of the fraction of the experimental oil for field work. The critical molecular size indicated by efficiency curves from the author's laboratory work was used to choose mid-boiling points for the fractions in the range of 410–15° F. at 10 mm. of Hg. Several other fractions tested involved variations of 50% distillation or of per cent carbon atoms in paraffinic structure. The results for pest control and for avoiding interference with tree function or adverse effects on the crop or fruit quality have been very satisfactory. These results indicate that the combination of mid-boiling point at the level of 410–15° F. and reducing the 10 to 90% range to less than 60° F. for distillation at 10 mm. of Hg provides a definite way to improve spray oils for citrus pest control. Spray oils conforming to the properties of the oils listed in Table III were marketed in California in 1966 under the designation of narrow-range spray oil to be used in accordance with issued recommendations (California University Agricultural Experiment Station, 1966).

Table III. Selected Properties of Two Experimental Narrow-Range Spray Oils

Property		Value[a] Oil A	Oil B
Distillation at 10 mm. Hg. ° F. (A.S.T.M. method D 1160)			
50% point		412	416
10–90% range	Maximum	60	60
Percent carbon atoms in paraffinic structure[b]	Minimum	75	62
Per cent unsulfonated residue (A.S.T.M. method D 483)	Minimum	92	92
Pour point, ° F. (A.S.T.M. method D 97)	Maximum	+20	+20

[a] Oils A and B and their properties supplied by Esso Research and Engineering Co. and Union Oil of California.
[b] Smith (1953).

In laboratory studies of the effects of spray oils on the physiological functions of citrus (Riehl *et al.*, 1958b; Riehl and Wedding, 1959), transpiration and photosynthesis were inhibited approximately 60% within the first day after application. Recovery occurred with time. The rate correlates well with available evidence on the decrease, or dissipation, of the oil deposits from citrus foliage. Spray oils in the lower temperature distillation range dissipate more rapidly than those in the higher range. The dissipation rate of spray oils from citrus foliage probably is temperature-associated. Therefore, climatic conditions may be taken into account in the choice of the distillation range of a spray oil for a given area. Experiments in Texas (Dean and Bailey, 1963) directed toward gaining information on properties most suitable for citrus spray oils indicate that oils with higher distillation temperatures may be acceptable there.

Investigations of spray oils for use on citrus in Florida are in progress (Trammel and Simanton, 1966). Trammel (1965) reported the results of laboratory studies of efficiency against citrus red mite eggs of narrow-cut fractions of naphthenic, paraffinic, and re-formed composition of oils produced by the recent newer processes of petroleum refining of spray oils (Riehl *et al.*, 1964, 1965). The efficiency of paraffinic composition in Trammel's results is better at an average molecular weight of 320 than for this level in earlier experiments (Riehl and LaDue, 1952). These results are in accordance with the effects associated with differences in the refining treatment of the oil and the use of an oil-soluble surfactant (Riehl *et al.*, 1964, 1965) instead of blood albumin spreader (Smith, 1932).

Pearce and Chapman (1952) compared the efficiency curve obtained for a series of 11 isoparaffins prepared synthetically to include a range of 16 to 34 carbon atoms per molecule with the efficiencies of serial narrow-cut fractions of naphthenic and paraffinic composition. They concluded that the efficiency was better for the isoparaffins. They generously made samples of the isoparaffins available for trial in the work at Riverside. The results as LD_{95} in micrograms of oil per square centimeter for citrus red mite eggs and California red scale are given in Table IV. Also available for trial were limited samples of serial fractions of an ethylene alkylate polymer. The mortalities obtained with them are listed in Table IV. For comparisons, the results obtained with the paraffinic oil (46-M20) (Riehl and LaDue, 1952) and the viscosities of the various oils are given in Table IV for the average molecular weight values within a comparable range. In Table IV, LD_{95} values for citrus red mite eggs are essentially equal for the three oil types below an average molecular weight level of 325; however, in the range of 350 to 366 for molecular weight, LD_{95} values are lower for the monomolecular isoparaffin series and the ethylene alkylate polymer than for the paraffinic oil. This level approaches but does not exceed the upper limit of size discussed earlier for the threshold of tree function interference. Against California red scale, the LD_{95} value for the isoparaffin, 7-*n*-hexyltridecane, indicates a potential for better efficiency for isoparaffinic composition in the molecular weight range of 270 to 300; however, this was not supported by the results with the ethylene alkylate polymer. In the range of 300 to 360, the three types of composition have nearly the same efficiency against

Table IV. LD_{95} Values in Micrograms of Oil per Square Cm. for Citrus Red Mite Eggs and California Red Scale and Viscosities of Fractions of a Paraffinic Oil, a Series of Monomolecular Isoparaffins, and of Fractions of an Ethylene Alkylate Polymer with Comparable Ranges of Average Molecular Weights

Paraffinic Oil[a]				Monomolecular Isoparaffins[a]						Ethylene Alkylate Polymer[b]			
		LD_{95}						LD_{95}				LD_{95}	
Av. mol. wt.	Vis. S.S.U. 100° F.	Citrus red mite	Calif. red scale		Carbon number	Av. mol. wt.	Vis. S.S.U. 100° F.	Citrus red mite	Calif. red scale	Av. mol. wt.	Vis. S.S.U. 100° F.	Citrus red mite	Calif. red scale
255	40.8	n.e.	122	7-*n*-Hexyltridecane	19	268.5	40.7	n.e.	78	276	48	n.e.	...
275	47.2	n.e.	89							288	52	...	86
290	52.4	69	85	9-*n*-Hexylheptadecane	23	324.6	49.7	33	67	298	56	28	86
312	58.9	34	69							310	63	...	78
323	67.0	29	85	11-*n*-Amylheneicosane	26	366.7	59.1	16	59	320	70	27	...
337	76.7	26	75							334	83	19	74
354	90.2	21	64	6,11-Di-*n*-Amylhexadecane	26	366.7	65.2	17	64	344	96	18	72
376	110.7	24	77							355	110	16	70
403	148.4	21	100	9-*n*-Octyleicosane	28	394.7	66.0	32	76	366	128	12	...
										378	152	15	60
				9-*n*-Octyldocosane	30	422.8	75.7	63	54	388	178	16	75
										398	200	15	82
										410	237	12	...

[a] Fractions of paraffinic oil and series of monomolecular isoparaffins and their properties made available by G. W. Pearce and P. J. Chapman (1952).
[b] Fractions of ethylene alkylate polymer and their properties supplied by Shell Oil Co.

California red scale. This evidence in combination with that of Pearce and Chapman (1952) furnishes reasons for a further interest in isoparaffinic composition for spray oil. On the other hand, in trials in this laboratory, an alkylate polymer of butylene was relatively inefficient against these test species compared to the paraffinic oil data given in Table IV. To date, alkylates of mixed olefins with molecular weights above 300 have not been available for testing, and no gain in efficiency was found for this type of oil below the level of 300. Comparison of the data of Table IV indicates that isoparaffinic composition offers a means of obtaining lower viscosity for given levels of molecular size. This feature has interesting considerations for spray oils.

Characterization of spray oils for citrus can be useful in summarizing the progress that has brought the current narrow-range spray oils that are better for citrus than the previous oils—i.e., California grades (Table I)—and that have good expectation of satisfactory performance. It can also reveal some leads for the future. Selectivity can be enhanced by making the distillation range narrower, but critical utilization will require a better analytical distillation method. Further advantage can be taken of the differences in efficiency associated with structural composition, and this will require better methods for its determination. Its manifestations in several properties such as viscosity and spreading coefficient offer promise for investigation. This would be helped by the availability of a critical method for measuring spreading coefficient. A good opportunity for useful information exists in the study of the new surfactants and their relation to the performance of spray oils. The interest in the application of concentrate spray mixtures brings additional importance to this problem. These comments present a few of the most important ideas and problems for spray oil research in the near future.

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