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Tree Spray Oils

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The early development and present status of petroleum oils as insecticides for use on deciduous fruit trees are reviewed. The biological groups of insects most susceptible to oil sprays are listed. Factors affecting oil deposit are discussed and data are cited to establish relationships between oil deposit and control. The relationship between chemical composition and control efficiency is also discussed. The possible modes of action by which petroleum oils kill insects are considered. Specifications are given for improved dormant spray oil. Current recommendations for the use of oil sprays in control of fruit pests occurring in New York State are listed. The possibility of developing more effective hydrocarbon insecticides is discussed.

Petroleum oils have for many years occupied an important place in the insecticide field. Perhaps the earliest written record of the use of petroleum oil as an insecticide is that of Goeze in 1787, according to Frear (10). References to the use of petroleum products as insecticides became more general during the latter part of the 19th century; however, Cook (6) is generally credited with the introduction of kerosene-soap emulsion in 1877. For a time kerosene emulsions using soap as an emulsifier were widely used, but were gradually replaced by crude oils and eventually by oils of the lubricating type.

Progress in the development of oil sprays was temporarily retarded by the introduction about 1900 of lime-sulfur solution as a more effective spray for control of scale insects. Ackerman (1) in 1923 demonstrated the superiority of light lubricating oil emulsion over lime-sulfur for control of San Jose scale and thus provided the impetus for renewed interest in development of oil sprays. From about 1925 oil rapidly replaced lime-sulfur as a scalecide. In the course of later investigations, methods were developed for determining the amount of oil deposited on sprayed surfaces under conditions of practical usage. This development logically led to a clearer understanding of the relationship between oil deposit and insect control. More recent investigations have been directed to the study of chemical composition of oils in relation to their insecticidal efficiency. Although much progress has been made, there is no indication that their potentiality as an insecticide has yet been developed fully.

General Uses of Petroleum Oils as Insecticides

In insect control petroleum oils may be used largely in three ways. First, they may be used as adhesives in the formulation of sprays and dusts—when used in this manner the inherent toxicity of the oil is not of primary interest. Second, they may be used as solvents which serve as carriers for toxicants such as rotenone and pyrethrin—"fly spray" is an example of this type. Third, they may be used as the principal toxic agent as in the case of horticultural sprays.

This discussion is confined to the latter class—i.e., oil sprays applied as oil-water

emulsions to fruit trees, and specifically to deciduous fruit trees. At present about 15,000,000 gallons of petroleum oil are used annually for horticultural sprays in the United States. Over half of this amount is used on the Pacific Coast.

The literature indicates that oils have been tested against a wide variety of pests. In some cases it is the egg stage against which oils are directed and in other cases the adults or partially mature insects. However, the oil-susceptible species fall into rather distinct biological groups.

Perhaps the best known of these are the scale insects, family Coccidae (order Homoptera), represented by the San Jose scale. This species has for many years been a serious pest of deciduous fruits. Another group within this family, the mealy bugs, are also susceptible to oil sprays. Oils used in control of these species are directed against the adults or partially grown forms.

The family Tortricidae (order Lepidoptera)—represented by such major pests as codling moth, oriental fruit moth, and fruit tree leaf roller—is also susceptible in the egg stage to oil sprays. In practice the fruit tree leaf roller is the only one of this group against which oil is used as the primary insecticide. The fact that the fruit tree leaf roller overwinters on the host plant in the egg stage and is susceptible to oil concentrations which can be applied with safety explains the general use of oil sprays for its control. Other Tortricid species, although equally susceptible to oil sprays, are not controlled by this means because the eggs are present over an extended period during the growing season when oil sprays of the concentration required cannot be applied to the foliage with safety.

The pear psylla, a representative of the family Chermidae (order Homoptera), is readily controlled by oil sprays directed against the adults as they appear on the trees in the spring. The egg stage of this species is not affected by oil sprays.

The apple red bugs, representing the family Miridae (order Hemiptera), are also readily controlled by oil sprays which are directed against the overwintering eggs. Oils are effective against the eggs of this species, in spite of the fact that the eggs are almost completely embedded in the tissue of the host plant.

Several species of mites (order Acarina) are effectively controlled by oil sprays. The European red mite, a major pest of fruit in the northeastern United States, is a member of this group. This pest appears to have become more severe as a result of the general use of DDT. Such a situation is explained by the fact that mites are not controlled by DDT, while certain parasites and predators of mites are killed by it. The continued use of DDT under these circumstances favors the build-up of mites.

Plant Tolerance in Relation to the Use of Petroleum Oil

Plant tolerance is a limiting factor in the use of oil sprays. The quantity and distribution of oils applied to trees have been controlled by applying them in the form of emulsions; however, it became apparent in the earlier use of oils that variations in oil deposit alone did not account for injury to plants (8). The aromatic or unsaturated constituents of an oil were also found to be a factor relating to the safety of oils applied to plants in foliage. This relationship was apparently first established by Gray and DeOng (11) in 1915. In spray oils the aromatic or unsaturated content is inversely indicated by the unsulfonated residue, that portion of an oil essentially nonreactive to strong sulfuric acid. The application of the inverse relationship between unsulfonated residue and plant injury became the basis of the well-known Volck (22) spray oil patents which were issued in 1929. Oils having an unsulfonated residue value of 85% or higher came within these claims. These patents have since expired.

Viscosity of an oil is also known to be related to plant injury (11). The heavier oils produce greater interference with the metabolic processes of the plant, which results in a reduction in vigor.

Deciduous fruit trees are much less susceptible to oil injury in the dormant stage than when in foliage. In practice today, oils having less than about 92% unsulfonated residue are considered unsafe for general use as verdant or summer oils. Less highly refined oil has been used for dormant applications. Within recent years, however, there has

been a tendency to apply these so-called dormant sprays after considerable new growth has appeared. This situation has resulted in the introduction of better type dormant oils having an unsulfonated residue more closely approaching the standard for summer oils. The chief difference at present between the so-called dormant and summer oil lies in viscosity, the former, of course, being heavier.

Factors Affecting Oil Deposit

In applying oil sprays to fruit trees, the objective is to apply an evenly distributed deposit of oil sufficient to effect control of the pest while remaining below the deposit that will produce plant injury. The margin of safety is relatively small in some cases. Recent attempts have been made to apply straight oils in the form of mists or as concentrated emulsions, but this method of application is still in the experimental stage. The quantity of oil deposited bears a direct relationship to both the effectiveness of insect control and safety of the tree. The most important factors affecting deposit are: concentration of oil in the spray mixture, the nature and concentration of the emulsifier used, and the quantity of spray applied.

Concentration of Oil in the Spray Mixture. Early recommendations for the use of oil sprays were apparently made on the assumption that concentration of oil in the spray mixture was the only factor determining the deposit of oil obtained. Consequently oils were recommended at a given concentration with no regard to the type or amount of emulsifier used, although a wide variety of emulsifying agents were in general use. It has been shown by Chapman *et al.* (3) that there may be little relationship between deposit and oil concentration when emulsions prepared with different emulsifiers are compared. For example, it was demonstrated by these workers that a 3% emulsion prepared with skim milk powder gave an oil deposit approximately 4 times as heavy as a 3% Goulac (lignin pitch) prepared emulsion. However, within practical limits the expected relationship between oil concentration and deposit is maintained when the same emulsifier is employed.

Kind and Amount of Emulsifier Used. Rather extensive laboratory studies have been conducted to determine the characteristics of oil emulsions prepared with various emulsifiers. These studies have led to the use of such terms as "quick breaking" and "tight" emulsions. In view of the many factors known to influence the characteristics of an emulsion, such classifications would appear to be of doubtful significance under practical conditions.

No generalities seem justified regarding the relationship between concentration of emulsifier and oil deposit obtained. An increase in the concentration of certain emulsifiers has been found to increase the oil deposit, while in other cases the reverse has been true. It is clear that both the individual characteristics of the emulsifier and the concentration used affect deposit, but, in spite of the extensive literature on the role of emulsifiers in emulsification and deposition, no satisfactory method of evaluating emulsifiers for spray oils other than by actual trial under field conditions has been found. A rather complete discussion of emulsifiers and the principles involved in emulsification is given in the work of Sutheim (21).

Quantity of Spray Applied. Petroleum oils exert a toxic effect through contact with the eggs or insects against which they are directed, and very thorough coverage is necessary to obtain satisfactory results. Poor coverage accounts for much of the failure experienced by growers using petroleum oil sprays. However, the possibility of excessive deposit through uneven coverage or overspraying should be considered. It has been shown by Chapman *et al.* (3) that there are definite limits to the quantity of oil which can be deposited in a continuous spraying operation. As will be seen in Table I, these workers applied twice the quantity of spray required to cover a tree and found that the oil deposit was increased approximately one third. However, when trees were resprayed after drying, the deposit was almost double that obtained from a single application. The practical significance of these findings is twofold. First, it is unlikely that excessive oil deposits can be accounted for by overspraying when standard concen-

trations of oil emulsions are used. Secondly, the common "spraying with the wind" practice used by growers may account for excessive oil deposit, as at least a portion of the tree is unintentionally sprayed twice by the overlapping of the two sprays.

Relationship between Oil Deposit and Control

A rather precise relation exists between dosage and insect response. The dosage, in the case of oil sprays, is generally expressed in terms of concentration of toxicant in the spray mixture, even though there may be little relationship between the actual oil deposit and the concentration of oil in the spray mixture (3). Comparisons made between oil emulsions of equal concentrations but prepared with different emulsifiers have resulted in considerable confusion. Dosage in terms of oil concentration in the spray is directly proportional to the actual dosage deposited on the host plant only when the emulsifier as well as the concentration is kept constant.

In the case of oil sprays a direct relationship has been shown by Cressman and Dawsey (7) between the amount of oil deposited and insect kill or control. A similar relationship has been shown by Chapman *et al.* (4) using oil as an ovicide in control of the fruit tree leaf roller. This relationship appears to hold regardless of the emulsifier used. The literature indicates that much attention has been given to the influence of emulsifiers on differences in effectiveness of oils. In many cases differences in effectiveness are attributed directly to the influence of the emulsifier. In spite of the various ways in which effects of emulsifiers have been interpreted, it appears that the basic influence of the emulsifier is on amount of oil deposited.

Relationship of Composition of Oil to Insect Control

All types of crudes have been used in the production of spray oils. On the West Coast the asphaltic base crudes occurring locally have been generally used, while oils derived from mixed base stocks are now most commonly used east of the Rockies.

Chemical composition of oils in relation to control has been considered for a long time. However, the evidence bearing on this point has not been conclusive until recently. Of the properties in question, viscosity was formerly considered most significant and most dormant oils had a viscosity of about 100 S.U.S. at 100° F. In 1942 Pearce *et al.* (15), using eggs of the fruit tree leaf roller *Archips argyrospila* (Walk.) evaluated approximately 40 oils of 100 S.U.S. viscosity representing a substantial cross section of all the oils being manufactured. These studies, conducted under conditions of practical usage, indicated a high correlation between control efficiency and paraffinicity. It was also brought out that the aromatic and unsaturated constituents contributed little to the efficiency of an oil.

Table I. Influence of Quantity of Spray Applied on Oil Deposit (3)

% Oil	Emulsifier	Tree Sprayed	Total Spray per Tree, Gal.	Oil Deposited, Mg./Sq. In. of Bark	Increase Due to Over-spraying, %
Ben Davis Series					
4	Goulac	Once	15	1.10	33.6
		Once	30	1.47	
4	Emulphor EL	Once	15	1.22	31.1
		Once	30	1.60	
4	Commercial emulsion	Once	15	1.85	36.8
		Once	30	2.53	
4	Triethanolamine oleate	Once	15	2.10	59.5
		Once	30	3.35	
Baldwin Series					
3	Goulac	Once	20	1.31	91.6
		Twice ^a	40	2.51	
3	Blood albumin	Once	20	1.47	95.9
		Twice ^a	40	2.88	
3	Commercial emulsion	Once	20	1.39	91.4
		Twice ^a	40	2.66	

^a First application was allowed to dry before second spray was applied; 4-hour interval between sprayings.

The relationship of paraffinicity to insecticidal efficiency was further shown by these workers (16) against the apple red bug, *Lygidea mendax* (Reut.); San Jose scale, *Aspidiotus perniciosus* (Comst.); scurfy scale, *Chionaspis furfura* (Fitch); cottony peach scale, *Pulvinaria amygdali* (Ckll.); European fruit lecanium, *Lecanium corni* (Bouche); European red mite, *Paratetranychus pilosus* (C. & F.); and against eggs of the codling moth, *Carpocapsa pomonella* (L.); the oriental fruit moth, *Grapholitha molesta* (Busck); eye-spotted bud moth, *Spilonota ocellana* (D. & S.); and grape berry moth, *Polychrosis viteana* (Clem.). It seems rather significant that the relationship between paraffinicity and insecticidal efficiency holds against species of such distinct groups. However, it should not be assumed, in the absence of specific data, that this relationship holds for all species.

In determining the value of an oil for spray purposes, both insecticidal efficiency and plant safety must be considered. Safety to foliage has been shown to be related to unsulfonated residue and insecticidal efficiency against certain species, at least, is related to paraffinicity. This being the case, the component of an oil largely responsible for plant injury is not the component largely responsible for insecticidal efficiency. Conversely, lowering the aromatic content for plant safety will not lower insecticidal efficiency. Likewise, increasing paraffinicity to obtain greater insecticidal efficiency will not reduce plant safety.

Mode of Action of Oils

Although petroleum oils have for a long time been used effectively as insecticides, the manner in which they produce toxic effects is not known. Relatively little work has been directed at this seemingly important point. In fact, the mode of action of oils when used as insecticides has been largely a matter of speculation. Undoubtedly, our meager knowledge on this point has hampered the development of more effective hydrocarbons.

Oils are used effectively against both the egg stage and hatched forms of insects. However, oil sensitivity varies not only among different species but also among life stages of the same species. For instance, eggs of the pear psylla are not highly susceptible to oil sprays, while the hatched forms are readily killed by these sprays.

Ovicide action. Theories on the mode of action of ovicides suggested by Hoskins (12) and Martin (13) are summarized as follows:

The oil may prevent the normal exchange of gases through the outer covering of the egg.

The oil may harden the outer covering so as to prevent hatching.

The oil may interfere with the water balance.

The oil may soften or dissolve the outer covering of the egg, through interfering with the normal development of the embryo.

The oil may penetrate the egg and cause coagulation of the protoplasm.

The oil may penetrate the egg and interfere with enzyme or hormone activity.

The oil may come in contact with the emerging insect and exert its toxic effect upon the delicate integument.

Upon consideration of these possibilities it seems reasonable that the precise mechanism of kill might vary with different species or that several modes of action might operate simultaneously or at different stages in the development of the embryo.

In their work on the mode of action of oils, Powers and Headlee (17) were unable to demonstrate the penetration of undiluted oils in eggs of the mosquito, *Aedes aegypti* (L.). They concluded that the killing of these eggs was due to oxygen deprivation. O'Kane and Baker (14), working with eggs representing six orders of insects, were clearly able to show traces of oil in the chorion and in tissues within the treated eggs. It would seem that the practical application of their findings might be limited as the technique used varied greatly from the practical application of oils in that eggs were immersed in undiluted oil for several hours.

Fox (9) attempted to determine whether oils penetrated the eggs of the leaf roller *Archips argyrospila*. Eggs were immersed in petroleum oils saturated with Sudan III

and oil red O. In a few cases faint red coloring was observed, but the results were not considered sufficient for definite conclusion by that author.

It has also been suggested that oils might penetrate the egg in the form of vapor. Shafer (18) pointed out that artificial fatlike membranes absorbed from the air highly volatile vapors of light petroleum fractions and that these rendered the membrane less permeable to oxygen. The possibility of similar effect by petroleum oils or their vapors is suggested. This point would seem at variance with the general observation of Powers and Headlee (17) and others that the lighter, more volatile fractions are less effective than heavier ones. It seems unlikely that under field conditions of considerable air movement volatile fractions would exert a marked toxic effect.

In considering the mode of action of petroleum oils when used as ovicides, it has often been suggested that the respiratory system is affected in some manner. Rather extensive investigations were undertaken by Smith and Pearce (20) to determine the effect of petroleum oils at concentrations of actual usage on the respiratory rate of eggs of the oriental fruit moth. These studies showed that the normal respiratory activity of developing eggs is markedly reduced by oil application. Furthermore, prolonged reduction of normal respiratory activity by oil is apparently directly related to lethal action. It would also appear that the lethal action consists of a slow reduction in vitality of egg with no sharply defined point of death. These observations strongly suggest that oil exerts its lethal effect through a mechanical interference with the normal gaseous exchange mechanism. Just how such interference eventually produces death is unknown. The possibility of mechanical rather than chemical interference seems to be further borne out by the fact that the less reactive paraffinic oils show greater ovicidal efficiency than do the more reactive unsaturated oils.

Insecticide Action. The mode of action involved in the toxic effect of oils on hatched forms is no better understood than in the case of ovicides. Several theories which have been advanced are summarized by Shepard (19) as follows:

Oil blocks the spiracles resulting in suffocation of the insects.

Oil penetrates the tissue in the liquid phase and kills by "corroding" them—by breaking down the tissue structure.

Volatile components of the oil are toxic and act as fumigants.

It seems unreasonable to assume that any one of these theories alone accounts for the toxic effect of oils on stages other than the egg. It is more likely that several operate simultaneously and that other modes of action are also involved. In generalizing, it would appear that the chemically active unsaturated oils might exert a toxic effect by virtue of their chemical structure. However, the highly refined saturated petroleum oils being less reactive would appear to exert their toxic effect chiefly through their physical characteristics.

As in the case of mode of action of ovicides, much work remains to be done before the mechanism whereby oils kill insects is clearly understood.

Oil Specifications

In the course of studies by Chapman *et al.* (3) on the composition and efficiency of spray oils applied to deciduous fruit trees, wide variations were found in the composition of oils supplied by insecticide manufacturers to New York growers. Industry in general, it seemed, had given relatively little attention to the specifications of oils offered for insecticidal use. In most cases oils were used which had been prepared primarily for other purposes. This situation is not surprising considering the quantity of oil used for insecticides as compared with the quantity used elsewhere. At the time of the studies (3), prepared emulsions were being widely used by growers in spite of their higher cost, largely because of the unsatisfactory results obtained with home mixed emulsions. A wide variety of emulsifying agents were used in the preparation of these products and products of certain companies varied greatly from year to year. The ideal solution to the problem involved would have been to adjust spray oil formulations to a standard deposition rate,

but this objective could not be readily accomplished. It was not surprising that variable results had been obtained by growers through the use of these products.

In order to gain greater effectiveness from oil sprays, it seemed desirable to establish specifications as a guide in selecting spray oils for use by growers of New York. The first such specifications were established by Chapman *et al.* (5) in 1942. After several years of practical usage, the advantage of more highly refined oils became further apparent and in 1946 specifications were established (2) for two grades of oil designated as "regular" and "superior." The superior grade was effective at lower concentrations and could be applied with safety later in the season. There has been a decided trend on the part of growers to use the superior grade. As a result of this trend the official recommendations for 1950 were limited to the use of the superior type alone. These specifications are as follows:

Viscosity (Saybolt, at 100° F.)	90-120 seconds
Viscosity index (kinematic)	90 (minimum)
Gravity (API degrees)	31 (minimum)
Unulfonated residue (ASTM)	90 (minimum)
Pour point	Not greater than 30° F.
Homogeneity	Relatively narrow boiling distillate portion of petroleum

The following methods of testing spray oils are to be used:

Viscosity, kinematic, ASTM Designation D 445-39T. Conversion to Saybolt Universal viscosity, ASTM Designation D 446-39. Kinematic viscosity index, ASTM Designation D 567-40T. API gravity, ASTM Designation D 287-39. Pour point, ASTM Designation D 97-39. Unulfonated residue, ASTM Designation D 483-40.

No specifications were established for prepared emulsions, owing to the difficulty of standardizing the kind and concentration of emulsifiers used by various manufacturers. Instead, a simple procedure was offered to growers whereby oil emulsions were prepared in the spray tank immediately before use. This procedure is generally referred to as "tank mixing." Blood albumin, being cheap and readily available, was selected as the most suitable emulsifying agent and was advised at the rate of 2 ounces for each 100 gallons of spray mixture. By standardizing both oil and emulsifier, growers were able to overcome many of the disadvantages previously experienced in the use of oil sprays. This method of preparing oil emulsions has been widely accepted by growers and the greater portion of the oil used by New York growers is handled in this manner.

Recommendations to Growers

The practices followed by growers of New York State are influenced in a large part by activities of the New York State College of Agriculture. The research bearing on practical problems is conducted by the New York State Agricultural Experiment Stations. The findings of the research staffs serve as a basis for recommendations which are formulated by extension specialists of the College of Agriculture. The current recommendations for control of fruit pests through the use of spray oils are given in Table II. In most cases oil is not the only insecticide recommended for control of these pests.

Need for Safer Oils

Not all the pests which overwinter on fruit trees are susceptible to oil sprays and for these oil-resistant species dinitro materials are currently being used. Unfortunately, oils and dinitro materials cannot be combined without undue risk of plant injury. This risk is avoided by applying the two materials in separate applications. The dinitro insecticides are usually applied in the dormant period, followed by oil application in the delayed dormant stage of bud development (when leaves of blossom buds are 0.25 to 0.5 inch in length). An additional reason for late application of dormant oil sprays which we have come to appreciate only recently is the fact that overwintering eggs of the European red mite are more readily killed at this time—i.e., just before hatching. The advantage

Table II. Recommendations for Use of Petroleum Oil in Control of Fruit Pests

Pest	Materials	Abbreviations for bud stages.		Remarks
		D = dormant	GT = green tip	
		Amount,	Time of	
		Gal./100 Gal.	Application	
Pests of Apple				
European red mite	Superior oil	2	GT, DD	DD preferred
Fruit tree leaf roller	Superior oil	3	GT, DD	
Apple red bug	Superior oil	3	GT, DD	
San Jose scale	Superior oil	2	D, GT, DD	
Scurfy scale	Superior oil	3	GT, DD	
Pests of Pear				
Pear psylla	Superior oil	2	D	Should be applied before eggs are laid
Pear psylla	Rotenone (5%) + summer oil	2 lb. 2 qt.	Summer	Emulsify with blood albumin
Fruit tree leaf roller	Superior oil	3	D	
Pear leaf blister mite	Superior oil	3	D	
Codling moth	Summer oil + nicotine sulfate	2 qt. 0.5 pt.	Summer	For second brood
Pests of Peach				
Cottony peach scale	Superior oil	3	D	
Cottony peach scale	Summer oil	1	Summer	One application at completion of hatch
European fruit lecanium	Superior oil	2	GT, DD	
Pests of Plum				
European fruit lecanium	Superior oil	2	GT, DD	
European red mite	Superior oil	2	GT, DD	

gained through late application of oils when trees are semidormant has emphasized the need of safer oils.

The use of summer oils, which for many years was a common practice, has been largely discontinued because of the incompatibility of these oils with sulfur and insecticides such as DDT. It is questionable whether this incompatibility can be overcome by changes in the formulation of the oil or the other insecticides intended for use with oil. If such changes could be made, summer oils would again find a useful place in the summer spray program, particularly for control of mites.

Discussion

Through successive developments in our knowledge of the use of petroleum oils, the earlier oils of practically unknown composition have gradually been replaced by safer oils which are effective at lower dosage than heretofore thought possible. Much work remains to be done before the fullest effectiveness is realized of petroleum oils as insecticides.

There is little doubt that the advent of DDT and other highly effective materials has brought about change in the nature of our insect problems. For example, the apple red bug which was formerly controlled by oil sprays has almost disappeared as a commercial pest in orchards following the adoption of a DDT spray program. On the other hand, the European red mite has become more severe as a result of the general use of DDT. It seems safe to say that the advent of DDT has not decreased the over-all use of petroleum oils as insecticides.

Many new insecticides are rapidly being introduced, but in general they appear to have several serious disadvantages. They are costly and many of them create a health hazard to the operator or the consumer. In addition, insects have developed resistance to certain insecticides. In other cases the use of newer insecticides has been a factor in the outbreak of so-called minor pests. In short, there is little indication that the long-sought cure-all insecticide is in sight.

Many of the objectionable features referred to above are not possessed by petroleum oils. In the matter of safety and economy they measure up well. Although oils have been employed as insecticides for over 50 years, no cases of the development of resistant strains have been reported.

In considering the continued use of petroleum oils as insecticides, it should be noted

that it has been only within recent years that intensive cooperative studies between petroleum chemist and entomologist have been undertaken. It is likely that before newer developments in the use of petroleum oils as insecticides are made it will be necessary to determine more precisely the specifications of the hydrocarbons responsible for highest insecticidal efficiency. Studies toward this end are currently being conducted at the California Agricultural Experiment Station, Riverside, Calif., and at the New York State Agricultural Experiment Station, Geneva, N. Y.

Present specifications, although useful from the practical standpoint, still call for oils which are composed of numerous types of carbon structures. It would be most desirable if, through the joint effort of petroleum chemist and insect toxicologist, specifications for the ideal hydrocarbon could be established. Industry could then attempt to meet or at least approach such specifications. One is likely to reason that economics would discourage such a venture on the part of industry. However, it should be kept in mind that increased effectiveness, together with the advantages already possessed by petroleum oils, would greatly enhance their value as insecticides.

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Insecticidal Efficiency of Petroleum Fractions and Synthetic Isoparaffins

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Two series of petroleum fractions and a series of synthetic isoparaffins prepared by the New York State Agricultural Experiment Station are described briefly. Their insecticidal efficiency on three unrelated pests—oriental fruit moth, European red mite, and cottony peach scale—is reported.

The relation of the constitution of saturated petroleum fractions to their insecticidal efficiency was shown in the case of a single insect species in a previous paper (9). To extend this study the Citrus Experiment Station of the University of California, the Shell Oil Co., and the New York State Agricultural Experiment Station cooperated to include other species and to examine the insecticidal properties of various hydrocarbon compositions derived directly or indirectly from petroleum as well as synthetic hydrocarbons of known constitution. Part of the program planned for the New York Station consisted of:

The preparation of suitable quantities of narrow boiling petroleum fractions for insecticidal and phytotoxicity evaluation at cooperating laboratories.

The preparation of sufficient quantities of individual hydrocarbons of known structure in the range of C₁₆ to C₃₄ for biological evaluation.

Two series of petroleum fractions and a series of synthetic isoparaffins which were prepared are described briefly in this paper together with a report of their insecticidal efficiency on three unrelated pest species. The materials were tested on the eggs of the oriental fruit moth, *Grapholitha molesta* (Busck), the winter eggs of the European red mite, *Paratetranychus pilosus* (C. & F.), and the newly hatched nymphs of the cottony peach scale, *Pulvinaria amygdali* (Ckll.). Riehl and LaDue (11) are reporting results on the evaluation of the two series of petroleum fractions against California red scale and citrus red mite.

Isoparaffins

Eleven isoparaffins having 16 to 34 carbon atoms per molecule were prepared in quantities of 600 to 1000 grams. Table I presents a brief description of the compounds. Details of the methods used in their synthesis and additional important physical properties will be presented elsewhere (10). The purity of all compounds is estimated to be 95 mole % or better.

Petroleum Fractions

The quantities of individual petroleum fractions necessary for the planned biological testing required the construction of a special vacuum fractionating column. A column of suitable size and efficiency was built and utilized in the fractionation of two waterwhite

Table I. Description of Isoparaaffins

Designation	Name	Empirical Formula	Theor. M.W. ^a	Viscosity at 100° F. ^b	
				Kinematic CS	Saybolt seconds
P1	7 <i>n</i> -Propyltridecane	C ₁₈ H ₃₄	226.4	2.69	35.0
P2a	7 <i>n</i> -Hexyltridecane	C ₁₉ H ₄₀	268.5	4.50	40.7
P3	8 <i>n</i> -Hexylpentadecane	C ₂₁ H ₄₄	296.6	5.82	44.9
P4	9 <i>n</i> -Hexylheptadecane	C ₂₃ H ₄₈	324.6	7.31	49.7
P5	9 <i>n</i> -Octylheptadecane	C ₂₅ H ₅₂	352.7	8.93	55.2
P27	11 <i>n</i> -Amylheptadecane	C ₂₆ H ₅₄	366.7	10.08	59.1
P22	6,11-Di- <i>n</i> -amylhexadecane	C ₂₅ H ₅₄	366.7	11.80	65.2
P6	9 <i>n</i> -Octyleicosane	C ₂₈ H ₅₈	394.7	12.03	66.0
P7	9 <i>n</i> -Octyldocosane	C ₃₀ H ₆₂	422.8	14.61	75.7
P8	9 <i>n</i> -Octyltetracosane	C ₃₂ H ₆₆	450.8	17.68	87.5
P9	9 <i>n</i> -Octylhexacosane	C ₃₄ H ₇₀	478.9	21.04	101.9

^a Calcd. using C = 12.01; H = 1.008.

^b Values will vary slightly from final values of Pearce and Schiessler (10).

oils representing a paraffinic type and a naphthenic type. The paraffinic oil was the same as that employed by Pearce *et al.* (9) except that it was from a different year's manufacture and is designated as 46-M20. The naphthenic oil, supplied by the Shell Oil Co., consisted of an exhaustively refined California spray oil blending stock. The two oils were separated into 10% fractions by vacuum fractional distillation; corresponding fractions obtained in replicated distillations were combined as composite fractions. These composite fractions were used for all physical property data and biological tests to be reported.

Figures 1 and 2 show the Engler boiling point characteristics at 1 mm. of mercury of the two oils and their fractions. A summary of the boiling point data is presented in Table II. These data were obtained in a specially designed vacuum Engler distillation apparatus at pressures ranging from 0.2 to 2.0 mm. of mercury; all values were extrapolated to 1 mm. by means of a Brown-Coats chart (1).

A summary of important physical and other characteristics of the parent oils and their fractions is presented in Table III. The molecular weights were estimated from the viscosity correlations of Hirschler (6, 7) and by direct determination with a modified Menzies-Wright apparatus (8). The other data were obtained essentially by the same methods used by Pearce *et al.* (9).

Insecticidal Evaluation

Oriental Fruit Moth Tests. In general the methods utilized in previous studies (9) were employed for the insecticidal evaluation of the materials. The results have

Table II. Summary of Boiling Point Data on Oils 46-S1 and 46-M20 and Their Fractions

	Cumulative % of Original Oil	% Distilled			B.P. Range 10-90%, ° F.	50% B.P. 760 Mm.	
		10%	50%	90%		° F.	° C.
		B.P. at 1 mm., ° F.					
46-S1 Fract.	1	263	315	367	104	660	349
	2	210	235	251	41	560	293
	3	246	261	275	29	590	310
	4	30	258	276	32	610	321
	5	40	274	289	30	625	329
	6	50	287	302	29	640	338
	7	60	302	312	22	655	346
	8	70	314	324	21	670	354
	9	80	326	336	22	685	363
	Residue 10	90	340	350	22	700	371
	100	361	381	423	62	740	393
46-M20 Fract.	1	289	353	435	146	705	374
	2	220	254	270	50	580	304
	3	271	286	299	28	620	327
	4	30	290	308	31	650	343
	5	40	310	325	29	670	354
	6	50	328	342	28	690	366
	7	60	346	362	28	715	379
	8	70	360	376	28	735	391
	9	80	378	395	28	755	402
	Residue 10	90	404	420	32	785	418
	100	429	454	483	54	830	443

Table III. Physical Properties and Ring Analysis of Oils 46-S1 and 46-M20 and Their Fractions

Oil	Mol. Wt.	Viscosity			Density, d_4^{20}	API Gravity, 60° F.	Ref. Index, n_D^{20}	Sp. Refract. n_D^{20}	Ring Analysis		Waterman chains
		Kinematic Centistokes		Lipkin-Kurtz rings					Waterman rings		
		100° F.	210° F.							Wt. %	
46-S1 Fract.	294	15.85	3.119	80.51	0.8794	1.4793	0.3226	55.0	45.0	46.0	53.1
	230	5.982	1.784	45.45	0.8784	1.4753	0.3207	66.8	33.2	37.0	37.0
	245	9.264	2.277	56.30	0.8766	1.4781	0.3218	63.3	36.7	59.4	43.9
	260	11.18	2.528	62.95	0.8775	1.4760	0.3219	60.7	39.3	59.7	47.0
	274	12.82	2.741	68.93	0.8778	1.4776	0.3222	56.8	43.2	60.4	46.0
	287	15.02	3.009	77.30	0.8776	1.4781	0.3225	56.1	43.0	47.4	52.4
	297	17.44	3.278	86.89	0.8779	1.4786	0.3228	55.5	45.0	45.2	55.3
	306	20.40	3.575	99.16	0.8780	1.4791	0.3230	53.8	46.0	44.2	53.9
	323	24.56	3.976	117.0	0.8782	1.4801	0.3232	51.9	48.1	43.4	56.9
	337	30.26	4.489	142.0	0.8793	1.4809	0.3236	50.0	50.0	40.3	56.7
Res. 10	61.26	6.682	263.2	0.8880	27.2	1.4857	0.3231	48.1	51.9	39.5	60.5
46-M20 Fract.	330	13.24	3.102	70.51	0.8394	1.4632	0.3282	29.3	70.7	21.6	77.4
	255	4.520	1.576	40.76	0.8170	1.4519	0.3301	25.9	74.1	22.4	78.6
	275	6.525	2.001	47.18	0.8241	1.4555	0.3295	27.1	72.9	21.6	78.4
	290	8.123	2.308	52.42	0.8293	1.4581	0.3291	28.4	71.6	21.6	78.4
	312	10.04	2.622	58.94	0.8341	1.4602	0.3285	28.0	72.0	22.5	77.5
	323	12.30	2.960	67.01	0.8382	1.4622	0.3281	29.8	70.2	23.3	76.7
	337	14.88	3.347	76.74	0.8418	1.4640	0.3278	30.0	70.0	23.6	76.4
	354	18.24	3.800	90.18	0.8458	1.4655	0.3271	30.8	69.2	25.5	74.5
	376	23.09	4.369	110.7	0.8500	1.4678	0.3269	31.0	69.0	25.3	74.7
	403	31.71	5.268	148.4	0.8564	1.4709	0.3263	32.9	67.1	26.8	73.2
Res. 10	54.38	7.345	251.5	0.8655	31.4	1.4742	0.3248	34.0	66.0	30.6	69.4

been expressed in terms of the minimum dosage per unit of leaf surface area required to produce a kill or control efficiency of 95% of the eggs of the oriental fruit moth on that surface. This value is termed the "minimum effective dosage." The minimum effective dosage values for all materials tested are presented in Table IV. These values were arrived at from dosage-control efficiency curves which are not reproduced, with the exception of those shown in Figure 3. All dosage-mortality curves were prepared from data from at least two and in many cases from three seasons' results. Each minimum effective dosage value is based on replicated tests and involves the use of a minimum of ten thousand eggs. It is believed that the results as a whole are reproducible to well within $\pm 10\%$.

Some of the minimum effective dosage values given in Table IV were obtained using a diluent in the form of Deobase kerosene which is completely nontoxic to oriental fruit moth eggs under the experimental conditions. The purpose in using a nontoxic petroleum derived diluent is accounted for as follows: First, it should be clear that the minimum effective dosage values do not include the quantity of diluent added—in other words, all values are directly comparable. In the course of the insecticidal work erratic results were sometimes obtained when testing the compositions of higher molecular weight, particularly if they were also highly paraffinic. Reports from co-operating laboratories indicated that similar difficulties were encountered. Superficially, at least, the data available suggested that the higher molecular weight compositions were less effective insecticidally than compositions intermediate in molecular size. This was not in agreement with the correlation shown by Pearce *et al.* (9) in which no substantial decrease in efficiency was observed in the higher molecular weight range considered. A closer study had led the authors to believe that the apparent poorer

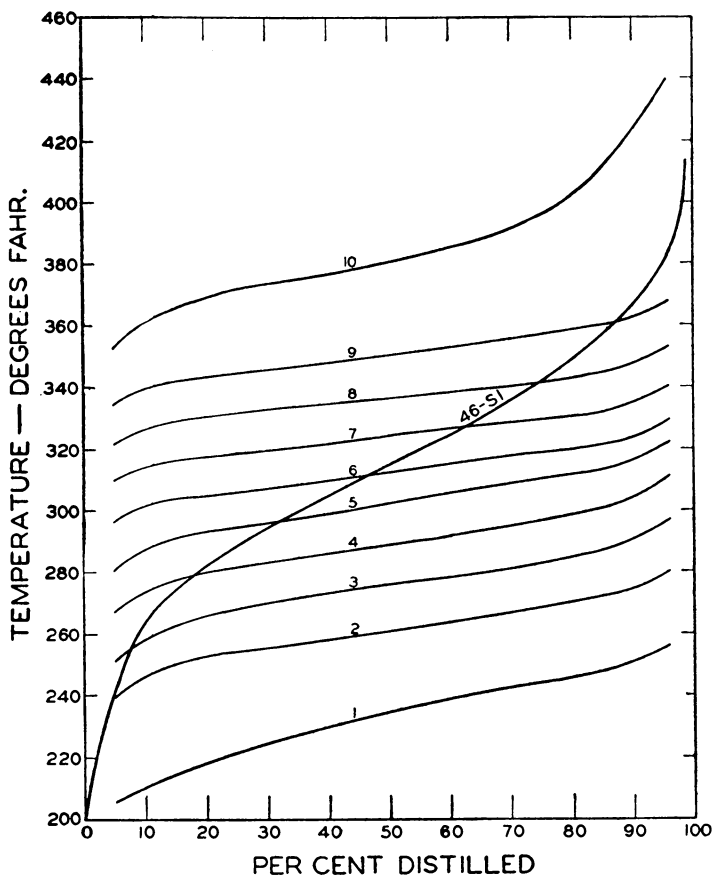


Figure 1. Boiling Point Curves for Oil 46-S1 and Fractions at 1 Mm. of Mercury

efficiency of the heavier compositions was not real but was due to poor distribution of the materials on the leaf or other plant surface. Evidently blood albumin, which has been used throughout this work as an emulsifying agent, is not sufficiently surface-active to promote good distribution of materials containing highly nonpolar and large molecules on the leaf surfaces involved. It is difficult to prepare relatively stable emulsions with the more highly refined oils and especially those from paraffinic stocks. Thus, it is reasonable to expect that the heavier materials and especially those highly paraffinic in nature would be difficult to deposit uniformly on a plant surface from a dilute emulsion of the type used in this study. The authors have been interested from a practical standpoint in the possible use of inert solvents as diluents for hydrocarbons of high insecticidal efficiency. Earlier work had indicated that a light petroleum solvent such as a highly refined kerosene would aid the distribution of oils applied to plant surfaces in the form of emulsions. For this reason Deobase kerosene was employed as a diluent.

Figure 3 is offered to illustrate the point under discussion as well as to present evidence with respect to the authors' interpretation of the data. These graphs are dosage-control efficiency curves for the isoparaffin of highest molecular weight (P9) tested and one of intermediate size (P22). The points obtained when P9 was used alone fall well on the initial part of the curve, but at the higher dosage levels the effectiveness appears to be proportionately much poorer. The highest kill (control efficiency) obtained with this compound was about 83% and this was at the comparatively low dosage level of 0.9 mg.

per 100 sq. cm. As already indicated, the erratic nature of such results is thought to be caused by nonuniform distribution of the compound over the host plant surface. The use of a diluent, as can be seen in the solid-line curve for P9, appears to correct this experimental difficulty. The results shown for P22 indicate that the diluent has no effect in the case of a material of lower molecular weight. The points fall well along the curve drawn, whether the compound was diluted or not. As suggested by the data in Table IV, no difficulties were experienced in arriving at reliable minimum efficiency dosage values for compounds having up to 28 carbon atoms per molecule. Above this molecular size, increasing variation in the results was encountered when the compounds were tested without the aid of a diluent. Satisfactory results were obtained for P7, P8, and P9 only by use of the diluent. Similarly, the values obtained for fractions 7 and 9 from the paraffinic oil (46-M20) were best when tested with a diluent. The authors believe that the insecticidal evaluations of the materials presented in Table IV represent the true relative efficiencies against the eggs of the oriental fruit moth.

European Red Mite Tests. The European red mite eggs used occurred as natural infestations on apple wood. Branches were collected in March, and from

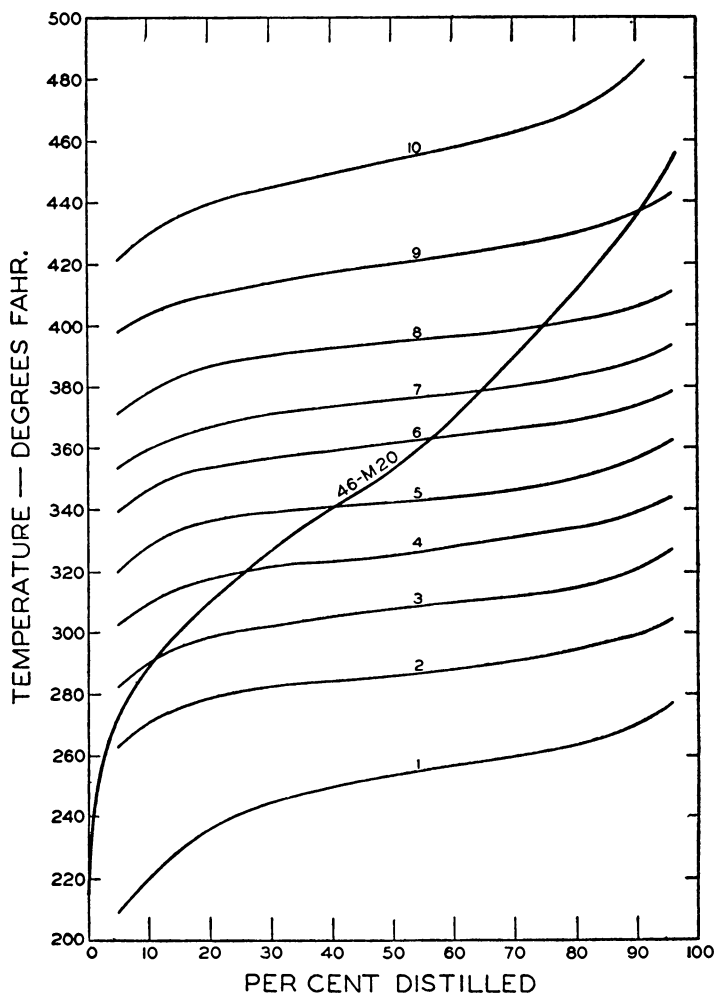


Figure 2. Boiling Point Curves for Oil 46-M20 and Fractions at 1 Mm. of Mercury

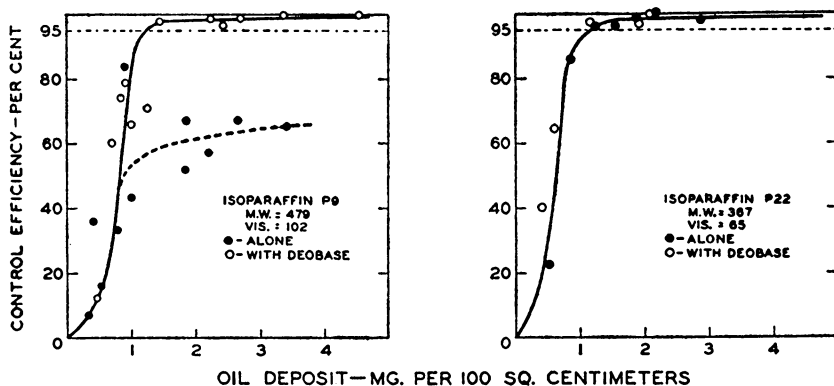


Figure 3. Doseage-Control Efficiency Curves for Isoparaffin P9 and P22 with and without Deobase

Oriental fruit moth eggs

this gross material infested fruit spurs or other small diameter twigs were cut into 1- to 3-inch sections. The egg population present on each section was then counted with the aid of a binocular microscope. Only the turgid, fully colored, and presumably healthy eggs were included in the record. After counting sections were impaled on brads which had been driven through $0.25 \times 4 \times 5$ inch pieces of plywood. Each such impaling block accommodated 12 twig sections which usually bore a total of from 750 to 1000 eggs. These blocks were the basic experimental units employed in the present studies. Three such blocks were treated at each spraying, giving three replicates per test.

Except for the time required to count and treat them, these eggs were maintained under outdoor conditions continuously until shortly before the beginning of the normal hatching period. At this time each impaling block was ringed with a sticky barrier and placed under greenhouse conditions. The purpose of the barrier was to entrap any mites that hatched from eggs which survived treatment. An illustration and further details of

Table IV. Insecticidal Evaluation of Petroleum Fractions and Isoparaffins

Materials	Minimum Effective Dosage, Mg./100 Sq. Cm.	
	Alone	With Deobase ^b
Naphthenic series		
46-S1	3.8	..
Fract. 1	α^a	..
3	18.0	..
5	7.0	..
7	2.5	..
8	2.6	..
9	2.6	..
Paraffinic series		
46-M20	2.5	..
Fract. 1	α^a	..
3	3.6	..
5	1.6	..
7	..	1.6
9	..	1.6
Isoparaffin series		
P1	α^a	..
P2a	45.0	..
P3	3.2	..
P4	1.2	1.2
P5	1.2	1.2
P27	1.2	1.2
P22	1.2	1.2
P6	1.2	1.2
P7	..	1.2
P8	..	1.2
P9	..	1.2

^a α signifies that material was tested at concentrations well beyond any practical limit and found noneffective at all levels.

^b Value when diluted 1 to 1 by weight with Deobase kerosene, a product of L. Sonneborn Sons, Inc., New York, N. Y.

the techniques employed will be found in the Chapman and Avens (2) paper on work with aphid eggs. Almost all of their practices were followed with the mite eggs.

All test treatments were applied approximately 1 month ahead of hatching and over a 2-day period. The writers (3) have shown that mite winter eggs become increasingly more susceptible to oil sprays as the hatching time approaches. Possible errors arising from this cause were avoided in these studies by limiting treating time to a 48-hour period.

Methods used in the preparation of the samples into emulsions, in applying treatments, and in making oil deposit determinations were the same as described by Pearce *et al.* (9). In the present situation an impaling block bearing 12 uninfested twigs was included in each test run for oil deposit determinations.

A sample of the data obtained in these studies is given in Table V. Control efficiency calculations in insecticidal studies must make a correction for the "natural" mortality which usually occurs in untreated controls. Abbot's equation, which is used for this purpose, follows:

$$\% \text{ control efficiency} = \frac{A - B}{A} \times 100$$

where A = % hatch in the untreated and B = % hatch in the treated

Table V. Sample of Data Showing Typical Response of Winter Eggs of European Red Mite to Oil Sprays

Test material, isoparaffin P5 used alone and diluted with equal volumes of Deobase (1950)								
% Oil	Additive	No. of Eggs	No. of Mites Hatched	% Hatch	% Control Efficiency	Oil Deposit, Mg./100 Cm.		
0.125	None	795	497	62.5	21.9	0.30		
		688	371	53.9	32.6			
		743	431	58.0	27.5			
	Deobase	780	408	Av.	27.3			
		894	524	52.3	34.6			
		846	435	58.6	26.7			
				51.4	35.7			
				Av.	32.3		0.83	
	0.25	None	753	219	29.1		63.6	2.84
			789	206	26.8		66.5	
1,022			318	31.1	61.1			
Deobase		752	228	Av.	63.7			
		944	191	30.3	62.1			
		797	139	20.2	74.7			
				17.4	78.2			
				Av.	71.7	2.40		
0.50		None	803	82	10.2	87.2	7.30	
			848	50	5.9	92.6		
	1,065		92	8.6	89.2			
	Deobase	752	62	Av.	89.7			
		659	51	8.2	89.7			
		778	57	7.7	90.4			
				7.3	90.9			
				Av.	90.3	6.74		
	1.00	None	979	22	2.2	97.2		15.2
			913	13	1.4	98.2		
1,033			11	1.1	98.6			
Deobase		768	30	Av.	98.0			
		955	19	3.9	95.1			
		757	18	2.0	97.5			
				2.4	97.0			
				Av.	96.5	16.4		
2.00		None	777	5	0.6	99.2	28.7	
			891	9	1.0	98.7		
	859		1	0.1	99.9			
	Deobase	764	16	Av.	99.3			
		783	10	2.1	97.4			
		778	5	1.3	98.4			
				0.6	99.2			
				Av.	98.3	21.5		
	Controls (no treatment)		14,298	..	80.0 (av. of 17 lots)			

Dosage-mortality curves have been plotted from data of the type shown in Table V and some of these are shown in Figures 5 and 6. Minimum effective dosage values, or the point of 95% kill, have been derived from these curves. These minimum effective

dosage figures have served as the basis for making comparisons between the various hydrocarbon compositions tested. Evaluation tests were conducted on winter eggs of the European red mite in 1948 and 1950. Some of the 1950 testing was done to check on the reproducibility of such data. Other work was done to extend the concentration test range below or beyond that of the 1948 test series, so that more complete or accurate curves could be plotted. Figure 5 shows that data obtained in 1948 and 1950 were similar.

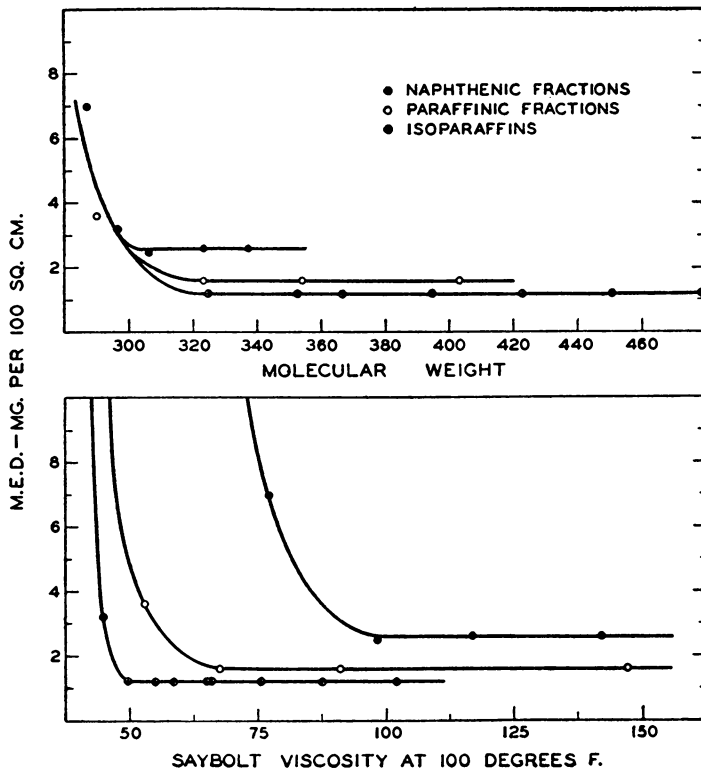


Figure 4. Correlations between Minimum Effective Dosage of Hydrocarbon Compositions and Molecular Weight and Viscosity

Oriental fruit moth eggs

Cottony Peach Scale Tests. Studies made on the cottony peach scale were limited, but the results obtained are considered reliable. All of the tests reported here were conducted in 1947 under orchard conditions. A heavily infested peach orchard at Hamlin, N. Y., was used for the experiment. Because the supply of the isoparaffins available was very limited, it was necessary to devise a procedure whereby satisfactory tests could be conducted with only 600 to 1000 ml. of spray mixture per test. Treatment was usually restricted in each test to two carefully selected attached branches 1 to 2 feet in length. A third branch was sprayed at the same time to provide leaves for oil deposit determinations. Treatments were applied on July 18 and 19, 1947. At this time all the eggs produced by the overwintering females had hatched, and the resultant new generation scales had largely moved to the leaves where they occurred on the lower surface along the midrib. A compressed air paint spray gun, operating at 30 pounds' pressure, was used to apply the spray treatments.

Treated branches were allowed to remain under natural conditions attached to the trees until August 13 and 16, when they were removed so that results on scale kill could be taken. This record was obtained through the aid of a binocular microscope. The ap-

pearance of oil-killed and live scales at this time is well illustrated by Harman (5, plate 2). The population of nymphs on treated and control leaves in these studies averaged 32.8 per leaf. Forty-four such leaves, on the average, were examined to obtain results on each test.

Table VI. Sample of Data Showing Typical Response of Newly Hatched Nymphs of the Cottony Peach Scale to Oil Sprays

Test Product	% in Spray	No. of Scales Examined		% Alive	% Control Efficiency	Oil Deposit, Mg./100 Cm.
		Total	Alive			
P1	0.50	1410	921	65.3	16.5	3.04
	1.00	1165	330	28.3	63.8	4.94
	2.00	1262	184	14.6	81.3	7.66
P4	0.25	1176	161	13.7	82.5	1.54
	0.50	1436	79	5.5	93.0	2.92
	1.00	1483	14	1.0	98.7	3.45
Deobase (alone)	2.00	1242	970	78.1	1.3	..
Deobase (plus dye)	2.00	1601	1140	71.3	8.8	..
Controls (no treatment)		2083	1592	76.4		
		854	730	85.4		
		1409	1066	75.7		
		832	626	75.2		
			Av.	78.2		

A sample of the data obtained in the cottony peach scale studies is given in Table VI. Data are included on Deobase kerosene used alone and combined with the dye which was added to all test lots for oil deposit determinations. The dye as tested apparently is nontoxic to the scale nymphs. The efficiency of various isoparaffins against the scale is presented graphically in Figure 7.

Correlations between Constitution and Insecticidal Efficiency

The three series of hydrocarbon compositions considered represent essentially three levels of paraffinic character. From the ring analysis data (Table III) the naphthenic fractions average about 50% paraffin chains; the paraffinic fractions around 75% and, of course, the isoparaffins are 100% paraffinic in structural character. To illustrate the relation of both molecular size and structural constitution to insecticidal properties, the minimum efficiency dosage values have been plotted against both molecular weight and viscosity of the three series of compositions as shown in Figures 4 and 7. Key information on the three series of hydrocarbons and their insecticidal efficiency against the three test species is summarized in Table VII. A plot of isoparaffin data on the three species is presented in Figure 8.

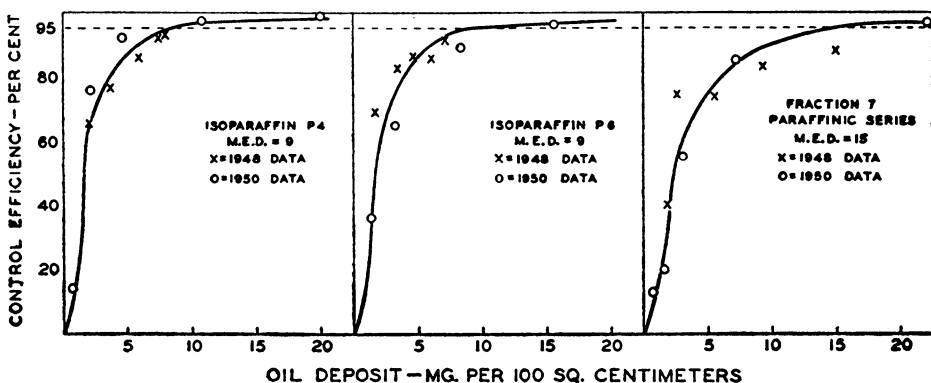


Figure 5. Dosage-Control Efficiency Curves Based on Data Obtained in 1948 and 1950

The data on oriental fruit moth eggs, Figure 4, are similar to those submitted by Pearce *et al.* (9). Considering the difference in the fractionation procedure and the fact that a different naphthenic oil was employed for the present study, the points of maximum efficiency at the lowest viscosities in the two series of oil fractions agree very well between each study. The level of maximum efficiency for the paraffinic fractions is the same as obtained previously—1.6 mg. per 100 sq. cm. The molecular weight correlation in Figure 4 shows a convergence of the curves at a molecular weight of 300. The data of Pearce *et al.* (9) suggested a small separation of the curves for the two series considered

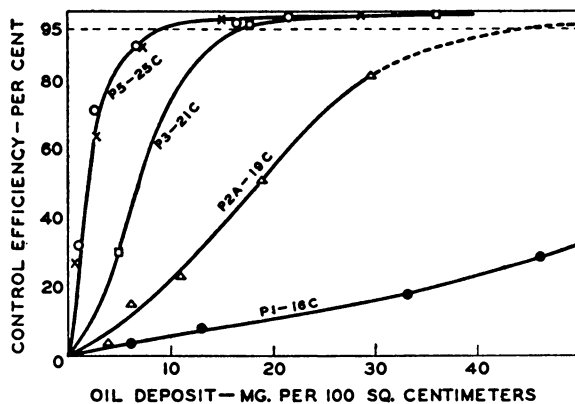


Figure 6. Dosage-Control Efficiency Curves for Isoparaffins P1, P2a, P3, and P5

European red mite eggs. On P5 curve O points with Deobase 1:1

Table VII. Insecticidal Evaluation of Three Series of Hydrocarbons against Three Species

Materials	No. of Carbon Atoms	Molecular Weight	S.U.S. Viscosity at 100° F.	Minimum Effective Dosage		
				Winter eggs European red mite (on apple bark)	Eggs oriental fruit moth (on quince leaves)	New nymphs cottony peach scale (on peach leaves)
Naphthenic series 46-S1 (original oil)						
Fract. 1	..	294	81	25	3.8	..
3	..	230	45	α ^a	α ^a	..
5	..	260	63	52	18	..
7	..	287	77	21	7.0	..
8	..	306	99	17	2.5	..
9	..	323	117	..	2.6	..
10	..	337	142	18 ^b	2.6	..
10	..	387	283	18 ^b
Paraffinic series 46-M20 (original oil)						
Fract. 1	..	330	71	20	2.5	..
3	..	255	41	90	α ^a	..
5	..	290	52	17	3.6	..
7	..	323	67	15	1.6	..
9	..	354	90	15	1.6 ^b	..
9	..	403	148	15 ^b	1.6 ^b	..
Isoparaffin series						
P1	16	226	35	α ^a	α ^a	12
P2a	19	268	41	50	45	6
P3	21	297	45	17	3.2	..
P4	23	325	50	9	1.2	3
P5	25	353	55	9	1.2	..
P5	9 ^b	1.2 ^b	..
P27	26	367	59	9	1.2	3
P6	28	395	66	9	1.2	3
P7	30	423	76	9 ^b	1.2 ^b	..
P8	32	451	88	9 ^b	1.2 ^b	..
P9	34	479	102	9 ^b	1.2 ^b	..

^a Signifies that material was tested at concentrations well beyond practical limits and found noneffective at all levels.

^b Values obtained using Deobase as diluent at 1 to 1 by weight.

there. More accurate methods for estimating molecular weight were utilized for the present data, so that the correlation shown in Figure 4 is believed to be more reliable. From the nature of the vertical portion of the curves it is readily seen that errors in molecular weight evaluation could cause horizontal spread between the three curves. The horizontal spread in the viscosity correlation is obviously the effect of the differences in structural constitution between the three series.

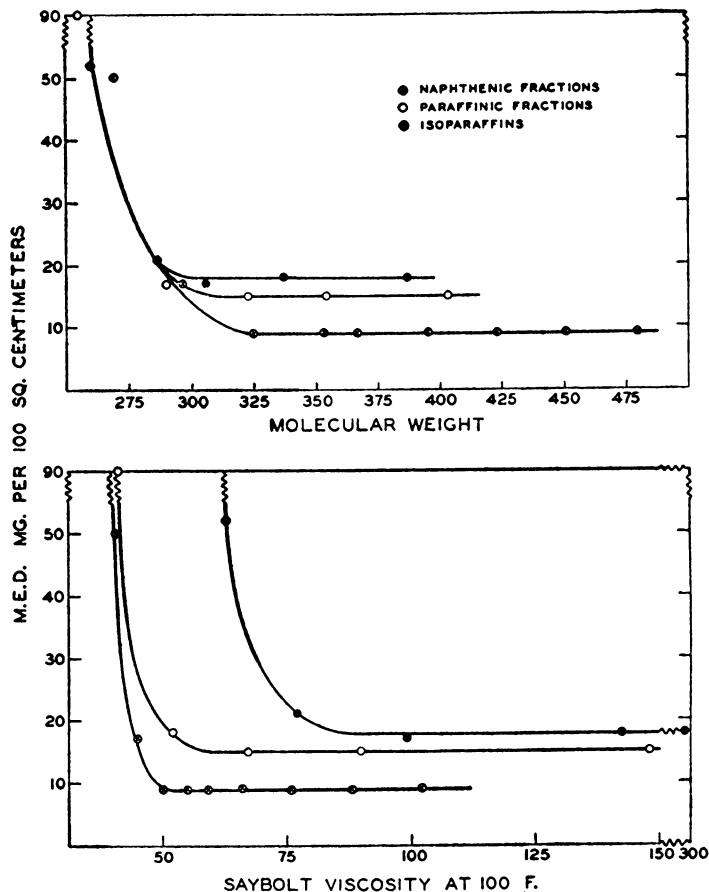


Figure 7. Correlation between Minimum Effective Dosages of Various Hydrocarbon Compositions and Molecular Weight and Viscosity

European red mite eggs

A striking similarity exists between the data plotted in Figure 7 and those shown in Figure 4. The break in toxicity occurs at much the same molecular size, around 300. However, at effective levels, along the horizontal portions of these curves, about seven times as much product is required to kill the mite eggs as is needed to kill the oriental fruit moth eggs. This situation may reflect a fundamental difference in hardness between summer and winter eggs. Strictly in the realm of speculation, a physiology which enables an egg to survive months of winter cold might better condition it to withstand other rigorous conditions, such as the presence of an oil film, than eggs like those of the oriental fruit moth which are dependent on mild summer temperatures for successful development. The comparison being made here is between a mite egg for one category and those of an insect for the other. However, essentially the same relationship can be shown

between the eggs of the oriental fruit moth and those of a close relative, the fruit tree leaf roller, *Archips argyrospila* (Wlkr.) (4). Even greater dosages of oil are recommended to destroy the winter eggs of this latter species than those of the European red mite.

The distinctly new information added to the work of Pearce *et al.* (9) is that submitted on the isoparaffin series. Further improvement in effectiveness is evident in the case of these 100% paraffinic materials. The data on this series represent an additional confirmation and extension of the authors' thesis that insecticidal efficiency is related to paraffinic character. Taking into consideration the molecular size factor, one can generalize to the extent that for saturated hydrocarbon compositions above a molecular size of about 310, insecticidal efficiency increases with increase in paraffinity. Although the data are incomplete, evidence is accumulating that this generalization will hold, approximately at least, regardless of the source of the hydrocarbons. In other words, there has been no indication as yet that such differences in structural character as degree of branching and position of paraffin chains are major factors in influencing toxicity. The principal consideration seems to be the proportion of carbon atoms in ring structures to those in the form of chains.

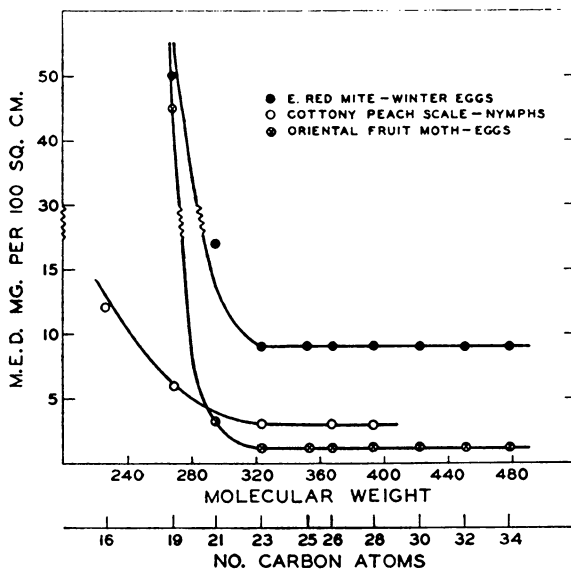


Figure 8. Correlation between Minimum Effective Dosages for Three Test Species to Isoparaffins Ranging from C_{16} to C_{34}

Figure 8 illustrates an interesting difference in response between the nymphs of cottony peach scale and the eggs of the other two test species. Again, while the molecular size break in toxic action occurs at about the same point for all test species, it is much less abrupt for the cottony peach scale. Possibly this can be accounted for by differences in the respiratory systems, since oils apparently effect kill through a smothering action (12). Exchange of metabolic gases takes place more or less directly through the wall in the case of eggs. Hatched insects, such as the scale nymphs, are equipped with a tracheal system and respire through openings in the body wall, the spiracles.

The question of the cause of the sharp change in effectiveness over a very small range in viscosity or molecular size is still not precisely known. However, it is believed from some limited data available that volatility is definitely involved. Certainly volatility accounts for the almost complete ineffectiveness of the lightest compositions as well as fractions of petroleum within the kerosene range. The studies of Smith and Pearce (12)

have shown that a minimum effective dosage of oil must be in contact with oriental fruit moth eggs for about 24 hours at $\approx 80^{\circ}$ F. to effect complete mortality. Any substantial loss in oil during the first 24 hours after application permits a high degree of survival of the eggs. Whether or not this time factor is the same for all oil-susceptible species of insect and mite pests is not known; however, the rapid change in effectiveness occurs at about the same molecular size for the three unrelated species tested. This suggests that the time factor may be much the same for various pest species and the possibility of using one product for the control of all horticultural pests. Tentative specifications for such an ideal product have been proposed (9). Evidence now available on the isoparaffins will permit an even more precise definition of such a product.

Acknowledgment

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Evaluation of Petroleum Fractions against California Red Scale and Citrus Red Mite

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The insecticidal efficiency under laboratory conditions of various members of two series of narrow boiling petroleum fractions was determined for adult female California red scale, *Aonidiella aurantii* (Mask.) and eggs of the citrus red mite, *Paratetranychus citri* (McG.). Correlations between efficiency and various properties of the fractions such as structural character, molecular weight, and viscosity were observed. These correlations indicate that conventional spray oils used on citrus in California may contain appreciable amounts of hydrocarbons of low insecticidal activity. The evidence indicates that the insecticidal efficiency of spray oils against citrus insect pests may be considerably improved by proper selection with respect to structural character and molecular size.

The use of petroleum substances to control insect pests on citrus apparently began about 1880. Riley and Hubbard (23) tested kerosene applied in aqueous emulsions. As kerosene was not completely satisfactory, unrefined distillates between it and lubricating oils were tried (25). A heavier petroleum component, an engine lubricating oil, was tried for the first time on citrus in Florida in 1906 (26). For some reason the use of cuts of petroleum in the light lubricating oil range as insecticides was not accepted rapidly. Experiments with distillates were continued, but damage to trees and loss of fruit followed application frequently and were deterrents to their use. In 1915 Gray and DeOng (14) reported that the observed injury to the tree resulted from substances in the oil which could be removed by treating the oil with sulfuric acid.

A premixed emulsion of a highly refined, heavy petroleum oil for horticultural sprays was marketed in California in 1924 by W. H. Volck. This seems to have been the first high unsulfonated residue (per cent of oil essentially nonreactive to sulfuric acid) spray oil offered commercially. The emulsion was a mayonnaise type and was recommended for use on citrus at 10 to 13%.

The quick-breaking emulsion concept developed by DeOng *et al.* (6) in 1927 materially improved the insecticidal efficiency of spray oils against insect pests of citrus. After announcement of these results, a large number of proprietary spray oils was placed on the market in California. During the next several years considerable variation in pest control and in damage to citrus orchards occurred with oil sprays.

Smith (24) conducted intensive studies of the factors involved in the use of oil sprays to control California red scale and other pests of citrus in southern California. He found that insecticidal efficiency and deleterious effect on the trees were closely related to the so-called weight of the spray oil, as indicated by the distillation range, and that this provided a better basis for classification of spray oils than viscosity. The relationship of the unsulfonated residue of petroleum oils to tree injury had been clearly established previ-

ously by Gray and DeOng (14) in 1915. A third factor of primary importance to insecticidal efficiency and to the effect of the oil on the tree is the quantity of oil deposited. Investigation of this phase of the use of oil sprays led Smith (24) to the development of the tank-mixture method, employing blood albumin for the emulsifying and spreading agent. English (9) proposed the first method for the direct measurement of the oil deposit on sprayed foliage.

Although spray oils marketed during this period were described in terms of general classes somewhat similar to those used today, confusion existed regarding selection of the proper oil for a given situation, because some of the oils were labeled according to viscosity and others according to distillation range. The California Department of Agriculture, Division of Chemistry, the agency charged with the registration of such products, recognized the need for standardization, and in 1932 adopted a classification including five grades of summer or foliage spray oils, based on the percentage distilled at 636° F. and the minimum unsulfonated residue for each (10, 18).

Ebeling (8) found in field studies that the amount of oil deposited was directly related to the control of California red scale; that heavier oils gave better results than light oils; and that unsulfonated residue did not seem to be a factor insecticidally. In laboratory studies (7) with the same insect he found that newly born individuals were very susceptible to oil, that the scales became progressively less susceptible as they developed, and that heavier oils hindered settling of the nymphs to a greater extent than the lighter oils. Ebeling showed that oil reaches the body of the insect from the edge of the armor. Although oil does penetrate the armor, it enters much more readily at the edge than through the more central zones. The flow of oil under the edge of the armor thus constitutes the practical consideration in the relation between the amount of deposit of a given oil and the kill obtained.

Chapman, Pearce, and Avens (4, 20) investigated the relation between chemical composition and insecticidal efficiency of various dormant and foliage spray oils against several common insect pests of deciduous trees, and found it to be positive. They concluded that an oil which is highly paraffinic in character is the most desirable type. Saturated narrow-cut petroleum fractions were used by Pearce, Chapman, and Frear (21) in a study of the influence of molecular weight and structural constitution on the insecticidal efficiency of such oils to eggs of the oriental fruit moth, *Grapholitha molesta* (Busck). Correlations between efficiency and various properties were compared on the basis of composition. The value of paraffinicity was illustrated, and the importance of other properties was indicated.

Petroleum oils are widely used in the treatment of citrus crops in California. They have proved to be the most efficient insecticide per unit of cost for most of the dominant pests of citrus in this area. In an effort to improve oil sprays from the standpoint of both tree safety and insecticidal effectiveness, the research on oil sprays at the University of California Citrus Experiment Station has been intensified. Part of this new effort has involved close cooperation with other laboratories, particularly with the New York State Agricultural Experiment Station at Geneva. The same petroleum fractions and other hydrocarbon compositions were tested simultaneously against citrus and deciduous fruit pests. This coordinated approach has been mutually advantageous, and it is expected that it will lead to an understanding of the fundamental principles involved in the use of hydrocarbon oils as insecticides in general.

An initial report is made here on results obtained in laboratory studies of two series of petroleum fractions against adult females of the California red scale, *Aonidiella aurantii* (Mask.), and against eggs of the citrus red mite, *Paratetranychus citri* (McG.).

Experimental Oils

The two series of narrow-boiling petroleum fractions used in these studies were derived from two water-white oils, one of naphthenic character and the other highly paraffinic in nature. These fractions were prepared in the laboratories of the New York State Agricultural Experiment Station and supplied to the writers for evaluation against citrus

pests. A detailed description of these stock oils and their fractions is presented by Pearce and Chapman (19), who also present insecticidal data on these same materials used against eggs of the oriental fruit moth.

Species Tested

The two species selected for the laboratory studies—California red scale and citrus red mite—are dominant economic pests of citrus in southern California (3). Constant vigilance against infestations of these species is of primary concern to the growth and production of citrus in the area, and petroleum oil sprays are the most important means of control available.

California red scales were obtained from a laboratory colony reared and maintained on banana squash. Squash was first used as a host for the mass production of California red scale under laboratory conditions by Rush Bumgardner of the Orange County Insectary, Anaheim, Calif. (12). The suitability of banana squash for this purpose was shown by Flanders (13). Lindgren *et al.* (15, 17) adapted the rearing methods of the red scale to the requirements of insecticide studies and developed techniques for using this species as a laboratory test insect.

Field observations and experience in the control of the citrus red mite indicate that the adult mite is much more susceptible to oil sprays than its eggs. Attempts to rear citrus red mites continuously in large numbers from a self-sustaining laboratory colony have not been successful. However, infestations of citrus red mite occur in southern California throughout most of the year and constitute a reasonably reliable source of mites. Adult mites brought into the laboratory from the field lay eggs readily for a few days on grapefruit and other suitable plant materials. Eggs laid within the limits of a specified interval may be obtained conveniently by manipulation of the various items and factors involved. Since the egg is a major target for field control and offers the most direct source for uniformity of test material for this species, it was the stage selected for laboratory experiments.

Procedure

For the laboratory tests with California red scale reported here, slight modifications were made in the technique developed by Lindgren, LaDue, and Dickson (17). Grapefruit infested with red scale crawlers were placed in a room in which the controls were set for a constant temperature of 80° F. and 85% relative humidity. Since mating does not occur in a high proportion of females in the absence of sunlight, or of fluorescent light if artificial illumination is used, a mixture of incandescent and fluorescent light was used in the room. Under these conditions young scales begin to emerge 38 to 40 days after the crawlers are placed on the fruit. Infested fruit were subjected to applications of the oil sprays at 36 days. At this age the female scales are fully developed, but the contact between the scale covering and the fruit surface has not been loosened by emergence of young. Observations by Ebeling (7) indicate that scales in this condition have the greatest tolerance to petroleum oil.

Supporting evidence was given (7, 17) for restricting the count to scales sufficiently separated from neighboring scales to respond as independent individuals to the applied oil film. However, oil entered and was retained by scales too near each other for them to be used for mortality counts. If the number and density of these scales were variable, some influence may have been exerted on the relation of the oil film to the individuals counted. To enhance the independence of each scale counted, fertile female scales were hand-thinned to approximately 0.5 cm. apart. The adult male insect emerges from the shell covering at an age of about 21 days; only the cast shells of the males remain on the fruit at 36 days. These are loose and may be removed easily with an air stream. Any unfertile females are removed at the same time.

A special tool was made to facilitate the thinning operations. A needle with a chisel-type point $\frac{1}{16}$ inch wide was mounted on a welding tip in such a way that the point of the

needle would intercept the jet at a distance of 1 inch from the face of the tip. The diameter of the orifice of the welding tip was 0.036 inch. The force and velocity of the air through the tip was controlled at 8 liters per minute. Scales loosened by the point of the needle are blown away by the air stream, which does not have enough force to loosen the edge of the armor of the scales left on the fruit.

Citrus foliage heavily infested with citrus red mite was collected and brought into the laboratory. Open-top containers of 1-gallon capacity were filled loosely with the foliage. Clear, uncolored celluloid or plastic was used to form a cone having a base 8 to 9 inches in diameter and an opening 2 inches in diameter at the apex. The base of the cone was placed over the top of the foliage container, and a fresh grapefruit was placed on the opening at the apex of the cone. As the foliage dried, the mites moved away from it up the inside of the cone to the fruit, where they fed and laid their eggs. After the mites had been on the fruit for approximately 24 hours, they were removed with a gentle stream of air of the same velocity as that used to thin the scale.

The procedure adopted for applying the petroleum fractions to the infested grapefruit is a modification of techniques developed by Smith (24) and Lindgren *et al.* (17).

The oils were applied in the form of an aqueous emulsion prepared according to the tank-mixture method. Most of the time it is possible to approach a given oil deposit by proper adjustment of the concentration of oil in the spray mixture. The volume basis was used for the concentration of oil in the spray emulsion. The ingredients were emulsified and agitated by means of a high speed homomixer (made by Eppenbach, Inc., Long Island City, N. Y.).

Commercial blood-albumin spreader was used as the emulsifying agent at the rate of 4 ounces per 100 gallons of finished spray mixture (24). The emulsion was applied to the fruit by means of a commercially available air-pressure paint spray gun (Type MBC, made by the De Vilbiss Co., Toledo, Ohio). The paint spray gun was operated with compressed air at a pressure of 30 pounds per square inch. The fruit were placed singly on a small turntable, so that the center of the fruit was at the same height as the face of the nozzle of the spray gun and 30 inches in front of it. The turntable was set at 30 r.p.m. Each fruit received a uniform exposure of four revolutions to the spray stream in accord with the following routine:

Each fruit was placed on the turntable with its polar axis (the axis between the stem and the blossom end of the fruit) in a horizontal position, and was exposed to the spray stream for one revolution of the turntable. Then the fruit was rotated 90 degrees around the axis, in the horizontal position, and sprayed for another revolution. The polar axis was then turned to the vertical position, and the fruit was exposed to the spray stream for two revolutions of the turntable to complete the application. During the latter operation, the spray stream was centered on the equatorial band of the fruit.

The mean quantity of oil deposited, in micrograms per square centimeter for each lot of sprayed fruit, was determined colorimetrically according to a method developed by Riehl, Gunther, and Beier (22). Portions of the various oils were partially saturated with Oil Red O. Dyed oil was used to prepare the spray emulsion applied to the fruit. It was shown that the concentrations of dye used were not toxic to the insects and did not affect the direct relationship of amount of deposit to mortality.

The treated fruit infested with red scale were held for 21 days in a cabinet maintained at 80° F. and 85% relative humidity. By the end of this period the scale insects that had succumbed to the treatment had become desiccated and discolored. When live scales are punctured with a needle a drop of fluid, which may be seen readily under 5- to 7-power magnification, exudes around the puncture. Dead scales are dry and easily distinguished. The dead scales on an equatorial band about 1.5 inches wide were counted.

Low-power magnification (approximately 18 \times) is required to distinguish mortality of citrus red mite eggs. Freshly laid eggs are red, but only a clear egg shell remains when the egg hatches, and this often shatters. To avoid the influence of color on choice of eggs counted, the locations of a number of eggs on fruit were marked 24 hours after the spray had been applied. Under low-power magnification of a stereoscopic microscope, a circle was inscribed with India ink around individual viable eggs selected at random from an equatorial band approximately 1.5 inches wide. The fruit were held post-treatment for 7 days in a cabinet maintained at 80° F. and 65% relative humidity.

Several follow-up observations indicated that this time-temperature interval provides ample allowance for incubation of the eggs. Accordingly, on the seventh day after application of the spray, the marked circles were examined, and hatched and unhatched eggs were tallied.

In the tests with both California red scale and citrus red mite, untreated lots of fruit selected at random from infested fruit prepared for a given day were held with the treated lots and counted for natural mortality. The corrected percentage of kill for each treatment was calculated by means of the Abbott equation (1).

Table 1. Efficiency of Petroleum Fractions of Paraffinic (46-M20) and Naphthenic (46-S1) Composition against Adult Female California Red Scale

Stock and Fraction No.	Molecular Weight	Viscosity, S.U.S. at 100° F.	Viscosity Index	Slope of Regression Line	LD ₅₀ , γ/Sq. Cm.	Limits at 5%, in % of LD ₅₀
Paraffinic Stock 46-M20	330	70.51	110.0	4.896	65	1.3
Fraction 1	255	40.76	..	5.175	122	24.2
2	275	47.18	105.4	5.575	89	6.4
3	290	52.42	107.9	5.884	85	11.4
4	312	58.94	99.7	4.552	89	4.9
5	323	67.01	90.8	3.870	85	11.8
6	337	76.74	99.2	2.250	75	8.1
7	354	90.18	110.3	4.899	64	10.8
8	376	110.7	112.5	4.504	77	1.8
9	403	148.4	109.8	3.015	100	7.8
Residue 10	453	251.5	102.4
Naphthenic Stock 46-S1	294	80.51	36.4	3.615	98	2.3
Fraction 1	230	45.45	..	n.e.*	n.e.*	..
2	245	56.30	54.5	5.218	116	6.9
3	260	62.95	32.5	4.946	117	11.1
4	274	68.93	28.3	5.303	104	17.7
5	287	77.30	35.8	3.367	83	9.4
6	297	86.89	40.3	4.240	84	1.8
7	306	99.16	37.3	3.755	107	8.2
8	323	117.0	36.0	3.603	109	6.8
9	337	142.0	39.9	2.121	124	7.2
Residue 10	387	283.2	54.3

* "n.e." signifies that fraction was noneffective at all concentrations tested.

It is possible to increase the precision of a dosage-mortality line by the use of a large number of replications or a large number of individuals per trial. Thinning limits the number of scales available per single piece of fruit. The number of fruit per trial and the number of replications for each dosage indicated by the heterogeneity would have prolonged the period of the trials considerably because of the limited number of infested fruit that were available and that could be handled per day. It was therefore decided to use three pieces of infested fruit, involving approximately 150 insects per spray trial, and to repeat each dosage level three times. As the dosage range required was wider for some fractions than for others, 21 to 30 points were determined for each material tested. Fractions, dosage levels, and replications were taken at random until all the spray tests had been completed. This required a fairly long period, but the points for any given line occur throughout the period and are comparable in this respect to those for any other line.

Mortalities observed in tests of a series of oil dosages against adult female California red scale or eggs of the citrus red mite indicated a positive relation between increased dosage and increased kill. The fit of the points to the line was much better for oil dosages expressed as deposit than for those expressed as spray concentration. However, the variance observed indicated that statistical procedures would be required to arrive at the best fit for a line through the observed points. The method of probit analysis chosen was that proposed by Bliss (2) and modified by Finney (11) for data adjusted for mortality in the controls.

Heterogeneity of Mortalities

Limitations imposed by the nature of the infested material and by the operations of spray application could not be adjusted to permit insecticidal evaluation of the oils in-

volved in the two series of fractions on the same day or within a relatively short interval. It was recognized that the tolerance of the test subjects might vary with time, and that heterogeneity might occur from this factor. Results of some earlier trials showed that the response to increased dosage of the stages of the two species used was somewhat heterogeneous, although the positive relationship was clearly evident.

Cressman (5) observed large differences in the susceptibility of adult females of *Aonidiella aurantii* to oil sprays. The mortality of those treated with a light-medium grade oil ranged from 87% with an oil deposit of 126 micromilliliters per sq. cm. to 11% with a deposit of 115 micromilliliters per sq. cm. His studies indicated that the differences were not associated with inherited resistance. No reference to such differences in susceptibility of eggs of the citrus red mite has been found.

Although it might have been reasonable to expect parallelism in the dosage-mortality lines, it was considered advisable to use a rather wide dosage range for each oil tested. It was planned to select spray concentrations to provide expected mortalities of 30 to 95%. After a little experience it was possible to judge the range of concentrations needed from the results of one or two exploratory trials. The probit method was applied to data for dosage-mortality series for several oils for each species. The chi-square values for these curves were a number of times larger than the maximum permissible for the number of degrees of freedom involved. For example, for red scale the chi-square values were 133 for 17 degrees of freedom, 140 for 19 degrees of freedom, and 198 for 22 degrees of freedom; for red mite eggs they were 257 for 17 degrees of freedom, 334 for 19 degrees of freedom, and 270 for 21 degrees of freedom. Yet the curves did not show departure from the linear relationship. This indicated that considerable heterogeneity in the fit of points to the line might be expected.

To gain further information on the heterogeneity observed for scale, and the possibility that it might be associated with lack of uniformity of the oil film over the surface of the fruit, or with the nature of the contact of the oil with the scale, the probit regression line for observed mortalities of nonresistant adult California red scale at increasing concentrations of hydrogen cyanide was determined. Availability of the fumigant to the scale does not appear to be a factor of consequence in the heterogeneity. Chi-square for this line was 423 for 28 degrees of freedom; yet the linear relationship of mortality to dosage was clearly evident. Thirty fumigation trials were made (16), and approximately 1100 scales were counted for each trial. The mean fiducial limit of the LD_{95} (11) for t at the 5% level was 3.3% of the LD_{95} .

Table II. Efficiency of Petroleum Fractions of Paraffinic (46-M20) and Naphthenic (46-S1) Composition against Day-Old Eggs of Citrus Red Mite

Stock and Fraction No.	Slope of Regression Line	LD_{95} , γ /Sq. Cm.	Limits at 5%, in % of LD_{95}
Paraffinic Stock 46-M20	2.562	25	17.2
Fraction 1	..	n.e. ^a	..
2	..	n.e.	..
3	4.656	69	7.0
4	3.408	34	13.6
5	2.652	29	13.8
6	2.626	26	8.6
7	2.866	21	11.1
8	2.402	24	11.5
9	2.464	21	13.6
Residue 10
Naphthenic Stock 46-S1	2.660	59	11.8
Fraction 1	..	n.e.	..
2	..	n.e.	..
3	..	n.e.	..
4	..	n.e.	..
5	3.229	144	12.8
6	4.284	80	11.5
7	2.189	71	14.7
8	3.255	39	11.6
9	4.445	20	14.2
Residue 10	3.244	15	11.0

^a "n.e." signifies that fraction was noneffective at all concentrations tested.

The factor for heterogeneity for each line was used in the determination of the fiducial limits of the *LD* values selected on that line. More than 1300 separate lots of treated fruit were used in these tests and mortality counts of approximately 250,000 insects were involved.

LD₉₅ as a Basis for Comparisons of Efficiency

Since English (9) demonstrated a method for recovering petroleum oil from sprayed foliage, numerous workers have recognized the value of stating their observations in terms of the quantity of oil present per unit area of plant surface. It became evident that insect control could be enhanced by increasing the amount of oil deposit, but the reaction of the plant, particularly of citrus, became a limiting factor in this direction. Numerous studies have been conducted in the field and in the laboratory in search of solutions for such problems in the use of oil sprays. It has been noted frequently in the reports that appreciable fluctuations may occur in the results from various applications of a given spray formulation. To eliminate such contingencies Pearce, Chapman, and Frear (21) used a rating for efficiency as a basis of comparison. They elected to define the efficiency of an oil in terms of the relation between the amount of deposit in contact with the insect and the observed mortality. A mortality of 95% was chosen as the fixed point for expressing the efficiency rating in terms of the amount of deposit.

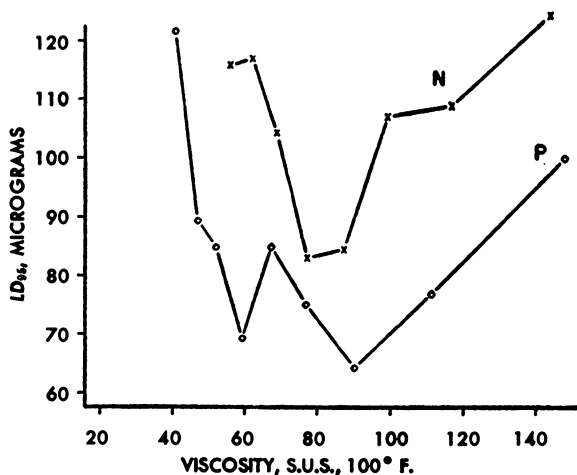


Figure 1. Correlation between Efficiency and Viscosity

Series of fractions of paraffinic (P) and naphthenic (N) composition against adult female California red scale.

Calculation of the probit regression lines and inspection of their slopes revealed that the lines for the various fractions are not parallel. For this reason the comparative efficiency of fractions changes with the mortality level chosen as the reference point. It seems logical, therefore, to make the comparisons on a basis similar to that on which they would be judged under field conditions. A mortality of 95% provides a suitable reference to field conditions in citrus pest control and offers the advantage of expressing the efficiency of the oils against citrus insects on the same basis as that used previously for similar fractions against deciduous pests (21).

Inspection of several representative curves indicated that 95% mortality might lie beyond the inflection of the sigmoid curve for data for most of the fractions. However, it seems reasonable to assume that the deposit-mortality relationship may be projected through the 95% level with confidence by the use of the probit method. No advantage

is apparent at this time for projecting the relationship above the level of 95%. Therefore, the efficiency of each oil is stated in terms of the LD_{95} expressed as the oil deposit in micrograms of oil per square centimeter of fruit surface required to kill 95% of the individuals. The values for LD_{95} , the reproducibility of the value for t at a probability of 0.05, the slope of the dosage-mortality regression line, and pertinent properties for each fraction are listed for adult California red scale in Table I, and for citrus red mite eggs 24 hours old in Table II.

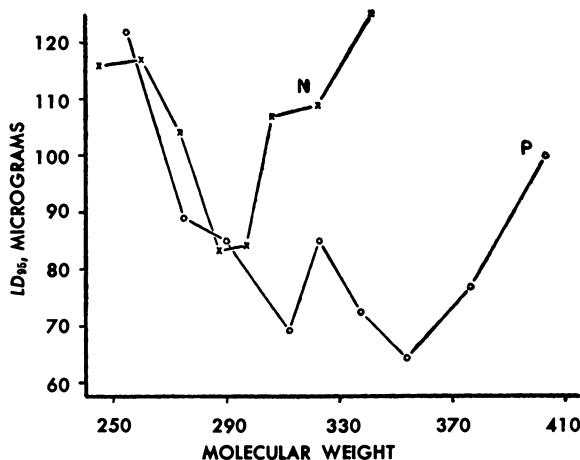


Figure 2. Correlation between Efficiency and Molecular Weight

Series of fractions of paraffinic (P) and naphthenic (N) composition against adult female California red scale

The same oil fractions were used for each species; therefore, any given property of an oil may be used with either set of efficiency data (19).

Correlation between Constitution of Oil Fractions and Insecticidal Efficiency

Molecular Weight and Viscosity. The values for LD_{95} have been plotted against molecular weight and viscosity values. The curves are shown in Figures 1, 2, 3, and 4 (data from Tables I and II). The values for each axis have been plotted in the increasing order of magnitude. As the 95% level of mortality was used in all cases, the efficiency relationship appears in the inverse form—i.e., the oil with the lowest LD_{95} is most efficient. Plotting the values for LD_{95} against molecular weight and viscosity values seems valid, since the ring-analysis data indicate that within each series of fractions the structural constitution is essentially constant.

The curves have been drawn from one coordinate point to the next. It is entirely likely that the slight deviations of these points from a smooth curve are within the limits of variation, such as those for the data for eggs of the citrus red mite, and for the correlations of the series of fractions of naphthenic composition against adult female California red scale. However, the deviation of fraction 5 (46-M20) of the paraffinic (P) series, as illustrated in Figure 1 in the viscosity range between 60 and 80, appears to exceed the limits of normal variation. In this connection, and as a check on the actual reproducibility of the mean position of these regression lines, it was decided to conduct a second completely independent set of spray trials for fraction 5 against red scale. The LD_{95} value determined for this set of data is 82 micrograms of oil per sq. cm., with fiducial limits of ± 4 micrograms at a probability of 0.05. The difference of 3 between the two LD_{95} values

substantiates the conclusion that the deviation from a smooth curve at this point is greater than might occur from chance alone.

The properties and characteristics available for paraffinic fraction 5 appear to be in line with those of the other fractions of the paraffinic series and do not indicate an explanation for a difference in performance against adult California red scale. A similar deviation did not occur in the case of the correlations established for eggs of the citrus red mite. Since the work of Ebeling (7) indicated that contact of oil with the scale insect is generally accomplished by penetration of the oil under the scale armor, the spreading ability of the oil film appears to be an important factor in the efficiency of an oil against adult California red scale.

It is known that the viscosity of a lubricating oil can be reduced by the addition of kerosene. Spray trials showed that kerosene was not appreciably toxic to the red scale. The effect of kerosene additions on the efficiency of paraffinic fractions 5 and 9 (46-M20) against red scale was therefore of interest. One-to-one mixtures of the two oils with kerosene were made on a volume basis. These mixtures were used in spray trials to establish dosage mortality values. Since the kerosene in the amounts used was not toxic, the deposit values used for the probit analysis were based on the actual amount of the oil represented.

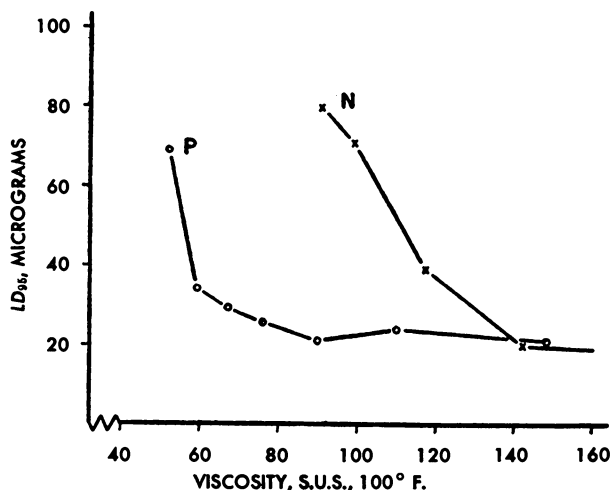


Figure 3. Correlation between Efficiency and Viscosity

Series of fractions of paraffinic (P) and naphthenic (N) composition against citrus red mite eggs 24 hours old

In mixture with kerosene, the LD_{50} value for paraffinic fraction 5 was found to be 63 micrograms per sq. cm., with fiducial limits of -10 and $+11$ micrograms at a probability of 0.05; and the LD_{50} value for fraction 9 was found to be 67 micrograms per sq. cm., with fiducial limits of -10 and $+12$ micrograms at a probability of 0.05. Further studies of this nature are in progress.

Figures 1 and 2 indicate that the insecticidal efficiency of oils of paraffinic composition against adult female California red scale is better than that of oils of naphthenic composition. The curves show that the toxicity to red scale of the lighter portions of the two oils tested is low, and that there is an increase to a peak of maximum efficiency with increase in molecular size. These findings agree in general with field experience in California in the application of spray oils for the control of California red scale. However, the correlations shown in Figures 1 and 2 indicate that an optimum is reached, and that beyond this point efficiency against the scale decreases with further increase in molecular size.

Paraffinic oils may be more efficient than naphthenic oils by virtue of the shape of the

molecules. An interaction of viscosity and molecular size is indicated. While the peak of maximum efficiency for the naphthenic oil occurs at a molecular weight of 287, as compared with an optimum molecular weight of 354 for the paraffinic oil, the spread between the optima for the two oils is smaller for the correlation with viscosity—a viscosity of 77 for the naphthenic oil as compared with a viscosity of 90 for the paraffinic oil. Figure 1 indicates that insecticidal efficiency of both oils against red scale begins to fall off above a viscosity of 90 S.U.S. at 100° F., and that the rate of decrease beyond this level is approximately parallel for the two oils, although there is a large difference between the oils in the molecular weight at which the curves turn upward.

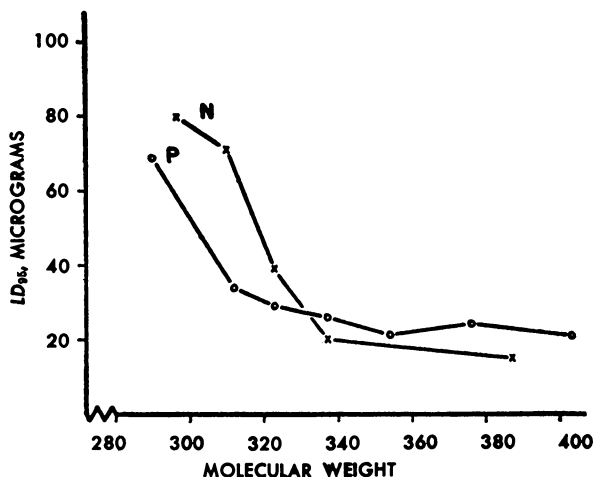


Figure 4. Correlation between Efficiency and Molecular Weight

Series of fractions of paraffinic (P) and naphthenic (N) composition against citrus red mite eggs 24 hours old

It is interesting to note in Table I that the LD_{95} of the paraffinic parent stock is practically as low as that of fraction 7, the most efficient fraction of the series. A reason for this is not clearly evident at this time, but the reduction in the LD_{95} observed when kerosene was mixed with fractions 5 and 9 suggests that although the lighter portions of the oil are low in toxicity they contribute to spreading of the oil film. The average LD_{95} is 71.8 micrograms of oil per sq. cm. for the series of 46-M20 fractions, and 105.5 for the series of 46-S1 fractions. The difference between the LD_{95} for the parent stock and the average value of the fractions tested is about the same for both oils.

Figures 3 and 4 indicate that the relations of composition and molecular size to the efficiency of petroleum oils against eggs of the citrus red mite are of the same type, with essentially the same critical values, as those found by Pearce, Chapman, and Frear (21) for eggs of the oriental fruit moth. The ovicidal efficiency is nearly constant above a molecular weight of 340 and falls off very rapidly to indeterminate amounts below this level.

It is interesting that the amount of oil deposit required for 95% kill is approximately the same for eggs of the oriental fruit moth and of the citrus red mite. For eggs of the oriental fruit moth, Pearce *et al.* (21) report lowest minimum effective dosage values of 1.6 mg. per 100 sq. cm. for a paraffinic oil and 2.3 mg. per 100 sq. cm. for a naphthenic oil. Equivalent values for 95% kill of citrus red mite eggs in the present studies were 21 and 15 micrograms per sq. cm., respectively.

The LD_{95} of the paraffinic stock oil 46-M20 (25 micrograms per sq. cm.) listed in Table II is almost as low as that of the best fraction of the paraffinic series. The average

molecular weight of 46-M20 is 330, which is only slightly lower than the critical value of 340 observed in Figure 4. It is also interesting that the paraffinic (P) curve of Figure 4 intersects the molecular weight (294) of the naphthenic parent stock 46-S1, at approximately 59 micrograms per sq. cm., the value of the LD_{50} found for this oil.

Other Properties. Since 1932, the spray-oil classes established by the California Department of Agriculture, Division of Chemistry (10, 18), have been used as general reference points for the performance of petroleum spray oils applied in California for control of insect pests of citrus. Minimum unsulfonated residue and the percentage distilled at 636° F. at atmospheric pressure are the specifications used for these classes. Minimum unsulfonated residue has served principally as a guard against plant injury, especially foliage burn. Boiling point has been a convenient means of reference to molecular size, the so-called weight or heaviness of the oil. Observations made in field practice indicate that heavier oils depress the citrus tree and limit its activity, and that the response of the tree to this factor varies with environmental conditions. On the other hand, it is the general observation that the degree of control of citrus insects is directly related to the weight of the oil, and that heavier oils provide better control. The compromise involved provides a sort of rule-of-thumb for choice of the class of oil for a given situation.

Pearce *et al.* (21) pointed out that changes in boiling point, number of carbon atoms, aniline point, refractive index, density, and gravity within a series of fractions of an oil are proportional to the change in molecular weight. The relationships observed in plotting correlations of efficiency to these factors would be similar to those illustrated by correlation with molecular weight.

Functions of properties such as the viscosity index or the viscosity gravity constant may be useful. However, the values of a function for a series of fractions of the same oil may be of approximately equal magnitude or may not be serial, as illustrated by the viscosity index (Table I).

Pearce *et al.* (21) suggest that some property of the fractions which has not been evaluated is probably related to the killing mechanism of hydrocarbon oils to oriental fruit moth eggs. It is thought that this may be true for eggs of the citrus red mite as well, and may be particularly applicable to the performance of the oils against adult female California red scale.

Application of Data

Field tests of the value of the relationships observed in the laboratory studies of petroleum fractions against the California red scale and the citrus red mite are planned for the California red scale and are in progress for the citrus red mite. In addition, field experiments offer opportunities to observe the response of citrus trees to differences in molecular size and to paraffinic *vs.* naphthenic composition of the oils.

The LD_{50} for fraction 7 (46-M20), 64 micrograms per sq. cm. (Table I), is about one half, or a little less than half, the average deposit of conventional spray oils used for commercial control of California red scale in the field in California. The results obtained in the laboratory studies indicate that proper selection of spray oils may make it possible to obtain the same degree of control with less oil deposit.

Until further information is obtained on the response of citrus trees to differences in the composition of petroleum oil, estimation of the practical value of the differences indicated between the two series of petroleum fractions on the basis of viscosity, in the control of citrus red mite, is limited. However, the conventional spray oils used in southern California for the control of citrus red mite are applied at dosages six to seven times the LD_{50} values indicated in Figure 4 for oils having a molecular weight of 340 or above. Proper selection of oils with respect to molecular weight might make it possible to achieve good field control of citrus red mite with applications of much smaller amounts of oil.

Acknowledgment

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Phytotoxic and Insecticidal Study of a Petroleum Isoparaffinic Fraction

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A single isoparaffinic fraction in the approximate distillation range of kerosene was studied as an insecticide and ovicide, and for quality control in storage. Evidence indicates the isoparaffinic fraction to be relatively low in toxicity toward several plant species, yet capable of a high percentage of insect kill when used alone or in combination with other insecticides. Increased phytotoxicity of stored isoparaffinic oils, considered to be due to oxidation products, was shown to result from light conditions and length of storage.

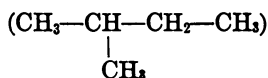
Since the development of emulsions for horticultural use about 1870, petroleum oils have been employed in many fields of insect control. On horticultural crops they serve as dormant sprays for scale insects, mites, insect eggs, and certain hibernating caterpillars; as summer sprays for mites and scale insects; as attractants in poison baits; as additives to increase the effectiveness of other insecticides; and as carriers for many toxicants.

Present-day oil insecticides are employed only at concentrations which satisfactorily control specific insects without injuring plant tissue. Many additional entomological problems might well be solved by increasing the dosage rate of oils, if it were not for the fact that plant foliage rarely tolerates oil deposits greater than those currently recommended. Furthermore, in the field of solvent carrier oils, the development of the newer insecticides and oil-soluble fungicides has increased the need for oils of lower phytotoxicity than is characteristic of naphthenic, paraffinic, or mixed base types.

The relatively recent development of isoparaffinic fractions from petroleum has resulted in experimental products of a very low order of toxicity to plant tissues. Initial studies have also indicated that selected isoparaffinic fractions are of a high order of toxicity to some insects or their eggs. The future development of isoparaffinic oils may result in new and important contributions to pest control on agricultural crops.

Physical Characteristics

This study is concerned with a single isoparaffinic fraction in the approximate distillation range of kerosene. Isoparaffinic oils are complex mixtures of saturated branched-chain compounds as illustrated by isopentane



and many other compounds with greater numbers of carbon atoms. The fraction employed in these studies is in a distillation range characterized by compounds believed to contain from 12 to 18 carbon atoms. It is a highly refined oil more viscous than kerosene.

The typical characteristics of the material reported in this work are as follows:

Gravity, ° API	49.5
Specific gravity	0.7818
Flash point, Tag, ° F.	160
Viscosity, S.U.S. at 100° F	33
Aniline point, ° F.	194.7
Unulfonated residue, %	97
Acid number	0.04
Distillation, ASTM, ° F.	
Initial boiling point	384
10%	394
50%	419
90%	477
Final boiling point	502

Insecticidal Properties

In screening tests it was observed that this isoparaffinic oil, at 100% concentration, killed from 85 to 95% of mealy bugs and aphids in the greenhouse. Test plants such as peach, gardenia, squash, corn, and bean were uninjured at this concentration.

Additional studies were made of the oil as an insecticide and ovicide, when applied as an emulsion. In all cases the isoparaffinic fraction was solubilized by the addition of Triton B-1956, a nonionic phthalic glycerol alkyd resin. The emulsions were applied to the point of runoff (200 to 400 gallons per acre). The results of these tests are shown in Table I.

Table I. Effect of Isoparaffinic Oil on Red Spiders and Certain Insect Eggs

Oil Concentration, % Emulsion	Insect	% Kill
1.5	Red spider adults	77
1.5	Red spider eggs	74
8.0	Colorado potato beetle eggs	74
10.0	Mexican bean beetle eggs	99

The isoparaffinic oil under study is much lower in boiling range than conventional tree spray oils and, being more volatile, would normally be at a disadvantage with regard to insecticidal properties. This results from the fact that the ovicidal performance of petroleum fractions is largely a smothering action requiring oils of relatively low volatility.

The fraction, nevertheless, exhibits a high degree of insect control which may be increased within certain limits by increasing the dosage rate. As shown in Table I, 1.5% oil gave 77% kill of red spider adults and 74% kill of red spider eggs. On larger eggs of the type not usually controlled with oil, 8 and 10% oil gave, respectively, 74% kill of Colorado potato beetle eggs and 99% kill of Mexican bean beetle eggs.

Phytotoxic Properties

In tests performed in 1944, Crafts and Reiber (2) demonstrated that heavy isoparaffins (slightly heavier than mineral seal oil) are less toxic to barley than odorless kerosene. These workers also showed that heavy isoparaffins have little or no toxic effect upon *Amsinckia*, *Lactuca*, and *Stellaria* species, or upon grasses. Heavy naphthenes, olefins, and aromatics were toxic, in ascending order, to these species.

In the work here reported the relatively low phytotoxic qualities of isoparaffinic fractions were evident from the inception of the screening tests in 1945. In order to evaluate this characteristic more precisely, applications of the fraction previously described were made on the foliage of plants in the greenhouse and in the field, employing the oil at full concentration and at several dilutions in emulsion form.

Comparisons were made with odorless kerosene and conventional summer tree spray oils. All applications in these studies were made to the point of runoff (200 to 400 gallons per acre). As shown in Table II, emulsions of the isoparaffinic oil were safe at concentrations far in excess of the usual 1.5% maximum recommended for foliage sprays.

At a concentration of 100%, the isoparaffin did not injure the foliage of bean or apple.

Table II. Phytotoxic Effect of Oil Sprays of Different Chemical Characteristics upon Foliage of Bean and Apple

Oil Concentration, %	Injury Index ^a , 7 days					
	Bean			Apple		
	Isoparaﬃnic oil	Odorless kerosene	Summer oil	Isoparaﬃnic oil	Odorless kerosene	Summer oil
1.5	1	1	1	1	1	1
3.0	1	1	2	1	1	3
5.0	1	2	3	1	3	6
10.0	1	4	4	1	5	8
100.0	1	9	9	1	9	9

^a Index 1 signifies no injury to plant; index 9 signifies complete kill or defoliation.

Odorless kerosene, representative of the highly refined types employed in household insecticides, resulted in significant injury to bean and apple foliage at 5% concentration. Conventional summer spray oils of higher viscosity than the isoparaﬃnic oil or kerosene caused significant injury at 3% concentration.

These data should not be interpreted as indicating that the isoparaﬃnic fraction is totally innocuous to all plant tissue. This fraction has been employed on only a few species. Some, such as the cucurbits, may be chronically injured to a variable degree, as characterized by chlorosis—the delayed formation of necrotic areas—and a retardation of growth. In addition, oxidation products, resulting in acute toxicity to plants, may accumulate in isoparaﬃnic fractions. The accumulation of toxic compounds, presumed to be organic acids, bears no relationship to the toxic unsaturates found in unrefined oils. The formation of toxic oxidation products occurs during long-time storage and primarily in the presence of light.

Relation of Unsulfonated Residue to Phytotoxicity

In 1927 DeOng, Knight, and Chamberlin (3) showed that injury to citrus trees was associated with a high content of unsaturated hydrocarbons, that these toxic materials could be removed by sulfuric acid treatment, and that a high unsulfonated residue (92% or greater) indicated that a tree spray oil was nearly devoid of unsaturates and thus safe for use at recommended dosages. Since the general acceptance of this work, the per cent unsulfonated residue (1) has been the primary indicator of acceptable quality for petroleum products marketed as foliage sprays.

Tucker (5), however, in 1936 demonstrated that oxidation products, formed in the oil after removal of unsaturates, caused serious toxic effects on apricot leaves.

Crafts and Reiber (2) in 1948 showed that low boiling isoparaﬃnic fractions, although having an unsulfonated residue of 100%, developed an acute toxicity to plants upon exposure to light. A chronic toxicity was developed in heavy isoparaﬃnic fractions under similar conditions. This increase in toxicity was considered to be due to oxidation products, the nature of which was not determined. It was believed, however, that acids rather than unsaturates are the cause of the increase in toxicity of isoparaﬃnic fractions upon exposure to light.

At the inception of the present studies, it was observed that the isoparaﬃnic oil when applied to plant tissue shortly after acid treatment resulted in no injury. However, after storage in glass in light of varying intensity for periods up to 325 days, this product

Table III. Phytotoxicity and Unsulfonated Residue Exhibited by Isoparaﬃnic Petroleum Fraction after Storage under Different Light Conditions

Light Intensity in Storage	Days Stored	% Plants ^a Injury	% Unsulfonated Residue
Control	0	0	97
No light	325	0	98
Difuse light	325	5	97
Brilliant light	141	65	97
	187	90	96
	325	100	96

^a Beans and corn employed as test crops.

showed an increasing toxic effect. Standard laboratory tests showed no significant change in unsulfonated residue. This is illustrated in Table III.

It is observed from the above data that the control (freshly refined oil) had an unsulfonated residue of 97%, indicating a nearly complete absence of unsaturates. This material, prior to light exposure for variable periods of time, gave no injury when applied at 100% concentration. However, after 141 days of storage in brilliant light, 65% of the leaf surface of plants sprayed to point of runoff showed acute toxicity. The unsulfonated residue remained unchanged. After 325 days of storage in brilliant light, the test plants were completely killed, while the unsulfonated residue had dropped to 96%. This reduction of 1% in unsulfonated residue is within the error of reproducibility of this test; thus no significance may be attached to it. It seems apparent from these data that the per cent unsulfonated residue cannot be employed alone as a test for the quality control of isoparaffinic fractions designed for horticultural application.

Relation of Acid Number to Phytotoxicity

Crafts and Reiber (2) suggested that oxidation, accelerated by light, may account for the increased toxicity of stored isoparaffinic oils. Although the oxidation products formed are not known, they appear to be primarily organic acids.

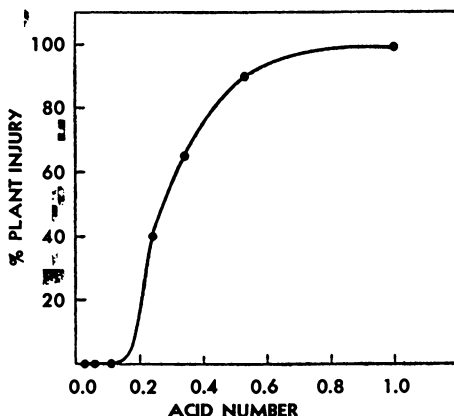


Figure 1. Correlation of Acid Number with Plant Injury

It appeared desirable to use a method which was relatively simple, and generally known, in initial efforts to correlate data on the phytotoxicity of isoparaffinic fractions with an acceptable quality control procedure. The determination of acid number (value), a common petroleum laboratory procedure, was employed in the current study.

The method employed in these studies for determining acid number is described by Snell and Biffin (4). The acid number is defined as "milligrams of alkali calculated as potassium hydroxide, required to neutralize the free acids in 1 gram of oil."

The acid number determinations were made immediately after refinement of the oil and were continued at every biological test period for 325 days. The oil was applied at 100% concentration to the point of runoff on immature bean and corn plants in the greenhouse. The temperature at which the plants were grown for the duration of each test was 80° F., and the relative humidity was approximately 85%. Phytotoxicity was determined on the second, seventh, and fourteenth day after the plants were sprayed. Figure 1 demonstrates the relationship obtained in these tests between acid number and per cent of plant injury.

Until the acid number increased to approximately 0.16, no apparent injury of either an acute or chronic nature occurred. Between 0.16 and 0.19, a very slight amount of

leaf tip burning appeared within 48 hours after spray application. No chronic injury was observed.

As the acid number increased from 0.19 to 0.24, foliage injury increased to 40% of the entire leaf area. Forty per cent injury was considered to constitute complete economic loss in terms of commercial crop production. Based on this relationship, an acid number of 0.15 to 0.17 may be considered the threshold between slight or no injury and economic injury.

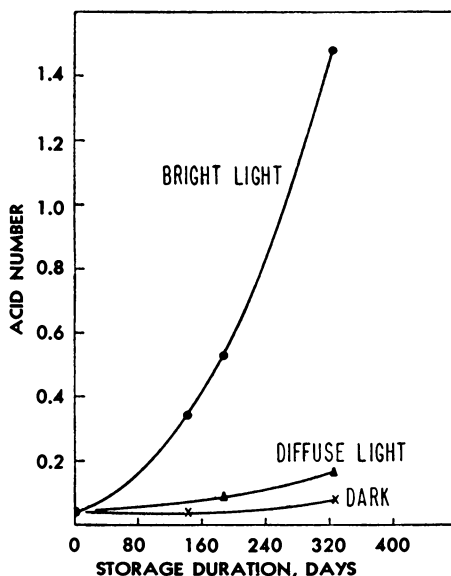


Figure 2. Effect of Light on Acid Number

Inasmuch as Table III shows that there is no correlation between per cent sulfonated residue and plant injury, and Figure 1 shows a measurable relationship between acid number and degree of phytotoxicity, it would appear that the acid number may be employed as indicative of the phytotoxicity potential of highly refined isoparaffinic fractions.

Effect of Light on the Acid Number

As suggested by Crafts and Reiber (2), refinement by sulfonation results in the removal of the natural antioxidants occurring in unrefined oils. Some highly refined oils, therefore, are subject to relatively rapid oxidation in the presence of oxygen and light, and this process is hastened by elevated temperatures.

During the initiation of this study, it was observed that peroxides increase rapidly during the earlier periods of storage of an isoparaffinic oil in bright light. However, the peroxide curve often breaks and lower peroxide numbers are obtained before 100% plant mortality is achieved. Although the mechanism was not determined, it was assumed that at some stage of the oxidation process peroxides were decomposed and acids were formed.

In view of the general relationship apparent between acid number and phytotoxicity, it seemed desirable to establish some measure of the rate of acid number increase when an isoparaffinic fraction is stored under different conditions of light intensity. Figure 2 shows this relationship for a 325-day storage period. Tightly stoppered glass bottles containing freshly sulfonated isoparaffinic oil were stored in the dark, in diffuse light, and in brilliant light at a temperature range between 75° and 95° F.

In bright light the acid number increases rapidly. The threshold of initial phytotoxicity (0.16) is reached in approximately 80 days. In diffuse light initial visible injury does not occur until near the end of a storage period of 325 days, at which time an acid number of approximately 0.16 has been reached. Material stored in the dark reached an acid number of 0.08 in 325 days and, at this time, caused no injury to beans or corn. If we may assume the same continuing rate of increase in acid number, the material stored in the absence of light will not reach the phytotoxic threshold point of 0.16 until it has been stored for approximately 450 days.

The above data indicate that highly refined isoparaffinic fractions may be stored in the dark for periods of approximately 1 year without serious increase in phytotoxicity. Future work may show that this period can be extended through the addition of oxidation inhibitors to refined isoparaffinic fractions.

Conclusions

Moderately light isoparaffinic fractions are relatively low in toxicity toward several plant species.

The isoparaffinic fraction employed in these studies is promising as an insecticide and ovicide—for use alone or in combination with other insecticides.

Highly refined isoparaffinic fractions have unsulfonated residues approximating 100%. The per cent unsulfonated residue does not change significantly when these fractions are exposed to light, although the oils become increasingly phytotoxic.

The increase in phytotoxicity of isoparaffinic fractions stored in light is believed to be due to the accumulation of acids resulting from oxidation.

The acid number test employed by many petroleum laboratories is indicative of the accumulation of acids, and is proposed as a measure of the phytotoxic characteristics of refined isoparaffinic fractions.

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Use of Petroleum Oils in Mosquito Control

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Petroleum oils in mosquito control are discussed from the pioneering experiments to their present-day status. Used alone or as carrying agents for other materials, such as DDT, petroleum oils have proved almost indispensable as larvicides and adulticides in the control of mosquitoes. Outdoor applications, from the ground and from the air, are described as well as indoor space and residual sprays. Standard specifications are urged for a petroleum oil that may be used as a mosquito larvicide.

Oils have been used for centuries to control certain insects, but the first known record of their use for controlling mosquitoes is found in Dunlap's *American Daily Advertiser* in 1793 (3).

As the late rains will produce a great increase of mosquitoes in the city, distressing to the sick, and troublesome to those who are well, I imagine it will be agreeable to the citizens to know that the increase of those poisonous insects may be diminished by a very simple and cheap mode, which accident discovered. Whoever will take the trouble to examine their rain-water tubs will find millions of the mosquitoes fishing (?) about the water with great agility, in a state not quite prepared to emerge and fly off: take up a wine glass full of the water, and it will exhibit them very distinctly. Into this glass pour half a teaspoon full, or less, of any common oil, which will quickly diffuse over the surface, and by excluding the air, will destroy the whole brood. Some will survive two or three days, but most of them sink to the bottom, or adhere to the oil on the surface within twenty-four hours. A gill of oil poured into a common rain-water cask, will be sufficient: large cisterns may require more, and where the water is drawn out by a pump or by a cock, the oil will remain undisturbed, and last for a considerable time.—A. B.

Undoubtedly the common oil referred to in this record is whale oil or a vegetable oil, as petroleum oils were not available before the middle of the nineteenth century.

Howard's (25) pioneer experiment on the use of kerosene against mosquito larvae, published in 1892, is well known. It is not so well known, however, that in 1867 he observed how "illuminating oil" killed mosquito larvae when he accidentally spilled some oil while filling a lantern over a horse trough infested with wrigglers. When called upon to devise a means for killing mosquitoes in later years, he remembered this incident on his father's farm in his early boyhood and so performed experiments that led to the universal use of petroleum oils as mosquito larvicides.

Of the 88 billion gallons of oil used annually in the United States, roughly 75,000,000 gallons go into the preparation of insecticides; of this quantity more than 1,000,000 gallons are used for controlling mosquitoes.

Petroleum Oils as Mosquito Larvicides

Oil as Toxicant. Crude petroleum and several petroleum products, used alone or with other materials acting as contact poisons, make effective mosquito larvicides.

For over 50 years they have been indispensable except between 1921 and 1942 in places where Paris green was used for controlling malaria mosquitoes.

It is generally understood that oils designed to control mosquito larvae should kill within a reasonable time; have a low surface tension; penetrate debris and aquatic plants easily; have a low toxicity to plants and wildlife; be free from disagreeable odor and prevent discoloration of vegetation; be nontoxic to humans; leave a long-lasting film; be generally available; and be low in cost. An oil with all these qualities is not essential and may be impossible to obtain, but in describing a good mosquito larvicide, it is well to consider these properties as important guides.

Table I. Per Cent Mortality of Fourth-Instar Larvae of *Anopheles quadrimaculatus* Say at Various Intervals after Treatment with Several Oils at 1 Gallon per Acre

Kind of Oil	(Laboratory tests)			
	5 Minutes	20 Minutes	1 Hour	24 Hours
Kerosene				
Refined	0	0	0	10
Commercial	0	10	20	65
Fuel oil (Diesel oil)	0	15	25	30
Stoddard's solvent	0	25	50	50
Monomethylnaphthalene	60	100	100	100

For years we assumed that oil killed mosquito larvae by suffocation brought about by the formation of an impenetrable layer of oil on the water surface through which the larvae were unable to thrust their breathing tubes to get oxygen. Freeborn and Atsatt (14), however, showed that the toxicity of petroleum oils as mosquito larvicides increases with their volatility, that the volatile constituents of the oils contain the principles that produce the primary lethal effects, that these lethal effects are produced by the penetration of the tracheal tissue by the volatile gases of the oils, and that the heaviest and least volatile oils (boiling point higher than 250° C.) may cause death by actual contact and mechanical suffocation. Ramsay and Carpenter (49) conclude that the toxic effect of oils diminishes appreciably when the boiling point is over 200° C. In other words, the light, highly volatile petroleum oils, such as gasoline and kerosene, paralyze the larvae and pupae, causing death within a few minutes, whereas the nonvolatile viscous oils, such as lubricating oil, gradually accumulate in their respiratory systems until suffocation takes place, after several hours.

Murray (39) thinks that a good mosquito larvicide is an oil that readily penetrates the tracheae of the larvae, and that actual toxicity is of secondary importance because the mere presence of oil prevents ordinary development. He further explains that penetrating oils are of a medium boiling range, not nonvolatile enough to be markedly viscous, and not volatile enough to give that immediately irritating effect which causes the larva to collapse its tracheae and dive without receiving a lethal dose of the oil.

Murray further explains that the inner surface of the larval trachea is composed of a waxy material, which is wetted by oil but not by water. According to Watson (55), the presence of any kind of oil in the tracheae is ultimately fatal. He shows, however, that survival time may vary from a few minutes to a week, depending on the toxicity and the amount of oil taken into the tracheal system. This amount varies with the number of times the larva contacts the oil film.

Considerable differences in resistance to mosquito larvicides were shown by larvae of *Aedes*, *Culex*, *Theobaldia*, and *Anopheles* (48). *Aedes vexans* (Meig.), for example, was slightly more resistant to oil and pyrethrum-oil emulsion than *A. sticticus* (Meig.). *Aedes* and *Culex* pupae were more resistant to pyrethrum-oil emulsion than to Diesel oil. *Theobaldia* larvae and pupae showed equal kills by pyrethrum-oil emulsion and Diesel oil. Unfortunately, insufficient basic research has been conducted to determine exactly why one mosquito species is more resistant to a larvicide than another.

The relative toxicities of several oils to malaria carrying mosquitoes, as determined by the Tennessee Valley Authority (52), are given in Table I.

A larvicidal oil should also spread upon the water surface to be treated. Oils differ in their ability to spread upon water; likewise different waters offer different resistance to

oil spread because they have different biological or mineral surface films. These may or may not be visible. The foundation of most of them is thought to be a bacterial slime, although the mineral surface films include dusts and inorganic colloids, often of a ferruginous nature. According to Williamson (56), a light breeze can cause these natural films to move to the leeward margins of the water surface, but they still adhere to the surface and are so rigid that they resist displacement and lateral compression by small forces.

Murray (40) has found that some substances, such as cresol, which have been considered valuable in improving the spread of oils, are ineffective. After a study of the spreading power of oils and methods for increasing it, Murray (41) concluded that spreading properties were due, not to the nature of their hydrocarbons, but to substances that might be classed as impurities. It is now known that compounds having polar groups increase the spread—for example, sulfonated derivatives and oxidized polymers of olefins all contribute to the spreading power. Concentrates from high-boiling residues, cracked spirit gum, and the alkali salts of the water-soluble petroleum sulfonates are considered satisfactory spreaders.

Several workers (1, 41, 44, 50) have investigated natural surface films in relation to the spreading of larvicidal oils upon water. Toms (50) has prepared "spreading standards" of oleyl alcohol and liquid paraffin, and of terpeneol and liquid paraffin. By using drops of these spreading standards on natural waters he measured the "resistance" of the existing surface film that would hamper the spreading of oil and expressed the results in dynes per centimeter. For example, the resistance of a film pressure classed in the range of 30 to 35 dynes per centimeter at 20° C. prevented spreading of a spreading standard of 3.9 grams of oleyl alcohol in 100 ml. of liquid paraffin, whereas a mixture of 6.5 grams of oleyl alcohol and 100 ml. of liquid paraffin displaced the surface film slowly.

There are two methods by which the suitability of a larvicidal oil can be assessed from the spreading standpoint: by determining the spread when drops are placed on a large selection of the accessible water surfaces; and by determining the resistance to spreading of the accessible water surfaces.

While carrying out tests on mosquito larvicides in Florida, Burrell *et al.* (8) found that oils were not spreading properly on most of the waters in September, and that some type of inhibiting biological film had formed on these breeding areas after control operations had been initiated early in the summer. They compared the spreading properties of Triton X-100 and of a Span 20-Tween 20 mixture (equal parts when used in No. 2 fuel oil); the results are given in Table II.

The pond with stagnant water thick with algae showed the greatest inhibition to spreading; the pond with smartweed and floating grass showed the best spread. The fuel oil containing equal parts of Span 20 and Tween 20 spread better than that containing Triton X-100.

Table II. Effect of Adding Triton X-100 and Span 20 plus Tween 20 on Spread of No. 2 Fuel Oil

[Figures represent diameter (in inches) of the oil film resulting from the application of one drop of material, October 1944]

Treatment	Stagnant Water Thick with Algae	Permanent Pools		Temporary Pools		
		Old brown grass and smartweed	Smartweed and floating grass	Fresh clean water, grass, and weeds	No grass	Roadside ditch grass and weeds
Fuel oil alone	2	8	10	4	3	6
Fuel oil plus 2% of emulsifier Triton X-100	6	30	24	24	30	20
Span 20 plus Tween 20 (equal parts)	12	24	30	24	40	36
Fuel oil (4 parts) plus DDT emulsion concentrate ^a (1 part)						
Triton X-100	8	18	30	36	30	18
Span 20 plus Tween 20 (equal parts)	12	20	40	24	36	36
Used crankcase oil	8	12	30	36	24	24

^a DDT 25%, xylene 65%, Triton X-100 10%.

The ranges of surface tension and spreading coefficient for several oils on water as determined by Gray and Bent (23) are shown in Table III.

Table III. Spreading Coefficients of Oils^a

Kind of Oil	Surface Tension, Dynes/Cm.	Interfacial Tension between Water and Oil, Dynes/Cm.	Spreading Coefficient
Neutral white oil	31.3	56.6	-15.9
High-grade kerosene	26.1	50.5	-4.6
Low-grade kerosene	26.5	45.0	+0.5
Light stone oil	27.3	32.9	+11.8
High aromatic kerosene extract	30.5	22.9	+18.6
Diesel oil	29.2	23.1	+19.7
Special mosquito oil ^b	29.4	15.0	+27.6

^a Spreading coefficient as used here is surface tension of water minus surface tension of the oil minus interfacial tension.

^b Diesel oil plus additional materials to increase spreading coefficient.

Unfortunately, the superintendents of many mosquito abatement districts know too little about the resistance of the surface films existing on their mosquito-breeding areas. Here is an excellent opportunity for a cooperative study between the oil company furnishing the larvicide and the mosquito control agency using it.

Murray (41) has recommended that, so far as film stability of larvicidal mixtures is concerned, the oil should have either a small or a very high aromatic content (it should not contain 50% of aromatics unless they are very high boiling—e.g., of lubricating base fraction); consist of a mixture of wide and overlapping cuts of oil; and should not contain fats or fatty acids added as "spread-aiders." If a spreading agent is desired, resins should be employed.

Knipling, Gjullin, and Yates (29) tested 26 emulsifiers and found only three that were particularly effective as spreading agents. They were sulfonated sperm oil (Nopco 1216), a phthalic glyceryl alkyd resin (Triton B-1956), and an 18-carbon-chain complex amine (Amine 230x). By adding 3 to 5% of one of these spreaders to Diesel or stove oil, these workers obtained adequate coverage and complete control with about 6 gallons instead of the usual 20 to 40 gallons of oil per acre on fresh water.

Specifications. The New Jersey Agricultural Experiment Station has prepared specifications for mosquito larvicides as a result of experiments conducted by Ginsburg (19).

H. F. Gray (23), director of the Alameda County Mosquito Abatement District in California, gives the following specifications for his district:

Oil furnished shall be homogeneous, and shall not separate into fractions of different densities on prolonged standing, nor shall the oil deposit any solid or semisolid material on prolonged standing. Oil shall be free from granular, flocculent, fibrous, or other material which might cause clogging of spray nozzles. Oil shall not be subject to change or deterioration by oxidation, or otherwise, on prolonged standing in tanks. The bidder shall state the range of American Petroleum Institute gravity of oil proposed to be furnished. Proposals are requested on a Diesel oil having an API gravity in the range from 27 to 30, and generally conforming to Pacific Specification No. 200.

The Tennessee Valley Authority (52) gives the following specifications for black oil as a mosquito larvicide:

Black oil should be a pure petroleum product free from fatty oils, fatty acids, resins, soaps, or other nonhydrocarbons. Sediment and sludge, insoluble in paraffin naphtha, should not exceed 12% when determined by the methods of the American Association of State Highway Officials. The product should be a distilled or fractionated oil, and should contain no oil-well water or residue therefrom. The product should be free of or contain no more than traces of naphthenic acids, naphthenes, mercaptans, soluble sulfide, and volatile sulfur derivatives. The oil should flow freely from the tank car at temperatures above 32° F.

Nelson, Pierce, and Donlan (42), at the author's request, prepared the following specifications.

Aromatic content	15%, preferably higher
Viscosity	Not above about 45 seconds at 100° F.
Interfacial tension	(Spreading coefficient) 25 dynes/cm. at 25° C. max
Specific gravity	0.75 minute to less than 1.0 max.
Kauri butanol value	
(toluene = 100)	35 minutes, preferably higher
Aniline point	+60° C. or lower
DDT soluble	Not less than 5% at 0° C.
Distillation	
Initial boiling point	Not below 350° F.
50%	440–480° F.
Final boiling point	Not above 600° F.

These specifications were suggested because older specifications had been prepared before some of the new, higher aromatic oils were available. These new oils appear to be much more toxic to mosquito larvae than the older type oils. Nelson, Pierce, and Donlan have therefore included values that are ordinarily indicated in an aromatic type of oil, mainly kauri butanol and the aniline point. The distillation range as given is a little too wide to be satisfactory, but it is difficult to say definitely just how broad a range should be allowed. The specific gravity has been widened slightly and a surface tension figure has been omitted as compared with older specifications. An interfacial tension between oil and water is given, however, because of its importance in obtaining a proper distribution of the oil. It is an index of water surface coverage—i.e., whether the oil will spread rapidly and evenly so as to produce a thin, uniform, unbroken film on the entire water surface or whether it will remain in thick localized spots.

These samples of specifications illustrate the inconsistencies now existing in the petroleum oil requirements of mosquito abatement districts. In general, the greatest emphasis should be placed on interfacial tension, toxicity, and film stability. Specific gravity, viscosity, and boiling range within the ranges given in the examples are also important. A final distillation point of 800° F. as given by some workers is entirely too high for safety.

In an effort to reduce costs, civic organizations have from time to time gathered waste crankcase oil for use in controlling mosquito larvae. Usually such mosquito control programs have failed, because waste crankcase oils are low in toxicity to mosquito larvae, they contain dirt and other materials that clog spray nozzles, and the collection and supply are undependable.

Oil as Carrying Agent. Means for increasing the effectiveness of oils or of adapting them to mosquito control include the addition of a toxic agent such as pyrethrum or one of the chlorinated hydrocarbons—e.g., DDT and benzene hexachloride. Pyrethrum has been rather widely employed since it was suggested by Bradley in 1928 and developed by Ginsburg in 1930 (6).

The use of petroleum oils as solvents and carrying agents of DDT in mosquito larvicides was mentioned by Wasicky and Unti (54) and Barber (4), but in 1945, after military restrictions were removed, considerable information on the use of DDT larvicides that had accumulated from 1942 to 1945 was published (11, 13, 28). The adaptability of petroleum oils made possible a wide application of DDT where larvicidal oils had been used. Moreover, No. 2 fuel oil containing DDT was more toxic, cheaper, more effective, and more easily applied than phenothiazine, Paris green, or cresol larvicides. The usual rate of application was about 1 or 2 quarts of oil containing 5% of DDT per acre of water surface. During the last months of the recent war, control of mosquitoes and the diseases they carried was largely effected by oil sprays containing DDT.

Foreign countries are now using large amounts of petroleum oils to which DDT has been added—e.g., Venezuela now uses nearly 1,500,000 liters of DDT solutions and emulsions annually in fighting malaria (5).

Lindquist (34) and his associates have applied Diesel oil containing DDT or other chlorinated hydrocarbons as a prehatching treatment for controlling snow-water mosquitoes. Late in the fall Lindquist applied several oil formulations containing chlorinated hydrocarbon insecticides to swales and depressions that had produced mosquitoes in season. These oil formulations remained on the ground during the winter and when flooded with snow water proved toxic to the newly hatched mosquito larvae. A dosage of 2 pounds of DDT per acre (10 quarts of a 5% DDT-oil solution) prevented mosquito development in some instances for 2 years.

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Since DDT became available, the volume of oils used in mosquito control work has dropped considerably. For example, Ginsburg (20) has recorded the following figures for the State of New Jersey:

Year	Gallons of Oil
1943	173,000
1948	80,000
1949	90,000
1950	81,000
1951	100,000

Where mosquitoes have developed resistance to petroleum oils containing DDT, they have been controlled with oils containing chlordan or benzene hexachloride (37). Normally, a dosage of 0.4 pound of DDT in 2 quarts of Diesel oil per acre will give from 75 to 100% control of nonresistant larvae, the results depending on the species of mosquito and on the thoroughness of the coverage (58).

In Florida late in 1949 King (27) found that oil solutions of dieldrin, parathion, lindane, and toxaphene gave excellent control of resistant strains of larvae and that any of these insecticides would be effective substitutes for DDT. However, some of them are very toxic to animal life and must be used cautiously.

Petroleum Oils as Adulticides

Out of Doors. Control measures against adult mosquitoes out of doors have been discussed by Ginsburg (21), Covell *et al.* (9), Russell and Knipe (45), and others. These workers used pyrethrum in oil sprays and were instrumental in reducing malaria or mosquito annoyance.

Applications from the Ground. Early in the war the Orlando, Fla., laboratory of the Bureau of Entomology and Plant Quarantine demonstrated the effectiveness of DDT sprays and aerosols as a means of controlling adult mosquitoes under outdoor conditions (33, 35, 36).

Many observations on the effects of DDT-oil aerosols dispersed from the ground as a means for controlling salt-marsh and anopheline mosquitoes have been summarized by La Mer *et al.* (30). The effects of particle size meteorological conditions, various emulsions, time of exposure, and the relationship of the habits of various mosquitoes to the use of thermal generators are given. This report discusses experiments of a pioneer nature.

In Alaska, Wilson and others (57) have tested ground aerosol generators for controlling adult mosquitoes. In one test they used 25 gallons of Navy fog oil, 15 gallons of fuel oil, 8 gallons of Velsicol AR-60 (chiefly di- and trimethylnaphthalenes), and 25 pounds of DDT; and in another test 5% of DDT in fuel oil. Satisfactory controls were obtained for only a few hours.

Brescia (?) conducted field tests in Florida and Alabama with thermal aerosols in which DDT was used in an oil emulsion. The generator had a capacity of 16 to 18 gallons per hour, and the areas were treated by the aerosol cloud drifting on winds of various velocities across them from a road traversed by the equipment at varying speeds. The author concluded that a dosage of 15 gallons per 1000 feet of front—50 parts each of oil and water plus DDT equal to 10% of the weight of the oil—will give effective control of adult mosquitoes up to a mile away in open country and 1000 yards into a forest.

Dickinson and associates (12) reported that the Consolidated Mosquito Abatement District of Fresno County, Calif., stopped a large population of *Aedes* mosquitoes from biting as soon as the clouds produced by an insecticide fog applicator had passed the field. This machine was also used to treat 160 acres of irrigated pasture land that had been considered untreatable. After 24 hours no adult mosquitoes were observed.

Thermal-aerosol applicators are employed to a considerable extent in the outdoor application of adulticides (sprays designed for killing adult mosquitoes). Well over 2,000,000 gallons of oil are used annually in these applicators.

Applications from the Air. Solutions of DDT in fuel oil or other solvent applied from airplanes as fine sprays have been found to destroy a large percentage of adult mosquitoes even in dense tropical jungles.

Following earlier and promising investigations in Florida against adult salt-marsh

mosquitoes (32), the first demonstration of the effectiveness and practicability of treating jungle forests against adult mosquitoes with oil sprays containing DDT was made in the Panama Canal Zone during 1944 by Lindquist and McDuffie (33). Lindquist *et al.* found that oil sprays containing 5% of DDT in fuel oil, dispersed at the rate of 2 or 3 quarts per acre over jungle forest area from a Cub airplane, reduced *Anopheles* and *Mansonia* mosquitoes 98% during a 4-day period. Because these early tests were so successful, malariologists were given much encouragement in fighting a disease that had been reducing our military strength.

To determine the influence of wind, velocity, and particle size on the toxicity of oil aerosols containing DDT, Latta and coworkers (31) conducted experiments in a wind tunnel at wind speeds of 2, 4, 8, and 16 miles per hour. The median lethal dose for a female mosquito was 1 particle 83 microns in diameter from a 10% DDT solution.

Indoors—Space Sprays. Petroleum oil sprays have been used for killing adult mosquitoes in homes for at least 30 years. These sprays, containing 95% or more of petroleum oil as a base, have been used around the world as a fairly effective weapon against malaria. In fact, a Flit gun is as familiar a sight to travelers in the tropics as are the inevitable bed nets. Before the residual insecticidal value of DDT against mosquitoes was discovered by entomologists of the Orlando laboratory (15, 17), these conventional sprays were applied as mists which killed the flying or resting mosquito upon contact. This type of spray gives temporary relief from mosquito annoyance and when regularly applied is of some value for the control of malaria. The aerosol bomb, patented several years ago by Goodhue and Sullivan (22) made available a unique device for applying space sprays effectively. Relief obtained by their use, however, is temporary.

Residual Sprays. It is possible to spray an oil solution containing 5% of DDT on the interior surfaces of a house and so deposit a residue of DDT crystals that will kill mosquitoes resting upon the treated area. This method of killing malaria carrying mosquitoes is especially valuable in malaria control. The mosquitoes rest on the interior walls or ceiling for several hours after feeding, and in so doing are destroyed and cannot bite the second time; hence the spread of malaria is immediately stopped.

The early development of DDT residual treatments for mosquito control was accomplished by the Orlando, Fla., laboratory (15, 17).

Some of the first large scale tests with residual oil sprays in other countries were made in British Guiana by Symes and Hadaway (49) in 1944 and by Giglioli (18) in 1945 against *Anopheles darlingi* (Root), a particularly potent malaria carrier. These workers sprayed a 4.6% DDT-oil solution at the rate of 2 quarts per 1000 square feet and recorded a 99% reduction of adult mosquitoes for more than 6 weeks. Many reports have been received from various parts of the world as to the effectiveness of DDT-oil residual sprays against malaria, including those of Gahan and Payne (16) from Mexico, Stage and Berti (46) from Venezuela, Trapido (51) from Panama, Aitken (2) from Italy, Muirhead-Thomson (38) from Africa, and Viswanathan and Rao (53) from India. Attempts are now being made to eradicate certain anophelines from several regions—e.g., Mauritius (47).

Davidson (10) reported on the use of petroleum oil containing benzene hexachloride as a means of malaria control by adult mosquito destruction in western Africa. He concluded that an oil solution containing 0.5% of the gamma isomer of benzene hexachloride (Gammexane) sprayed on the inside wall surfaces of all houses at the rate of 10 mg. of gamma per square foot (2 quarts of solution to 1000 square feet) practically eliminated mosquitoes in those houses for about 6 months.

Notwithstanding the present trend toward the use of DDT in oil as a mosquito control agent, petroleum oil alone will continue to be used, for the following reasons. First, on places charged with heavy pollution or industrial waste, where DDT rapidly loses its effectiveness, it is usually cheaper to apply a heavy layer of petroleum oil to assure complete kill of both larvae and pupae. Secondly, in places where the mosquitoes have reached the pupal stage and quick kill is essential, it may be more advantageous to apply a heavy dose of straight oil rather than DDT, which has a relatively low toxicity to pupae. Finally, the use of oil will be continued wherever DDT encounters objections.

Future Research Needs

Petroleum oils have proved almost indispensable in the control of mosquitoes. Certainly, the full potentialities for them in this field have yet to be explored and fully evaluated.

According to Herms and Gray (24), studies are needed on the chemical and physical properties of mosquito oils and on the basic effects of oils upon the mosquito larva's physiology, as well as physiochemical studies of oil films on water surfaces.

Jobbins (26), of the New Jersey Agricultural Experiment Station, has suggested the need for a list of adjuvants and the quantities to be used in oil sprays to be applied from aircraft that will permit control of particle size on the ground under various temperature conditions. He would also like to include in oil specifications some reference to their natural spreading coefficients when they are applied on clear water.

There is need for experiments on the effect of various solvents in formulation of mosquito larvicides and adulticides containing chlorinated hydrocarbon insecticides.

The miscibility and specific gravity of mosquito larvicides may greatly modify their usefulness. Likewise, information on the viscosity of petroleum oils in relation to their effectiveness as mosquito larvicides and adulticides may increase their value. There is much that we do not know about them and their place in mosquito control.

The effects of various types of petroleum-carrying agents—e.g., aromatic, paraffinic, and naphthenic—should also be studied.

The effects on the vaporization of petroleum-oil sprays after various periods of air suspension have not been explored, and little information is available on this phase of mosquito control.

Additional research to find a suitable carrying agent having low explosive and flammability properties is urgently needed as we increase the control of adult mosquitoes by fogs and sprays dispersed by the new types of applicators.

Finally, there is still a definite need for standard specifications for a good petroleum oil that may be used as a mosquito larvicide.

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Solvents for DDT

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The solubility of DDT in twenty materials—ketones, petroleum fractions, and several miscellaneous solvents—over the temperature range -30° to 76° F. was determined by the rapid density method developed by Mauke and Sheard. DDT was found to be most soluble in cyclohexanone and less soluble in aromatic petroleum fractions, but the solvent cost per unit of DDT dissolved with them was only one half that for cyclohexanone. Cyclic ketones were better solvents than acyclic ketones with the same number of carbon atoms and the solubility in ketones was found to decrease with increasing molecular weight.

With the increased use of DDT as an insecticide following World War II, interest in solvents for this material also increased. Data available in the literature (2) indicated that the solubility of DDT in regular petroleum fractions was low, and that these solvents, consisting primarily of paraffinic hydrocarbons, could not be used to obtain concentrated DDT solutions. The data also showed that ketones and aromatic materials were good solvents for DDT.

Information on the solubility of DDT at low temperatures was not available. Because of the wide variations in temperatures likely to be encountered in storing DDT solutions, the present work was initiated to determine the solubility at various temperatures in solvents that are miscible with inexpensive and widely available petroleum fractions. A second consideration was the economics of the DDT solvents.

Experimental

The method of Mauke and Sheard (3), used for the determination of the DDT content of the solutions, is based upon the density measurement of the DDT solution and assumes that the volumes of the solid DDT and the solvent are additive. The formula for this relationship is as follows:

$$W_{\text{DDT}} = \frac{100(d_s - d_a)}{d_{\text{DDT}} - d_a} \times \frac{d_{\text{DDT}}}{d_s}$$

where W_{DDT} = per cent by weight of DDT, d_s = density of solution, d_a = density of solvent, and d_{DDT} = density of DDT = 1.5. To check this relationship, three samples were prepared with known amounts of DDT in an aromatic solvent; the densities of these solutions were determined with a Westphal balance and the DDT content was calculated by the formula. The results were as follows:

Density at 76° F., G./Ml.	DDT Content, G./100 G. Solution	
	Actual	Calculated
0.934	0.0	0.0
0.952	5.0	5.0
0.987	15.0	14.3
1.028	25.0	25.6

Table I. Typical Physical Inspections of Petroleum Fractions

	Aromatic										Paraf- finic
	A	B	C	D	E	F	G	H	J	K	
Specific gravity at 60° F.	0.865	0.866	0.860	0.881	0.869	0.892	0.887	0.941	0.956	0.969	0.796
Distillation ^a , ° F.											
Initial	272	274	277	296	312	357	357	390	404	426	367
10% recovered	277	277	283	310	319	362	365	415	428	442	392
50% recovered	280	280	291	324	323	369	373	446	462	468	419
90% recovered	286	286	311	348	327	381	389	478	502	496	451
Maximum	306	306	331	406	337	401	423	515	562	518	491
Mixed aniline point ^b , ° C.	12.6	14.3	17.8	13.4	16.0	16.7	22.5	21.1	18.5	17.6	69.8
Aromatics by sulfonation ^c , %	95.8	94.6	90.9	94.9	93.8	91.6	86.3	83.0	79.2	81.6	2.6

^a ASTM method D 86-46 (1).

^b ASTM method D 611-47T (1).

^c ASTM method D 875-46T (1).

These data indicate that the accuracy of this method, as well as its simplicity and speed was adequate for the investigation.

Saturated solutions of DDT in the various solvents were prepared by heating and storing at three lower temperatures for at least 48 hours after crystal formation. Samples of the supernatant solutions at the test temperatures were taken and their densities were determined at room temperature 75° to 77° F. If the amount of supernatant liquid was sufficient a Westphal balance was used; for smaller amounts, the density was calculated from the weight of a pipetted volume.

The twenty solvents investigated were of commercial or technical grade. They can be divided into three groups: ketones, petroleum fractions, and miscellaneous. Typical inspection data for the petroleum solvents, consisting of ten aromatic fractions and a paraffinic fraction, are shown in Table I. The ketones and miscellaneous solvents investigated are listed in Table II.

Results and Discussion

The results of the solubility determinations are summarized in Table II and shown graphically in Figure 1. The ketones are good solvents for DDT. Of all the materials investigated, cyclohexanone had the greatest solvency. Cyclic ketones are better solvents for DDT than acyclic ketones with the same number of carbon atoms, as evidenced by cyclohexanone being better than methyl isobutyl ketone and isophorone being better than diisobutyl ketone. The DDT solubility in the ketones investigated decreased with in-

Table II. Solubility of DDT in Various Organic Solvents

Solvent	Solubility, G. per 100 G. of Solution				
	-30° F.	-20° F.	30° F.	40° F.	76° F.
Ketones					
Cyclohexanone	..	58	68	..	71
Isophorone	45	47
Methyl isobutyl ketone	37	..	39	..	47
Ethyl n-butyl ketone	31	..	38	..	46
Diisobutyl ketone	31	..	32	..	36
Petroleum fractions					
Aromatic A	30	..	33	..	43
Aromatic B	32	..	35	..	42
Aromatic C	22	31	44
Aromatic D	34	..	37	..	46
Aromatic E	16	29	37
Aromatic F	17	29	39
Aromatic G	15	27	32
Aromatic H	..	34	..	36	40
Aromatic J	30	..	34	..	39
Aromatic K	..	34	37	..	40
Paraffinic	..	3	..	5	7
Miscellaneous					
Nitrocyclohexane	41	..	44	..	47
Tetralin	32	..	36	..	45
Dipentene	22	..	25	..	30
Ethylene chloride	8	21	31

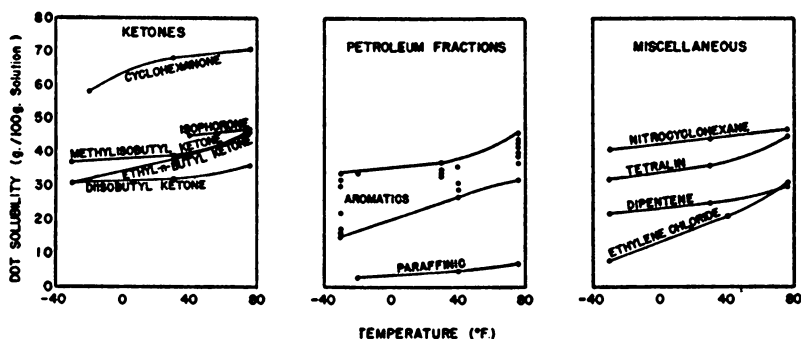


Figure 1. DDT Solubility in Various Organic Solvents

creasing molecular weight. Considerable difficulty was encountered in determining solubility at the lower temperatures with cyclohexanone and isophorone. This was caused by the increase in viscosity of the solution due to the reduced temperatures and high DDT content.

Of the petroleum solvents, the aromatic fractions are much better solvents for DDT than the paraffinic fraction. The limited solubility of DDT in the paraffinic fraction, representative of straight-run petroleum oils, shows that such oils alone cannot be used as solvents in concentrated DDT solutions. An auxiliary solvent would have to be used to prepare concentrated solutions with them. It was not possible to correlate solubility with mixed aniline point and aromatic content. This was presumably due to differences in the solubility of DDT in the individual hydrocarbons present which included both monocyclic and dicyclic types. No attempt was made to determine the amount of the individual hydrocarbons in the aromatic fractions.

Table III. Economic Evaluation of DDT Solubility in Various Organic Solvents

Solvent	Cost, \$/Lb.	DDT Solubility, Lb./\$ Solvent				
		-30° F.	-20° F.	30° F.	40° F.	76° F.
Ketones						
Cyclohexanone	0.29	..	5.2	7.4	..	8.6
Isophorone	0.24	3.4	3.7
Methylisobutyl ketone	0.145	4.1	..	4.4	..	6.1
Ethyl n-butyl ketone	0.30	1.5	..	2.0	..	2.8
Diisobutyl ketone	0.145	3.1	..	3.3	..	3.8
Petroleum fractions						
Aromatic A	0.038	11	..	13	..	19
Aromatic B	0.035	13	..	15	..	21
Aromatic D	0.028	19	..	21	..	29
Aromatic E	0.041	5.0	11	15
Aromatic G	0.041	4.6	10	12
Aromatic H	0.026	..	20	..	21	25
Aromatic J	0.025	17	..	21	..	26
Aromatic K	0.058	9.0	..	10	..	11
Paraffinic	0.021	..	1.3	..	2.2	3.3
Miscellaneous						
Tetralin	0.25	1.4	..	1.6	..	2.4
Dipentene	0.042	6.9	..	7.9	..	10
Ethylene chloride	0.09	1.0	3.0	5.1

Of the miscellaneous solvents investigated, nitrocyclohexane and Tetralin look promising for concentrated DDT solutions. Because nitrocyclohexane is not commercially available, only Tetralin represents a practical DDT solvent.

Economics of DDT Solvents

The cost of solvent per unit of DDT dissolved is a prime factor to be considered in the manufacture of DDT solutions. The amount of DDT that will remain dissolved in a dollar's worth of solvent is shown in pounds in Table III and Figure 2. The solvent prices upon which these data are based are also included in the table except for nitrocyclo-

hexane, aromatic C, and aromatic F, which were not available. It can be seen that cyclohexanone is the best ketone investigated on a cost basis as well as on the basis of solubility alone. Of the miscellaneous solvents investigated, dipentene is the most economical. It is comparable to cyclohexanone.

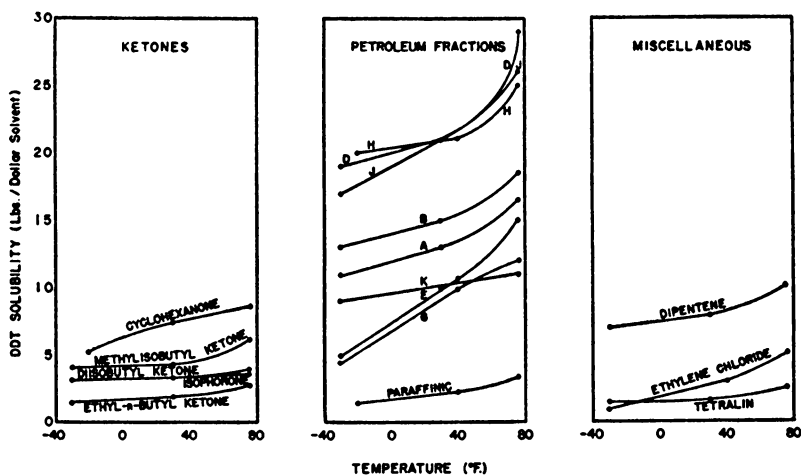


Figure 2. Economic Evaluation of DDT Solubility in Various Organic Solvents

There is a much wider range in the solubility of DDT in petroleum fractions when expressed on a cost basis than when expressed on a solubility basis. It is apparent that most of the aromatic fractions are more economical solvents than cyclohexanone. The petroleum aromatic fractions are a relatively inexpensive source of high solvency materials.

Summary

Cyclic ketones are better solvents for DDT than acyclic ketones with the same number of carbon atoms. The solubility of DDT in ketones decreases with increasing molecular weight.

Of the solvents investigated, cyclohexanone was found to dissolve the greatest amount of DDT on a weight percentage basis, but most of the aromatic fractions were more economical than cyclohexanone.

Among the petroleum aromatic fractions there appears to be no close correlation between DDT solubility and either mixed aniline point or aromatic content.

Acknowledgment

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Influence of Particle Size on Application of Insecticide Sprays

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Particle size is shown to have an effect on the distribution and deposit of the insecticide and on foliage injury. A brief description is given of methods of determining particle size. Examples are given of using aerosols and mist blowers in buildings and in the field, and airplanes in the field to illustrate the importance of particle size.

Particle size of insecticidal sprays has a bearing on the ability of airborne sprays to be transported and deposited, on foliage injury, and on the efficiency of residues in killing insects. Each problem should be carefully analyzed for the particle-size requirements.

In studying these problems the author applied the fundamental information available, such as Stokes' law for the settling rate of particles and Sell's work (3) on the efficiency of deposit of particles in a moving air stream. However, this fundamental work is based on ideal conditions never found in practical problems, so that the job was to correlate the fundamental information with actual conditions.

A standard method of determining the size had to be developed (5). None of the various methods used to atomize liquids give homogeneous particle sizes; therefore a representative value, such as mass median diameter, was used to compare particle size of insecticidal sprays. If the spray must be described more completely, this is done by breaking down the particle size range into several divisions and reporting the accumulative percentage of the mass of the spray according to each division.

Various methods of taking samples of spray were tested. Impinging the spray on a coated microscope slide and then measuring the deposited particles under a microscope was found to be the best method for computing the sizes accurately. One method of impingement is to wave a slide through the spray. Another is to air blast the spray against the slide, and, for very fine spray having a mass median diameter of less than 10 microns, to use settling or electrical precipitation. For non-volatile oil sprays the slides are coated with an oleophobic material that gives a uniform spread and maintains the round shape of the droplet. Methods of determining the spread of the droplet as it rests on the slide have also been developed (5). For volatile solutions the slides are coated with magnesium oxide or carbon soot, and the particle leaves a crater on contact. The thickness of this type of coating establishes the amount of deviation of the crater size from the actual particle size.

Although most oils have similar surface tension and density, they differ greatly in viscosity. The viscosity, the output of liquid, the efficiency of the application of energy to the liquid, and the degree of evaporation after the particle is formed are important factors to utilize in producing the desired particle size. In heat vaporization aerosols the distillation range of the solution is also important.

Three methods of applying atomized liquids were tested—by aerosols, by mist blowers, and by airplane. Sprays were released by the first two methods in buildings and by all three methods in the field.

Spray Particle Size in Indoor Treatments

Tests with Aerosol Sprays. One of the chief means of applying concentrated oil sprays is in aerosol form. An aerosol generally remains suspended in the air for some time and is carried by normal wind or air currents. Aerosols are probably best adapted to interior applications but have been used with some success outdoors. They may be produced by liquefied-gas formulations released through capillary nozzles, by steam and air atomization, by centrifugal disks and rotors, by extremely high pressure, and by heat vaporization.

Many factors influence the selection of the proper particle size when concentrated oil sprays are being used. In large closed warehouses, aerosol treatments can be used to protect stored products from exposed crawling and flying insects. Aerosols having various particle sizes were tested and the results compared by taking residue samples throughout the warehouse. Insect mortality studies also served as a basis of comparison. As a result, a particle size between 1 and 5 microns mass median diameter was selected. These small particles are produced by thermal aerosol generators that can be operated outside the warehouse and the fine particles introduced through an open door. The aerosol is carried first to the ceiling, but by the time the treatment is complete it is well distributed throughout the interior by convection currents. The warehouse door is then closed and overnight the particles penetrate into most of the cracks and crevices and settle on the top of the exposed horizontal surfaces. The small particles in this test gave the best penetration and insect control, and also were the easiest to apply.

For control of flying insects with aerosols, research showed that there is an optimum particle size needed to obtain maximum kill. The size was determined through extensive research in wind tunnels (2) and Peet-Grady chambers in which the most nearly homogeneous sprays possible were used. For adult mosquitoes the optimum particle size was found to be between 10 and 15 microns mass median diameter and for adult houseflies between 15 and 20 microns.

In treating some closed interiors with aerosols, it may be necessary to limit the time of application. In this case the particle size must be large enough to settle out in the time available. A 10- to 15-minute exposure time is the minimum for satisfactory results. An aerosol spray having a mass median diameter of 15 to 30 microns is sufficient for the short-exposure applications, but will not penetrate so completely as the smaller particle size. Furthermore, aerosols of this size must be released from more than one point if the radius of the area is more than 15 feet. When heat from thermal generators causes excess breakdown of the insecticide, equipment that produces larger particle sizes must be used.

The relationship between particle size and foliage injury was shown in work with liquefied gas aerosol formulations of hexaethyl tetraphosphate for greenhouse applications (1). Particles larger than 20 microns diameter injured some varieties of foliage. Increasing pressure and using smaller nozzles lowered the mass median diameter but did not eliminate the maximum sized particles. The problem was finally solved with a low-concentration formulation, in which the particles larger than 20 microns in diameter could be eliminated.

Tests with Mist Blowers. Work carried out in large open warehouses, such as those used for storing tobacco hogsheads (4), showed that the particle size must be about 50 microns mass median diameter to prevent too much loss through the large wall openings. The spray was blown over the tops of the hogsheads with a specially built mist blower in order to get proper distribution.

Spray Particle Size in Outdoor Treatments

Tests with Aerosol Sprays. Insecticide aerosols may be applied outdoors for controlling insects on crops. The aerosol is released from a line source and is carried by the wind across the area to be treated. A number of tests were made with aerosols of various particle sizes under different weather conditions (6). For satisfactory

results a surface inversion in the air is required to keep the aerosol close to the ground and a light wind of steady direction is necessary. Particle size should be selected according to swath width and wind velocity. For a 3 mile-per-hour wind the particle size should vary from a mass median diameter of 70 microns for a 100-foot swath to 18 microns for a 1500-foot swath. The swath width should not be so narrow that too large a particle size is necessary, for penetration is then poor and foliage is injured near the source. Deposit from this type of treatment was studied by insect counts across infested fields before and after treatment, by chemical analysis for insecticidal residue on foliage, by microscopic examination of droplets deposited on coated glass slides, and by dye samples recovered across the treated area. This type of sampling showed that even under the best conditions only about 25% of the insecticide can be recovered on the first swath, but that up to 50% can be recovered if there are many overlapping swaths. The deposit was also found to taper off from the source, the tapering being more pronounced as the particle size increased. This variation has been explained by the larger range of particle sizes contained in the larger mass median diameter sprays and, therefore, the greater differences in the settling rates of the particles. Most of the particles settle on low-growing crops, but if much of the foliage is exposed vertically and the wind velocity is greater than 5 miles per hour a substantial deposit is obtained on the exposed vertical surfaces. When dye is added to the solution, small vertical surfaces can be seen to have the heaviest deposit. This finding agrees with wind-tunnel data (?) and with Sell's work (3). Small surfaces are usually the most tender and are sometimes injured when application is made in windy weather. Moreover, applications are not usually recommended in wind velocities greater than 8 miles per hour, because much of the insecticide is lost.

Tests with Mist Blowers. Mist blowers are well adapted to laying down a uniform deposit across a low-growing crop. Several of these machines have an air output of about 10,000 cubic feet per minute. The relation between the velocity of the air and that of the liquid is one of the principal elements in controlling particle size. The size is adjusted mainly by the method of introducing the liquid, because the air velocity is usually maintained at the maximum. Sprays having particle sizes between 50 and 150 microns mass median diameter are the most useful. Mist blowers can apply larger particle-sized sprays than the aerosol machines, because the air nozzle can be pointed upward at an angle of about 45° and the large particles can be blown some distance from the machine. Swath widths up to about 500 feet can be treated in strong winds with a mist blower. From a machine having an air output of 8000 cubic feet per minute with the air nozzle pointed up 45° in an 8-mile-per-hour wind and a spray having a particle size of 65 microns mass median diameter, a relatively uniform deposit can be made across a 150-foot swath. About 50% of the insecticide is deposited in a swath of this size, and the recovery approaches close to 80% when several swaths overlap. Particle size should be varied according to wind velocity and swath width. With mist blowers the best practice is to use a particle size between 50 and 65 microns mass median diameter, and adjust the swath width to suit the wind. A wind between 5 and 10 miles per hour is most suitable for this type of application.

In treating tall trees with the mist blowers, selection of the proper particle size is of great importance. It has been difficult to secure sufficient deposit on the tops of such trees without overdosing the lower branches and wasting material. This was especially true in certain prefoliage treatments where a heavy deposit was required. It was found that the most efficient particle size was that predicted by Sell's data (3). The size depends on the diameter of the branches and the air velocity available at their elevation, in addition to the velocity required to overcome the force of gravity on the particles. For mist blowers having an air volume of about 10,000 cubic feet per minute, the optimum particle size for deposit at the top of a tree was found to be about 100 microns mass median diameter.

Tests with Airplane Sprays. In airplane spraying the selection of the proper particle size is difficult. Weather conditions, the type of plane and spray apparatus,

the habits of the insect, and foliage injury must be considered. The planes are flown into the wind as close to the ground as safety will permit. Calm, subsiding air, with a surface inversion—sometimes found in the early morning—is the ideal weather. The particle size should be between the large particles that fall rapidly and the small ones that give a wide, uniform swath. For control of forest defoliators, such as gypsy or tussock moth, a C-47 with a boom sprayer produced satisfactory results with a spray of 275 microns mass median diameter. For mosquito control where penetration below heavy foliage is required, particles of 100 to 125 microns mass median diameter are recommended.

A study of the effect on insects of varying the particle size of deposits on different surfaces indicated that the residues from sprays of fine particle size are most effective soon after application, but that residues of the large particles will weather best and be least absorbed in the material. Large particles, therefore, will give more effective residue over a longer period than the fine particles.

There is still much to be done in developing equipment and formulations, as well as in studying the best particle size to get the most out of concentrated-oil sprays. An occasional poor application, and especially one that injures foliage, will materially retard the widespread use of concentrated-oil sprays.

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Thermal Oil Fogs as Insecticides and Insecticide Carriers

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The principles of insect control by thermal aerosol fogs, developed from idea to practical application in five years, are reviewed. Two large scale experiments, one indoor and one outdoor, carried out by the New York State Science Service are explained in detail along with their chemical and physical data. Characteristics of a special oil developed for fogging are also given.

Thermal aerosol fogs have been of increasing interest to entomologists and others concerned with insect control since World War II, when thermal aerosols to a large extent came to supplement and then supplant chemical aerosols for use as screening smokes to cover military operations. The fact that petroleum derivatives were not only the common smoke-screen producers but also were solvents for DDT, the then new and seemingly universal insecticide, suggested the use of DDT oil solutions to produce fogs that would be lethal to insects—especially to those of military importance, such as disease-carrying mosquitoes and houseflies.

Smoke-screen generators were adapted, first in virtually their original form, later with many refinements for their specialized purpose, as generators of insecticide fogs. Insecticide fog generators are now in use in all parts of the world in practical insect control operations and under further experimental study. Most of them use petroleum products or oils as the insecticide or insecticide carrier, and the designation fog oil has become an accepted term with a meaning so clear that it no longer needs to be defined.

The New York State Science Service, under the leadership of Robert D. Glasgow, then state entomologist, and with the participation of the writer, initiated and carried forward some of the pioneering work in this field. The pioneering work was followed with studies of several potential practical applications.

The readiness with which many organizations and individuals collaborated with each other and with the Science Service made possible tests on an unusually large scale, and the principle of insect control by thermal aerosol fogs has been developed and perfected rapidly. It has taken only 5 years to progress from a mere idea to practical use with helicopters and jet engines.

In specific instances, the application of fogging outstripped the acquisition of prerequisite basic information, not only in the field of biology (entomology) but also in chemistry, physics, and the broad, ill-defined fields which embrace the safety factors—safety to man and animals, safety to vegetation, and safety with respect to fire and explosion hazards. Research in all these fields is under way and is catching up with, or has already caught up with, the practical applications.

The present paper contains data obtained in experiments in which the New York State Science Service participated, together with such chemical and physical data as have a direct bearing thereon. Much of the information was accumulated early in the work and, strictly speaking, does not relate to agriculture. Although most of the data have

not been published, applications based on figures in unpublished progress reports were developed so rapidly that some of the original data are presented.

Characteristics of Fogs

Aerosol fogs as used in entomological work are of three general types: an oil solution of the insecticide dispersed as microscopic droplets by a liquefied gas propellant, usually Freon; a mist or fog produced by mechanical means; a fog produced by means of a thermal aerosol fog generator.

For volume production of an aerosol fog of small particle size, on a large scale (suited to indoor use), the thermal aerosol fog generators appear to be very efficient. The Science Service experiments were mostly with this type. Two principal varieties have been developed. One discharges the insecticide solution or suspension as a relatively coarse spray into a jet of superheated steam delivered by a flash boiler of the tubular coil type. The other discharges that insecticide solution or suspension as a relatively coarse spray into a blast of hot gas emerging from a combustion chamber. The temperature is regulated by the controlled admixture of cold air.

With either method, a portion of the suddenly heated coarse spray droplet is vaporized. This serves as a propellant to disrupt the less volatile remainder of the droplets into smaller droplets, the diameters of which are determined by the temperature at which disruption occurs, by the rate of flow of the air, and by the pressure of injection, as well as by the particular characteristics of the solvent or formula used.

This last point is very important, yet it is commonly overlooked or ignored. A machine adjusted to deliver a certain particle size range with Diesel oil or fuel oil as the solvent or base liquid with the same setting may generate and deliver a fog of widely different average particle size and size range, when a different solvent is used. There is no universal setting for any specific size or size range, that will hold good for all solvents.

The military screening smoke generators, in which these principles were first applied, were built to generate and deliver from Diesel oil or fuel oil an oil fog in which the droplet diameter ranged between 0.5 and 0.75 micron. This particle size will give maximum dispersion of light rays within the visible spectrum. For insect-control purposes, however, these machines have been modified to deliver an oil fog in which the mass average droplet diameters may, in a limited sense, be selected at will, and the range of diameters held within fairly narrow limits. This control of droplet diameter or of particle size is essential because different types of insect control problems require aerosol fogs of different characteristics, associated with different mass average droplet diameters.

R. D. Glasgow compiled and adapted the following physical information from various sources. Three kinds of "aerosols" are distinguished:

Dusts or Mists. In these the particles are larger than 10 microns in diameter. Such particles settle in still air with increasing velocity. They do not diffuse, or tend, as does a gas, to escape through crevices in an enclosure.

Clouds or Fogs. The particles range in diameter from 10 microns to 0.1 micron. Such particles settle in still air at a constant velocity which varies with the diameter of the particle. They do not diffuse.

Smokes. The particles range from 0.1 to 0.01 micron. Such particles are small enough to be pushed about by the impact of surrounding air molecules (which are in constant motion at average velocities of about a quarter of a mile per second). They show Brownian movement and settle very slowly or not at all, in still air. They tend to diffuse slightly.

The force of gravity and the resistance of the medium vary in their effect according to the size of the droplet. Thus, in still air, a droplet 100 microns in diameter, at a height of 10 feet, would fall to the ground in 10 seconds. A droplet 0.1 micron in diameter would require 115 days to fall the same distance. Even within the comparatively narrow range which is called the "true fog," the larger or 10-micron droplets would fall 10 feet in 16.67 minutes, while the smaller 1-micron size would require 27.5 hours.

Particle size must be studied and understood for another reason, immediately evident

upon consideration of the relation between a given volume or weight of liquid and the number of droplets into which it can be divided. One gram (1 ml.) of water would make only 30 large raindrops, each 4 mm. in diameter. But it would make 30,000,000 droplets of mist (40-micron droplets) and 30 billion droplets of fog (4-micron size), having a total surface area of about 14,400 square feet.

The reactivity or effectiveness of the particles increases with the convexity of the exposed surface. Obviously, the surface of the droplets rapidly becomes more sharply convex as the diameter becomes smaller and smaller. It may happen, however, that smaller droplets may not carry a lethal dose for a given insect.

Suppose a bedbug requires, for a lethal dose, an amount of DDT equivalent to that carried by a 100-micron droplet of a 20% DDT solution. Suppose, further, that the bedbug is hiding in an out-of-the-way crack in a corner 2 or 3 feet above the floor. The lethal dose in the form of 100-micron particles might never reach the insect because the particles settle fast, and might not eddy into the cracks. But 10-micron particles would have easy access to the bug, and many times the lethal dose in the form of such particles could actually strike the insect.

With bedbugs, where a residual effect is also desired, and is perhaps as important as the original contact in its effect on a large population, a certain percentage of larger particles would also be of value, to settle out and form a residual deposit of DDT. Tests cited in later paragraphs and in Table I show where bedbugs exposed in the open received more and larger particles and died more quickly, than those in secluded retreats. There are also bedbug hiding places that are not reached by ordinary fumigation or fogging, so that a fog which not only reaches into obscure hideouts, but also leaves a residue to kill those not searched out, should prove most effective. Thus, it is important to know what particle sizes are needed for a particular purpose, and to be able to produce them.

Development of Basic Information from Tests of Fogs in Confined Spaces

The largest undertakings in the field of the Science Service experiments were the Sampson College project which involved the fogging of over a hundred buildings aggregating some 50,000,000 cubic feet of space; and the fogging of some 4000 acres of woodland and recreation areas in the town of Webb, N. Y., from a helicopter.

The first of these projects is of especial interest because of the varieties of insects employed as test animals, the number of formulas used, and the principles that were there first demonstrated; the latter because it was the first large scale use of a new fog oil developed especially for the work after studying and comparing the characteristics and behavior of the formulations used in the Sampson project, and because it was the first instance of fogging from a helicopter.

Because certain fundamental concepts were demonstrated for the first time in the Sampson projects, the tests will be described in sufficient detail to explain why fogs were used instead of standard fumigation procedures; the insects involved will be mentioned as well as what happened to them.

Sampson Project

The plan for converting a portion of the former Sampson Naval Training Station into a college included a provision that all the buildings be subjected to some sort of insect extermination program as a precautionary measure to rid the buildings of any insects that might have become established in them.

The first thought was fumigation. However, a fumigant insecticide such as hydrogen cyanide, methyl bromide, or chloropicrin in gaseous dispersion holds the individual gas molecules in constant motion at high velocities, and the smallest openings in an enclosure are avenues of escape for the gas. The fumigant then becomes so dilute, by diffusion, that it soon loses its insecticidal potency, and, in some cases, becomes a hazard in the immediate environs of the fumigated structure. In most indoor pest control operations by fumigation, therefore, expensive and time-consuming precautions to seal

up the room or building must be made. Further, exacting safety measures must be taken to safeguard both the operators and the general public.

Contrasted with gases, in an aerosol fog of droplets even as small as 0.1 micron in diameter, the individual droplets hang passively in the air, except for gradual settling in response to gravity and movement in air currents. They do not have the tendency to escape by diffusion, as gases do. For this reason, the sealing of windows and doors is unnecessary when aerosol fogs are used indoors.

Conditions. The principal buildings fogged were:

BARRACKS. Uniform two-story, boxlike frame structures covered by shingles or rectangles of corklike composition. Average dimensions were 200 feet long and 45 feet wide, with two floors and a loft, the walls each about 10 feet from floor to ceiling. Capacity figured at 200,000 cubic feet.

MESS HALLS AND GALLEY. Roughly T-shaped frame buildings. Ground dimensions of main structure were approximately 400×90 feet; several side rooms and wings not included. Capacity was approximately 1,500,000 cubic feet.

DRILL HALLS. Large buildings of typical drill-hall or armory style. Each was approximately 600×100 feet on the ground by 50 feet from ground to center of main arch. Capacity estimated at 3,000,000 cubic feet.

OTHER BUILDINGS. Dispensaries, ships service, administration, and school buildings. Frame structures larger than the barracks but smaller than the drill halls and galley units, some of them "rambling" in their layout.

Materials and Methods. FIRST SERIES. The formula used in most of the tests was 10 pounds of DDT in 5 gallons of a solvent which consisted of a mixture of 2 gallons of carbon tetrachloride and 3 gallons of a high-boiling aromatic petroleum solvent (SV PD 544C)—roughly, a 30% DDT solution. The latter was the predecessor of the special fog oil solution, Sovacide F, that was later developed, which in itself possesses certain insecticidal qualities.

The carbon tetrachloride was included in response to a demand that the solution be as safe as possible in regard to danger of fire or explosion. Later work and a more scientific appraisal of the factors involved indicated that this precaution was probably superfluous.

It was realized also that the carbon tetrachloride in the aerosol might in itself be a factor in the insect mortality which resulted. Therefore parallel tests were run in several instances in which carbon tetrachloride was omitted, and it was concluded that in the mixtures DDT was the principal toxic ingredient, at least when dispersed as a thermal aerosol.

SECOND SERIES. The second series included only barracks buildings. The formula used included the 20% DDT solution mentioned above, and chlordan, chloropicrin, nicotine alkaloid, and ryania extractives, with an aromatic petroleum solvent as the carrier in each instance. There were no established precedents that could be used as guides in formulating the solutions used. In most instances the concentrations were adjusted on what seemed to be a reasonable basis when compared with published data on the more conventional use of the chemicals.

In the routine that was developed, the fog machine was brought close to the structure to be fogged on a jeep, trailer, or truck. The fog was piped in through a door or window through flexible metal tubes 4 or 6 inches in diameter and up to 30 feet long. The two floors were either fogged separately, first the upper and then the lower, or simultaneously with two machines, one for each floor.

The dosage expressed in terms of pounds or gallons per cubic foot varied considerably, depending on the type of building. In the first series, for the barracks type it was more or less standardized at roughly 5 gallons of DDT solution containing 10 pounds of DDT. In the drill hall, 30 gallons of solvent carrying 60 pounds of DDT were used. This was about 1 pound of DDT per 50,000 cubic feet, or, in this instance 1 pound per 1000 square feet of floor area—a very high dosage—resulting in a heavy residual deposit on horizontal flat surfaces as shown in Figure 1. Neither the optimum nor minimum dosages which should be used under the different conditions were determined.

In order to evaluate the results of the operations, insects of several species were caged in the buildings that were to be fogged, both in the open and in places of difficult access, such as in cupboards and behind baseboards. In the first series of tests, the insects included bedbugs, cockroaches, houseflies, clusterflies, clothes moths, and carpet beetles.

Slides coated with fused zinc stearate were exposed with the cages to furnish records of the fog deposits, which might be correlated with the kills.

In the second series, the exposed insects included several of the above, and, in addition, two species of mosquitoes, mealworms, and milkweed bugs.

Results. Examples of the data obtained in the first series of tests at Sampson are given in Table I.

Figures 7 and 8 are especially significant in that the slides were in a vertical position, and the photomicrographs therefore represent deposits of fog particles which impinged on a vertical surface. The slide shown in Figure 7 was slipped edgewise into a vertical crack in a post near the center of the second floor, with about 1-mm. clearance between the coated surface and the side of the crack. The slide shown in Figure 8 was wedged just sufficiently to hold it in a nearby crack, also in a vertical position, but with the oleophobic surface fully exposed. The slide shown in Figure 4 was placed on its edge at an angle just sufficient to allow it to lean against the wall behind a warped portion of the coping board at the far end of the same room, at a height of 5.5 feet.

Table I. Deposits of Fog Particles and Conditions of Insects at Selected Test Locations

Building	Figure No.	Location of Slide and Insects	Fog Deposit at Test Location	Condition of Insects Caged at Test Locations, after about 24 Hours
Barracks L-1	1	In mail box with slot facing away from fog	Good deposit	5 bedbugs, all moribund ^a
Barracks SCPO-2	2	On ledge behind radiator at far end of closed room	Good deposit of small particles	10 bedbugs, all moribund
Barracks SCPO-2	3	Same relative position as Fig. 2 but room open	Heavy deposit of confluent droplets, with crystallization	10 bedbugs, 5 dead and 5 moribund
Barracks S-6	4	At far end of room behind coping at 5 $\frac{1}{2}$ -foot height, nearly vertical	Good deposit with some coalescence	9 bedbugs, all moribund
Drill hall	5	In rear room inside wall below hole closed by board nailed over it	Good uniform deposit of fine droplets	10 bedbugs, all moribund; 10 clusterflies, all dead
Drill hall	6	Behind baseboard along one side of main hall	Heavy deposit of small droplets	10 bedbugs, all moribund

^a No insects classified as moribund recovered.

In most of the photomicrographs discussed and reproduced here, especially slides that were exposed inside closed spaces and received only the smallest particles, the smallest droplets would not be registered, and those that did appear, at the magnification used, are indistinct and obscure the scale. In other instances, the photographs are not sharp because they were made in the field with the slides exposed at locations where dust could settle, and where firm supports for the camera and microscope close to a good light source could not always be obtained. These inferior photographs are included because they furnish a record of the deposit for correlation with kill, which was the chief purpose of exposure, whether or not fine measurements of individual minute particles can be made. In all cases, the proportions of particles in the different size ranges may be determined, and the general character of the deposit can be ascertained. In some photographs, as shown in Figure 4, the definition of individual droplets was much better than in others.

In the first series of tests, a particularly interesting result was the total destruction of a large natural infestation of German cockroaches (*Blattella germanica*) in the B mess hall. As fogging progressed, thousands of roaches emerged from their hiding places in cracks and crevices, and from the interiors of the walls. Hundreds of them came through the walls and under the doors to the outside of the building, but were so strongly affected before they reached the outside that none survived. All of those that crawled out onto the floors of the fogged rooms were also killed. The day following the fogging, 1500 dead and dying roaches were swept up from 1000 square feet of floor space. No active roaches

were seen in the building for several weeks, or for as long as the observations were continued.

None of the other chemicals tested in the second series showed more promise than DDT, although some of the data were rather fragmentary. Certainly, none of the materials would be expected to have the residual action of DDT, which, from the settling of the larger fog particles, produced a sufficient deposit of DDT on horizontal, face-up surfaces, to have a residual effect for several weeks.

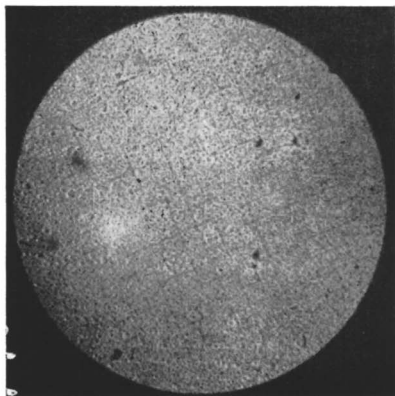


Figure 1

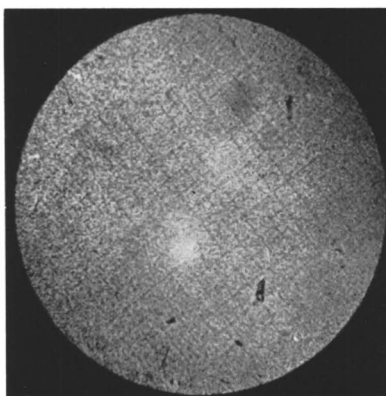


Figure 2

The tests in the second series included buildings fogged with the oil Sovacide 544C alone, and it was found to possess significant insecticidal action at stations where a high concentration of fog occurred. This was evident particularly with houseflies, German cockroaches, mosquitoes of the genus *Aedes*, and furniture carpet beetles.

Tests have not yet been made to determine accurately the separate effects of the oil and of the DDT in solvent mixtures of the two.

Other Experiments

Another interesting experiment was the treatment of a seed storage warehouse for suppression of the Indian meal moth. This warehouse was fogged more or less regularly for several months with 20% DDT in Sovacide (PD 544C) solvent. Scores of house mice and several rats were killed in the course of the operations, and the owner felt that the fogging was worth while for this alone. The meal moth infestation was greatly reduced, and it is believed that periodic fogging would keep such an infestation to a minimum. As the stored grain was used for seed only, the factor of possible contamination of foodstuffs did not have to be considered.

Several experiments have also been carried out in wool storage warehouses, with consequent reductions in clothes moth infestations. In one such experiment a check was afforded by the use of electric light-and-fan moth traps. During a 2-week period before the fogging, 11 traps captured 5589 moths. In the 2-week period after fogging, the same traps captured only 3 moths.

Discussion

The question of dosages—how much to use—is a very important question and one that must be answered before fogging methods can be standardized. Unfortunately, there is not yet sufficient information on this point.

So many basic factors must be considered that standard dosages are difficult to determine, and the closest estimate based on reasoning may be far off in either direction. In indoor work, especially, one effect which might be unfavorable under some, but not all, conditions has been the deposition of heavy DDT residues. However, it may be neces-



Figure 3

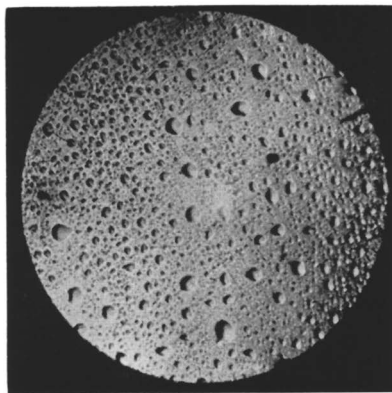


Figure 4

sary in many instances to get too much in one place in order to have enough in another. The possibility of staining or oil damage, when mixed size particles or uniformly too large particle sizes are used, must also be borne in mind and allowed for, under some conditions, in indoor work.

Also, the small particle size so desirable in situations where there must be penetration into closed spaces such as gymnasium lockers or desk drawers, at the same time facilitates penetration into cupboards which contain food or eating utensils. However, these items may often be sealed in, or tightly covered, and table tops are easily cleaned. The operator must bear all these things in mind and proceed with full knowledge of what is involved.

A chamber containing 1000 cubic feet can be visualized as one having dimensions of $10 \times 10 \times 10$ feet. It would be bounded by six plane surfaces of 100 square feet each, aggregating 600 square feet. A dosage of 0.05 pound per 1000 cubic feet, as used in the barracks buildings at Sampson, if depositing out evenly on all six boundary surfaces—which, of course, it would not do—would be the equivalent of 0.05 pound per 600 square feet, or 3.65 pounds per acre. It is obvious that normal settling would result in a much heavier deposit on floors and face-up horizontal surfaces than on under surfaces and vertical walls, and that in many buildings the fog seeping into cracks and other openings into hollow walls would find many more surfaces, including insects, on which a deposit could occur.

Dosages that were over as well as under an effective level were used, without knowing in advance whether they were over or under. For instance, in the barracks building the dosage of 0.05 pound of DDT per 1000 cubic feet in the first experiment at Sampson was apparently more than adequate. Therefore in the second set of tests in the same building a smaller dosage of DDT was used; however, this did not give such good results.

Many factors would influence the dosage to be used. In loose, frame structures such as the barracks, the high and irregular winds prevailing at the time of treatment undoubtedly were responsible for lack of kill in several instances, and made comparisons very difficult. The direction and velocity of the wind would influence the choice of a location from which to fog a building, and it might be necessary to fog from more than one position.

The temperatures occurring during the fogging would also be a factor, as well as an abnormal rise or fall of barometric pressure during the time the fog was expected to hang in the air within a building.

As implied above, the character of the building is also an important factor in determining dosage—whether the structure is large or small, loosely constructed or tight, with many partitions or compartments or with few, empty or well filled with furniture or merchandise.

And one must first of all consider the species of insect or insects involved, the stage they are in and to what extent they are known or expected to be hidden, whether they are active, sluggish, free flying, or crawling. Therefore, decision must be made as to whether the fogging is to be strictly spatial in intent, or whether residual effect is necessary to produce the desired kill and control.

Although the Sampson and other fogging projects were undertaken as research projects with the hope, at the same time, of achieving practical results, they were on such a large scale that a great amount of public interest was aroused. Even before all of the results could be determined and before sufficiently inclusive and conclusive observations could be made on such points as margins of safety, fogging as an indoor pest control procedure became a widespread practice. In those early days much fogging was done which might better have been left undone or have awaited a more thorough understanding of the principles involved. Owing to carelessness and ignorance, several accidents occurred, as can happen with any pest-control procedure when practiced without sufficient care or knowledge.

Fortunately, pest-control operators and others are now proceeding more cautiously, and fogging is recognized for what it is—a specialized control procedure for certain specific insect problems, not a cure-all for any problem that has presented unusual difficulties. As a specialized procedure it works best when special formulas and special equipment are used—formulas and equipment designed for the various special fogging problems, after research has first revealed the difficulties and how to overcome or avoid them.

Uses of Fogs Out of Doors

Thus far this discussion has centered around indoor experiments, because it was easier to control more of the conditions and therefore to make more precise studies as a basis for further work. The uses of fogs out of doors have been studied in connection with many insect problems. Fogs appear to be especially suitable as space insecticides against mosquitoes, houseflies, blackflies, sandflies, punkies, and similar insects that annoy man and carry disease organisms.

In 1947, a single mosquito abatement district in California reported using 10,029 gallons of aerosol mixture to treat 47,003 acres, mostly from the ground. The acreage treated by aerosols represented a little more than 10% of the district.

Webb, N. Y., Project

With ground-operated machines, the effects of fogging, while pronounced for a limited time, may be very local as well as temporary, even when a special fog oil is used. A rather spectacular development, but one which appears to have been successful to an unusual degree and to have wide potential usefulness, was the helicopter fogging for blackfly control

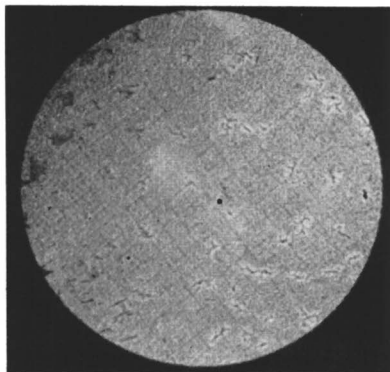


Figure 5

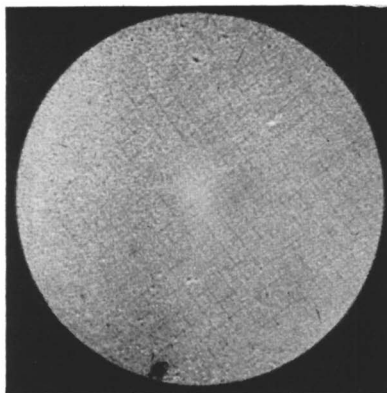


Figure 6

in the resort region of the central Adirondacks in New York—the Town of Webb project, which was carried out under the direction of the State Science Service.

The possibility of large scale abatement of blackflies in the Adirondack area by thermal fogs from DDT oil solutions was forecast in 1945 by the local success of early work with ground-operated generators using solutions of DDT in kerosene and Diesel oil. This work, however, showed the necessity for operations on a very much larger scale if the control was to be really effective. In a region with few roads through the extensive black-fly-inhabited wilderness, application from the air seemed to be unavoidable.

A better DDT solvent and a better fog producer than the fuel oils were therefore necessary to permit efficient and economical operations. A helicopter was considered more efficient than a fixed-wing plane in forcing the fog through the tree canopy, and in being able to treat slowly and topically when necessary. Through the agency of the New York State Science Service and largely under the guidance of R. D. Glasgow, collaboration between engineering and research units of the Socony Vacuum Oil Co., Todd Shipyards Corp., and the Bell Aircraft Corp. was brought about. This resulted in the adaptation of the Todd fog-head for use on the Bell helicopter, designed specifically to produce and disperse the optimum fog from a 15% solution of DDT in Sovacide F fog oil.

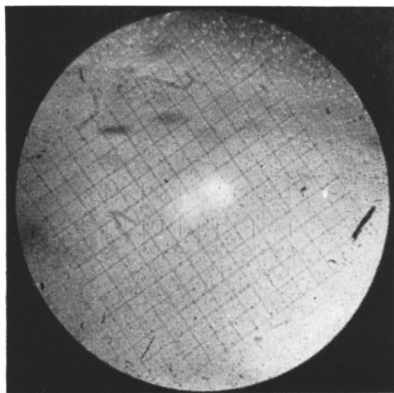


Figure 7

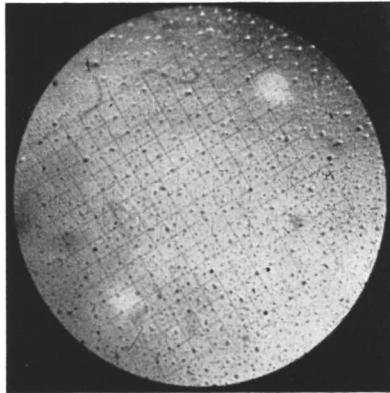


Figure 8

With this combination, 4000 acres of recreation area and woodland were fogged three times, and the blackfly nuisance was abated.

The success of these helicopter fogging operations in controlling blackflies in the Adirondacks resulted in plans to use similar equipment and formulations in other parts of the world for mosquito control on a large scale, notably in Sardinia and in Brazil. Many if not most of the mosquito abatement districts and organizations throughout the world now employ fog in one way or another as one of their routine treatments.

Conclusion

The chief interest of petroleum chemists in the information presented here may be in the fact that, although the earlier kerosene type of petroleum derivatives mixture will produce insecticide fogs—and is still used successfully for them—an analysis of fog production and its use, from biological, physical, chemical, and mechanical standpoints, has resulted in the evolution of special fog oils which combine higher DDT solvency, specific insecticidal potency, greater safety, and greater chemical and physical stability with consequent limited and therefore more desirable particle size range, at known temperatures and pressures.

In the California work already cited, aerosol solutions used ranged from 5 to 25% DDT in various solvents, such as Sovacide 544C and Velsicol. Specifications for the best of these stated that it is 75% aromatics, with a flash point of 220° F., and a distillation range of 520° to 700° F. This agrees in general with the findings of the Sampson College

fogging tests and other studies which, recognizing the limitations of kerosene, Diesel oil, and fuel oil as thermal fog oils when high DDT content and greater physical and chemical stability were required, led to the establishment of certain characteristics as being desirable in a fog oil, and to the development of an oil which embodied these characteristics.

Some of these desirable characteristics are:

The solvent should dissolve a minimum of 15% of technical DDT at field temperatures of 60° to 70° F. and should retain this amount of DDT in solutions at 32° F. In addition, the aerosol oil should readily dissolve other toxicants. This high solvent power is required in order that each fog particle may carry a maximum load of toxicant.

The fog formed with a solvent should be dense enough, fine enough, and persistent enough to ensure maximum penetration of underbrush and crop cover.

The solvent should be capable of forming uniform aerosol particles within a limited range under 100 microns in diameter.

The solvent should in itself have a certain degree of insecticidal power.

The solvent should be relatively nontoxic to human beings and to higher animals.

The solvent should be relatively nontoxic to vegetation over a wide range of species and under the conditions where it is most useful as an insecticide or insecticide carrier.

The solvent should offer a minimum hazard with respect to fire and explosion.

The solvent should be nonstaining, and at least in fog form, noncorrosive to paint, metals, plastics, and fabrics.

The solvent should be cheap enough so that the advantages of its specific superior qualities as an insecticide fog oil will encourage its production and use.

Actual tests on a sample of Sovacide F outdoor fog oil, according to data furnished by Socony-Vacuum Laboratories, showed the following characteristics:

Distillation, ° F.	399
I.B.P.	706
F.B.P.	
Gravity, ° API	23.1
Flash, C.O.C., ° F.	190
Saybolt Universal viscosity at 100° F.	34
Color, ASTM	2½
Technical DDT solubility at 32° F., %	15
Mixed aniline cloud pt., ° F.	120
Un sulfonated residue, %	37

It is not implied that other effective fog oils have not been devised or used, nor that other fog-producing mechanisms would not achieve the desired results. However, the circumstances and data cited constitute interesting and significant instances of how certain specific insect problems were analyzed, and how, through the coordinated collaboration of engineers, mechanics, chemists, physicists, and entomologists, effective control methods were evolved.

Acknowledgment

Principal collaborators in most of the developmental experiments were the Combustion Equipment Division of Todd Shipyards Corp. with the active participation of Frank K. Steinrock and his associates; and the Socony-Vacuum Oil Co., with the active participation of A. E. Griffiths, William Stevens, and Warren Beman.

The ryania formulas were prepared by and used through the courtesy of Merck & Co., Inc., which furnished many of the test insects and whose research representative, John V. Osman, participated in the tests.

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Herbicidal Uses of Oils

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Summarizing the growth of the utilization of petroleum oils in herbicides, an evaluation is made of the present-day chemical weed-control methods in which oils are employed—as toxicants, as solvents, as filming agents, and as carriers. The unique properties of oil in the pest control of the future are also indicated.

Early use of petroleum products in weed control was generally limited to the local area and involved mostly the use of waste materials—acid sludge, various aromatic bottoms, low grade oils, and by-products of little commercial value. With increasing emphasis on weed control and firebreak maintenance, particularly in the Southwest where roadside, fences, and ditch banks become unsightly and are a fire hazard during the summer, Diesel fuel and smudge-pot oils were used in increasing quantities. During the twenties and thirties, use of these oils for puncture-vine control by counties, firebreak maintenance by highways, and roadside and fence-line weed control by farmers had reached a volume of several million gallons annually in California alone. Oil sprays in lieu of tillage had been proved beneficial in citrus orchards. Various oils and emulsions were being used in increasing amounts in the control of Johnson and Bermuda grasses in many agricultural areas.

Throughout this period Avon weed killer, a highly aromatic residue from the Edeleanu process, was about the only oil sold for purely herbicidal purposes. Meanwhile, Diesel oil was becoming popular as an automotive fuel and attempts were being made to improve its quality by removing its aromatic ingredients, a process that decreased its toxicity to plants.

In 1936 Sinox, a dinitro selective weed killer, was introduced and widely used, not only in cereal crops but in peas, onions, flax, and other important crops. In the early forties a private dealer in the Salinas Valley of California discovered the selective herbicidal use of stove oil in carrot crops. As war conditions made labor scarce and military demands called for increased production, this proved a great boon to the vegetable growers.

Oil sprays in 1943 and 1944 saved many thousands of acres of carrots that would have been lost if hand labor had been required to weed them. Meanwhile, guayule production had utilized to the maximum the tolerance of that crop for Diesel oil emulsions. Oil sprays allowed complete mechanization of this crop, which was considered critical in our war production.

But stove oil, if not carefully used, left an oily flavor in carrots. Synthetic rubber reduced the need for guayule. Fuel oil prices had advanced to a level that almost prohibited their use for weed control. The future of oil in the herbicide field was in doubt. Yet farmers needed oil sprays for their irrigation systems, which were infesting their fields with weeds, and for their fence lines, which were harboring thrips and other insects and diseases. These problems of research were undertaken by the agricultural experiment stations in California, Massachusetts, New York, and other states.

Toxicity Research

One investigation (1) sought more definite information on the effect of molecular structure on toxicity. Although it had been well established that aromatic and olefin compounds were toxic as compared to alkanes, it seemed worth while to pursue this study further, with the idea that if some one compound or series of compounds could be identified as the significant factor in toxicity, it could either be isolated by some refining procedure or be synthesized from other substances.

In view of the development in synthetic toxic agents, described in this paper, this phase of the project has become somewhat less important. It was equally essential then, however, that some oil diluent should be available, so that toxicities of oil-soluble, water-insoluble substances could be studied.

Experiments (1) indicated that *n*-hexane or *n*-cetane was reasonably satisfactory as a nontoxic diluent for short-time tests. This was confirmed by the work of Leonard and Harris (2), although the higher alkanes, even decane, in the 9-week test, showed marked toxicity toward such plants as cotton, soybean, and others. They also found that *n*-tetradecane produced considerable injury below the surface of the soil. This result had also been experienced by the writers with *n*-cetane and had been classed as chronic toxicity. Leonard and Harris, however, subjected plants to six sprayings in a 6-week period, a much more rigorous treatment than the writers had applied. Their conclusions of the increasing toxicity of compounds from hexane to dodecane, with some decrease in tetradecane, were based on examination 9 weeks after the first application of oil. This general rule relating toxicity to molecular weight was evidenced in results of investigation by the writers, using appropriate fractions of gasoline and kerosene which had been subjected to the usual acid treatment.

In regard to unsaturation, on flax especially, a marked toxicity of cyclohexene, as compared to cyclohexane, was observed (1). Leonard and Harris (2) investigated this further and noted that while hexene differed little from hexane, both being relatively nontoxic, higher members of the series, even decene, produced severe burn or death in two sprayings, while with *n*-decane such severe damage was not noted unless five treatments or sprayings were made. This result was much more noticeable on cotton than on soybeans.

The aromatic fractions were recognized as of more herbicidal value. However, the use of pure compounds in relatively high concentrations with repeated sprayings at definite time intervals was required to prove that in general the toxicity varied directly with number of substitutions on the nucleus. Similarly, the toxicity was shown to increase with the length of the side chain, at least through C_4H_9 , the butyl group. Little effect was noted from the amount of branching on the side chain. These results were clearly shown by the work of Leonard and Harris as well as that of the writers.

Recently it has been noted that certain polycyclic aromatic compounds cause marked chronic toxicity, particularly on large grass plants. Killing such grasses is one of the most difficult weed problems under field conditions and its importance should justify further research. Possibly the phenolic constituents of oils should be studied further, in view of the now known toxicity of substituted phenols. Such compounds had been removed by chemical treatment from the oils used in most of the original work of the writers.

Refined Selective Spray Oils

Refined oils of the Stoddard solvent type, safe and effective for handling carrot crops, were developed after a relatively short period of research. Their use spread to celery, parsnips, parsley, and anise. Foresters, finding that conifer seedlings were tolerant to the refined oils, sprayed forest tree nurseries. Research proved that a somewhat less toxic oil could be used on flax and onions. The use of refined selective spray oils found a definite place in the agriculture of our country.

Fortified Oil Sprays

Research on activation of dinitro sprays had proved that the substituted phenols were more toxic than their salts. These compounds are oil-soluble and therefore could be used to bolster the dwindling toxicity of fuel oils. When dinitrobutyl and amyl phenols and pentachlorophenol were found effective, the general contact oil-emulsion sprays were developed.

Since the removal of aromatics from fuel oils lowered toxicity, attention was directed to other highly aromatic fractions. Avon weed killer, a very aromatic material, had proved toxic and it was soon proved that many other aromatic fractions were effective. Unfortunately, most of the old sources of aromatic fractions were soon exhausted, but tests proved that the bottoms from the catalytic cracked stocks were similarly toxic. Shell No. 20, Standard No. 2, and a host of other toxic weed oils soon came onto the market, and the demands on Diesel and smudge-pot oils were alleviated.

Since a few pounds of a substituted phenol fortifier will make 100 gallons of Diesel oil more toxic, the advantage of heavier fortification was in doubt. Tests proved that a little fortifier goes a long way as the covering capacity of the oil soon becomes the limiting factor. The problem of extending the oil itself was studied by agricultural experiment stations in California and Hawaii and by oil companies and herbicide manufacturers. It is now known that a fortified oil emulsion spray consisting of a few pounds of fortifier, 10 to 20 gallons of low grade fuel oil, having a viscosity of 50 seconds or less, some oil-soluble wetting agent, and 80 to 90 gallons of water will kill general weed growth almost as effectively as will a straight weed oil. The most effective wetting agents have been sulfonated naphthenic petroleum fractions. Likewise, the fortifiers may be made from phenols or substituted phenols derived from petroleum.

Aquatic seeds in irrigation ditches interfere with the flow of water and often result in serious loss to farmers. Chlorinated benzene with appropriate emulsion stabilizers has proved effective in the control of such weeds. The Bureau of Reclamation through its Denver laboratories tested methyl substituted benzenes and found them equally toxic to aquatic weeds. As a result, the aromatic solvents, both from coal and petroleum sources, are proving a boon to farmers.

And then came 2,4-D. Emerging from the war as a miracle weed killer, this material grasped the imagination of American farmers. Within three years it became the center of a multimillion-dollar business. Could oil fit into the 2,4-D picture? The answer is decidedly "yes."

Work with the dinitro selectives prepared the stage for 2,4-D. They were highly selective; they could be applied by airplane; they had been put on at volume rates as low as 25 gallons per acre. A hormonelike chemical, 2,4-D moves around in the plant. Work in California in the early spring of 1946 proved conclusively that 8 gallons of water were as effective as 160 as a carrier for 2,4-D. But below 5 gallons per acre, water sprays were hard to apply. Work in the lake states and in Canada in 1946 proved that 2,4-D could be applied in as little as 0.4 gallon of oil per acre and give good results. Distribution was the major factor and the agricultural engineers soon handled that problem. In the wheat belt of the United States and Canada, many millions of acres of grain have been sprayed with 2,4-D. Oil has been used as a carrier where water is not plentiful or where it is less practical than oil.

Oil is beneficial not only as a carrier but also as a spreading agent. Oil emulsions carrying considerable wetting agent as a stabilizer have proved effective as 2,4-D carriers on many hard-to-wet plants. Over 100,000 acres of rice are sprayed annually with 2,4-D in California alone, and practically all of this spray is in the form of an emulsion, for experience has shown that oil aids in the spreading of the herbicide on sedges, cattails, and tules. Oil-emulsion carrier has proved essential in the high-dosage application of 2,4-D to cattails and tules in ditches. It is proving essential in brush control, in the control of hoary cress and Russian knapweed—two deep-rooted perennial weeds that resist control efforts. In fact, oil as a filming agent is proving

beneficial in almost all 2,4-D sprays designed to control perennial plants. In all such sprays, the oil content should be around 4 gallons per acre, and the oil should be low enough in toxicity so as not to injure the foliage of the treated plants.

Oil in Present-Day Weed Control

Surveying the field of chemical weed control today, it is found that oils fit into it in many ways:

As toxicants, the aromatic and olefinic compounds are most effective.

As solvents, aromatic fractions are most useful with pentachlorophenol; aliphatic fractions are effective as solvents for 2,4-D esters.

As filming agents, cheap, readily emulsifiable oils are useful.

As carriers, oils enter the picture where low-volume airplane applications are made. The cheap oils are used in higher volumes in grass killers. Possibly new materials will displace the present wasteful high-volume spraying of grasses.

Oils form the base for a number of wetting agents and emulsion stabilizers. They are probably the cheapest source of such reagents.

Oils could and actually may supply many of the basic chemicals from which special herbicides are synthesized.

Economy of Oil Resources in Future Weed Control

As we turn to the future, we are faced with several serious questions. No one now doubts the essential role of agricultural production, and few would question the importance of weed control. But, as important as it is, how far should we go in using high-energy fuel such as oil for killing weeds? There are two criteria upon which this question must rest. The relative advantages of using oil must be considered. If oil can do a better job, if it can do it more quickly, more conveniently, or more effectively, the answer is clear. The use of oil for herbicidal purposes might prove as justifiable as its use as a motor fuel. A second and possibly more critical question is "Can pest control be done with less oil?" Undoubtedly, in planning future work with oil we must devise more economical and efficient methods for the use of our oil resources in pest control.

2,4-D. The most widely used herbicide at present is 2,4-D. As far as the selective use of 2,4-D on cereal crops is concerned, the amine formulations seem perfectly satisfactory. As a translocated herbicide, results are not too good. In some localities, 2,4-D has been effective in treating perennial weeds, but in other places results have been disappointing. The differences seem related to the movement of the material after it gets into the plant, and here the physiology of the plant, as well as the nature of the chemical, is concerned.

As 2,4-D is applied to the foliage, it first must penetrate the cuticle. The more oil-like the molecule, the more readily it may go in. This is evidenced by the superiority of the esters over the salts on an equivalent basis. When the 2,4-D has diffused through the cuticle, it must then move through several layers of living cells, the mesophyll, from whence it migrates into the phloem or food-conducting channels. Much evidence now indicates that 2,4-D accompanies foods in moving out of the leaves, through the stems, and on to points of utilization or storage, mainly the growing shoot tips and the roots. Here the molecules are in water solution and, as they move through the cuticle, across the mesophyll, and along the phloem, the partition of the chemical between these phases will depend on the nature of the molecule—oil-like molecules penetrate cuticle readily; more polar forms are compatible with the aqueous phases in mesophyll and phloem. Obviously, it is difficult to fill both these needs with a single molecular form. An oil-soluble amine salt of 2,4-D has been synthesized that has proved to be translocated effectively; possibly, the free acid may fit the requirements most accurately. Since the ester forms do translocate, possibly they hydrolyze readily within the plant, releasing the acid to move along the phloem channels.

Recent research has proved 2,4-D to be effective in brush control, and oil seems to be essential in the formulations. For spraying, a fairly heavy, low toxicity oil has proved best. There are indications that a coarse spray which only spots the leaves will foster translocation of the 2,4-D after it has been absorbed.

Oils are also essential as carriers of 2,4-D for basal treatments. Here penetration of the bark is essential. Whether killing the bark is desirable is yet to be determined. Much research is needed to define the role of oil in the basal spray and to find the particular oil best fitted to the method.

DN. The dinitro general contact weed killers are usually formulated with some oil. In these, the oil serves as both solvent and filming agent. The emulsifier is usually also incorporated to stabilize the emulsion and give wetting properties. To lower costs and conserve oil, it is desirable to use the minimum effective volume in these sprays. Possibly some of the penetrating oils may fit into this need. No research is known that is designed specifically to find the best oil for this purpose.

Maleic Hydrazide. Best results with this new chemical to date have followed aqueous sprays of the diethanolamine salt. Treatment of grass with comparable amounts of the chemical in oil has been less effective. This is contrary to the results with dinitro and 2,4-D sprays; possibly the partition coefficient of the oil-soluble material is not right. As with 2,4-D, penetration is only one aspect of the herbicidal action; translocation is involved where grasses having underground rhizomes or crowns are involved. For killing these, migration through the phloem channels may be the essential factor, and the more polar salts may prove best.

Pre-emergence Herbicides. Probably the first pre-emergence treatments were stove-oil sprays on carrots and onions in the Salinas Valley. Following their successful introduction, dinitro selectives were tried with success in the Tule Lake region of California. This trial was in early summer. The following winter similar trials on onions in the Sacramento delta were ruinous; the crop had to be plowed up and replanted. Evidently, weather played a decisive role in the use of pre-emergence treatments.

With the introduction of 2,4-D, pre-emergence methods again became prominent and again weather proved decisive. More recently, toxic oils and fortified oils have been used; some crops have been saved, and other crops have been ruined. There are two distinct pre-emergence methods, one a contact spray that kills weed seedlings emerging before the crop, the other a pre-emergence treatment through the soil.

For contact pre-emergence work light oils of high toxicity, such as Stoddard solvent, are safest although possibly relatively expensive. Stove oil is also relatively safe; Diesel oil can be used, but if the crop seedlings are pushing through, they will be injured. Crops having big, vigorous seedlings are less susceptible to injury than are small seeded ones. Aromatic oils have proved hazardous, as the oils or the vapors from them may severely injure seedlings of the crop. Fortified oils are even more hazardous, because the fortifying agents form highly toxic residues in the soil. Only under special circumstances, usually involving dry weather with no rainfall until after the crop is well established, may fortified oils or their emulsions be safely used for pre-emergence work.

Most effective 2,4-D pre-emergence treatments are through the soil. Pre-emergence sprays by the residual or soil-treatment method should be used with a crop that is relatively tolerant of the herbicide. Selectivity between the crop and the weeds depends upon the spread in susceptibility between them. For this reason, pre-emergence treatment with 2,4-D may be safely used on certain corn varieties, while on others it is hazardous. It is most successful on heavy to medium soils if soaking rains follow, and in light sandy soils if rainfall is scanty. The opposite pattern of rainfall will give less satisfaction. Oils play no part in this 2,4-D pre-emergence treatment. However, heavy weed oils have been used alone and with fortification in established crops like cane or alfalfa to kill weeds during the dormant season.

Oils have been pre-eminent in grass killing, but with the introduction of isopropyl *N*-phenyl carbamates, trichloroacetates, and maleic hydrazide, satisfactory

substitutes may be found. Though this may reduce the bulk use of low-grade oils, it should not discourage the use of oils in weed control. However, only where oils serve a useful purpose in better and cheaper herbicides should they be withdrawn from use as fuel to be applied in the control of weed pests.

Summary

In the utilization of petroleum oils in the field of chemical weed control, oils function as toxicants, as solvents, as filming agents, and as carriers. In view of the very effective synthetic compounds now used as toxicants (substituted phenols), the toxicity of the oils themselves is somewhat less important than it once was. Oils may serve as adjuvants in formulations involving 2,4-D, 2,4,5-T, dinitro compounds, trichloroacetates, and others. They have the unique property of aiding in the contact, spreading, and penetration of herbicides. In addition, synthesis of wetting agents, emulsifiers, and special herbicides may be dependent on petroleum products.

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Herbicidal Properties of Petroleum Hydrocarbons

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Toxicity tests on 31 pure hydrocarbons of aromatic, olefin, naphthene, and paraffin series are reported. The hydrocarbons, ranging in boiling point from 176° to 572° F., were representative of those found in petroleum naphthas. The work was done at Ithaca, N. Y., in both greenhouse and field plots.

For killing undesirable plants and for protecting crops against insect pests, it is highly desirable to understand the properties of the petroleum oils which are responsible for plant toxicity.

The work of several investigators (3, 5-7, 12) has indicated a general, although far from perfect, correlation between toxicity and percentage of sulfonatable residue of oil fractions. The sulfonatable hydrocarbons are the olefins and aromatics. The paraffinic hydrocarbons do not react in the sulfonation treatment. These results suggest that the olefin and aromatic groups are largely responsible for the herbicidal activity of oils.

The findings of Crafts and Reiber (4) were somewhat inconsistent with the above conclusions. After sulfonation, gasoline and the low-boiling fraction of stove oil were still toxic to broad-leaved weeds and grasses. The unsulfonatable residue of the heavier fraction of stove oil, boiling between 424° and 570° F., was not toxic.

When certain of the pure hydrocarbons were tested on growing plants (4, 11), the aromatics were found to be highly toxic, but the paraffins were not toxic. That the aromatics were the principal hydrocarbons responsible for toxicity was strongly suggested by the independent work of Lachman (8) and Sweet *et. al.* (10), who studied the suitability of light oil fractions for weeding carrots in the East. The Stoddard solvents have an aromatic content of 10 to 20% and a boiling range of 300° to 400° F. These oils killed weeds, but did not injure carrots. When the aromatic content was 6 to 8%, only moderate injury to weeds resulted. Oils with an aromatic content of 50% or greater were severely toxic to carrots as well as to weeds.

This is a report on tests of 31 pure hydrocarbons of aromatic, olefin, naphthene, and paraffin series with a range in boiling point from 176° to 572° F. The hydrocarbons were representative of those found in petroleum naphthas. The work was conducted both in the greenhouse and in field plots at Ithaca, N. Y. In the greenhouse, the chemicals were sprayed on test plants which included peas, lettuce, spinach, onion, carrot, and timothy. The field tests were made on carrots and naturally occurring weeds.

Toxicity Ratings

More than one method was used to evaluate the toxicities of the hydrocarbons. The first was to give a toxicity rating to each hydrocarbon based on the speed and com-

pletteness of kill when the test plants were sprayed with the pure hydrocarbons. The ratings thus obtained are presented in Table I. Certain generalizations can be made from a study of these data. The aromatics produced the greatest toxicity. Although the paraffins were generally the least toxic, certain paraffins produced considerable injury. Boiling point also appeared to influence toxicity. The hydrocarbons boiling below 280° F. and those boiling above 510° F. were generally less toxic than the hydrocarbons with intermediate boiling points. The high rate of evaporation from the plant foliage probably accounts in part for the relatively low toxicities of the hydrocarbons which boil below 280° F.

Table I. Toxicity Ratings for 31 Pure Hydrocarbons

	Hydrocarbon	Series	Boiling Point, ° F.	Toxicity Rating ^a
1	Benzene	Aromatic	176	1
2	Iso-octane	Paraffin	194	1
3	Methylcyclohexane	Naphthene	214	1
4	Diisobutylene isomers	Olefin	214-219	3
5	Toluene	Aromatic	231	5
6	<i>n</i> -1-Octene	Olefin	251	3
7	<i>n</i> -2-Octene	Olefin	257	3
8	<i>n</i> -Octane	Paraffin	258	3
9	Vinylcyclohexene	Olefin	264-266	5
10	Ethylcyclohexane	Naphthene	267	3
11	Xylenes	Aromatic	280-291	7
12	Isopropylbenzene	Aromatic	306	7
13	<i>n</i> -1-Decene	Olefin	342	7
14	<i>n</i> -Decane	Paraffin	345	5
15	Triisobutylene	Olefin	347-357	5
16	Diethylbenzene	Aromatic	357	7
17	Decahydronaphthalene	Naphthene	375-383	7
18	Tetrahydronaphthalene	Aromatic	405	9
19	Triethylbenzene	Aromatic	412	7
20	<i>n</i> -1-Dodecene	Olefin	415	5
21	<i>n</i> -Dodecane	Paraffin	421	3
22	Dicyclohexyl	Naphthene	446	7
23	Methylnaphthalene	Aromatic	464-473	9
24	<i>n</i> -1-Tetradecene	Olefin	482	5
25	<i>n</i> -Tetradecane	Paraffin	488	1
26	Diphenylmethane	Aromatic	504	9
27	Dimethylnaphthalene	Aromatic	507	9
28	<i>n</i> -1-Hexadecene	Olefin	536	5
29	<i>n</i> -Hexadecane	Paraffin	548	3
30	Amylnaphthalene	Aromatic	550-558	7
31	Amyldiphenyl	Aromatic	554-572	3

^a Toxicity rating: 1 = no toxicity; 9 = complete, rapid kill.

From a study of narrow distillate fractions of gasoline, stove oil, and Diesel oil, Crafts and Reiber (4) concluded that "acute" or rapid toxicity resulted from low-boiling fractions. High-boiling fractions caused "chronic" or delayed toxicity. The Stoddard solvents produce the acute type of injury and rapid kill of weeds but do not injure carrots. It has been frequently observed, however, that oils having an upper boiling range of about 500° F. or above cause chronic toxicity and are likely to injure carrots. It was found in the hydrocarbon study that the high-boiling olefins caused chronic injury beginning with *n*-1-tetradecene, which has a boiling point of 488° F. The paraffins and aromatics gave chronic injury at about 550° F. This suggests that olefins may be responsible for chronic toxicity produced by oils having a boiling range no higher than 500° F.

Selective Concentrations

The hydrocarbons were diluted with a nontoxic oil to provide a further measure of toxicity. It was thought that, if the toxic hydrocarbons could be diluted to a concentration at which carrots were not injured but at which the other test plants were killed, such selective concentrations might provide a more definite basis for comparing the toxicities than was previously possible. The diluent, Bayol D, is a highly refined paraffinic oil which boils between 400° and 500° F. The test plants sprayed with Bayol D exhibited a translucent appearance for 2 or 3 days; but neither acute nor chronic injury developed, and growth was not noticeably checked.

Clear-cut selectivity was not found in all cases. As used in this discussion "selective concentration" means the hydrocarbon concentration which resulted in no injury or only slight injury to carrot plants, but which killed or severely injured the other test plants.

The concentrations found to be selective in these tests are presented in Figure 1. The hydrocarbons are located on the abscissa according to their boiling points. A logarithmic scale is used for plotting the concentrations on the ordinate in order to show true concentration relationships. The points for hydrocarbons in a series have been connected for convenience in comparing the different series or the hydrocarbons within a series.

When the toxicity evaluations in Table I are compared with those in Figure 1, the two methods of evaluation agree very well. It would not be safe to assume that the selective concentrations in Figure 1 provide exact measurements of the phytotoxicities of the hydrocarbons. It is believed, however, that they do give a close approximation of their relative toxicities as they occur in petroleum naphthas.

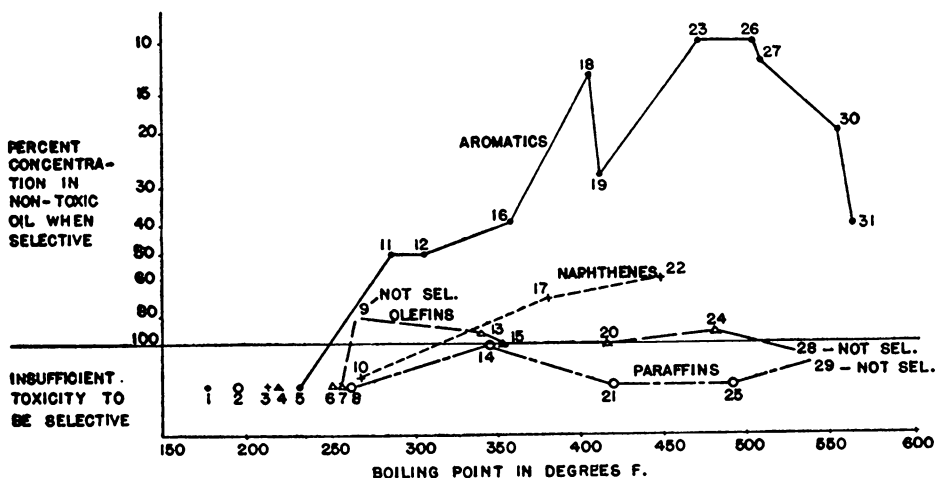


Figure 1. Concentration at Which 31 Hydrocarbons Were Nontoxic to Carrots But Toxic to Most Other Plants

Hydrocarbons listed in Table I

With all of the hydrocarbons except amyldiphenyl, phytotoxicity appeared to be a direct function of concentration of the hydrocarbon—i.e., the lower the concentration, the lower the toxicity. For amyldiphenyl, however, concentrations of 30 to 50% produced more rapid injury and a greater degree of injury than did higher concentrations. The reasons are not clear for the apparently anomalous action of amyldiphenyl and for the apparent decrease in acute toxicity of hydrocarbons with increasing boiling points above about 500° F. Chemical properties alone may be responsible, but it is more likely that some physical property such as viscosity, surface tension, or size of molecule may be involved. Viscosity is probably the factor determining acute or chronic type of injury.

As was pointed out by Bell and Norem (2) and Crafts and Reiber (4), toxicity increases with the addition of side chains on the benzene nucleus. This increase in toxicity, however, may be due to changes in physical properties—e.g., decreased volatility—rather than direct chemical effect. The data in Figure 1 suggests a tempering effect from side chains on the benzene ring. For example, isopropylbenzene, diethylbenzene, and triethylbenzene appear to be less toxic than aromatics which have similar boiling points but shorter or no side chains.

The most toxic hydrocarbons, tetrahydronaphthalene, methylnaphthalene, diphenylmethane, and dimethylnaphthalene, had selective concentrations below 15%. Petroleum naphthas which contain these hydrocarbons even in relatively small amounts would be very toxic to plants.

The studies of the pure hydrocarbons show further that the aromatics are not the

only hydrocarbons toxic to plants. Some of the cycloparaffins (naphthenes) gave considerable toxicity, and one of the straight-chain paraffins, *n*-decane, was toxic to all of the test plants except carrots.

The olefins were found to be much less toxic than the aromatics. It is thus apparent that in the sulfonation studies the aromatic hydrocarbons were largely responsible for the toxic properties of the sulfonatable portion of oils.

The usefulness of the information obtained in the hydrocarbon study may be illustrated by examining the data on the hydrocarbons which fall in the boiling range of the Stoddard solvents. Many of the Stoddard solvents used commercially for weeding carrots have a boiling range of 300° to 400° F. and contain 10 to 20% aromatics. It can be seen in Figure 1 that the paraffin falling in the 300° to 400° F. boiling range is selective for carrots. The two aromatic hydrocarbons in this boiling range have selective concentrations of 35 to 50%. It seems reasonable, therefore, that adding 10 to 20% of these aromatics to the base paraffin would appreciably increase the weed-killing properties but cause little injury to the carrots.

Other Methods of Evaluation

As an additional measure of toxicity, the hydrocarbons were diluted with the non-toxic oil to find the minimum concentration at which there was injury to Abutilon, a plant sensitive to oils. The ratings according to this evaluation agreed fairly well with the previous methods. These minimum concentration studies provided little additional information other than to be helpful in the valuation of some of the hydrocarbons that were not sufficiently toxic to be made selective. For example, of the hydrocarbons boiling below 280° F., the two paraffins iso-octane and *n*-octane were the least injurious.

Another type of test using young barley seedlings was developed by Green (?). This test is more quantitative for certain oil and hydrocarbon toxicity studies than those tests previously mentioned. Tests of hydrocarbons on barley seedlings were in general agreement with the evaluations obtained in the other tests.

From the commercial or practical point of view at the present time, the important factors characterizing oil sprays are boiling range and aromatic content. Boiling range, or viscosity, accounts for the speed and type of killing and such physical considerations as ease and safety of spraying and persistence. Aromatic content is the best single indication of the herbicidal properties of the oil. Although aromatic content is a good indication, it is not entirely satisfactory, since there is considerable variation in the quality of the various aromatic hydrocarbons. The only sure method of learning the herbicidal properties of an oil is actually to apply the oil to the plant.

Increased Toxicity in Storage

Crafts and Reiber (4) noted that certain of the petroleum products increased in toxicity when allowed to stand for some time. Their tests showed that kerosene stored 6 months in the light acquired high toxicity. Gasoline samples increased in toxicity on standing and lost their original selectivity for carrots. A heavy isoparaffinic fraction which was being used as a diluent also became more toxic. Stove oil apparently was unaffected by storage. The investigators believed that the stored kerosene and gasoline sample produced a new type of compound capable of chronic toxicity. It was believed that the new products were peroxides of aliphatic compounds. "Antioxidants" were believed to be responsible for the stability of the unrefined stove oil.

The highly refined paraffinic oil used as a diluent in the hydrocarbon investigations did not become toxic when stored in a metal container for 18 months. The hydrocarbons were stored in the light in both metal and glass containers. After the materials had been stored about a year, it was noticed that several had increased in toxicity. Fresh materials were obtained, and tests were made to compare the new materials with those that had been stored in glass containers. Hydrocarbons of the olefin series had increased in toxicity. No change was detectable in the aromatics or paraffins. These results suggest that olefins increase in toxicity during storage more readily than do other kinds of hydro-

carbons. Olefins seldom occur in crude oil. They are the result of cracking in the refining process and thus are present only in refined oil fractions.

Effect of Temperature on Toxicity

According to Lachman (9), little or no damage to carrots is likely to result from Stoddard solvent sprays when the temperature is below 80° F. At higher temperatures, however, the oil may cause some injury. Crafts (3) states that the toxicity of the oil both to the weeds and to the crop is increased by heat and that spraying while temperatures are above 90° F. may be dangerous.

Experiments were conducted at Cornell in an attempt to learn more about the effects of temperature on oil toxicity. Small carrot and parsnip plants were placed at four temperature levels: 40° to 50°, 50° to 60°, 60° to 70°, and 70° to 80° F. After 2 weeks at these temperatures, one sixth of the plants in each group were sprayed at the rate of 80 gallons per acre with a Stoddard solvent (Varsol No. 2) which contained an additional 4% diethylbenzene. One week after the first treatment a second lot of plants was sprayed in the same manner. Ten replications of carrots and five replications of parsnips were used. Harvests were made 2 weeks after the treatments.

Temperature had a marked influence on the growth of the plants. There was very little visible difference, however, in the effect of the spray on the plants at the various temperatures. As shown in Table II, the per cent reduction in fresh weight of carrots caused by the sprays was less at the 60° to 70° temperature than at any of the others. Similar results were obtained for parsnips.

Table II. Per Cent Reduction in Fresh Weight of Carrots Caused by Spray

(Varsol 2 plus 4% diethylbenzene applied as spray at different growing temperatures)

Temp., ° F.	First Spray	Second Spray	Average
40-50	26	10	18.0
50-60	3	22	12.5
60-70	2	1	1.5
70-80	11	13	12.0

The above studies dealt with temperature conditions during the growing period as well as at the time of spraying. Hence, it was not possible to distinguish between the effect of temperature on the structure and composition of the plant and the influence of temperature on the action of the oil. The following experiments were conducted to study the latter aspect of temperature effect.

Bean seedlings were grown at 60° to 70° F. until they reached a size at which the primary leaves had almost fully expanded and before the growth of the second internode had exceeded 0.5 inch in length. At that time they were placed at temperatures of 35°, 40°, 50°, 60°, 70°, 80°, and 85° F. Varsol No. 1 was carefully brushed on the upper surface of the primary leaves. After several hours, all the plants were moved back to the original temperature. Ten replications per treatment were used. Statistical analysis of the average fresh weights showed no difference between treatments.

Pea and barley seedlings were grown in the greenhouse at 60° to 70° F. The plants were placed in chambers at temperatures of 5° intervals from 40° to 85° F. After one day in the temperature chambers, the plants were sprayed at the rate of 100 gallons per acre with a 50-50 mixture of Varsol No. 1 and *n*-tetradecane. Injury ratings made 3 days after the treatment showed only a very slight tendency for toxicity to increase with a rise in temperature (correlation coefficient = 0.426, regression coefficient = 0.029).

The fact that temperature variations between 35° and 85° F. had little influence on the toxicity of hydrocarbons would seem strange, as certain properties of the hydrocarbons are influenced markedly by temperature.

Two of the physical properties which are affected by temperature are vapor pressure and viscosity. The vapor pressure of *n*-decane approximately doubles with each rise of 10° C. This increase would double the evaporation rate and should, theoretically at least, halve the contact time of the hydrocarbon on the plant. The effects of injurious oils are closely correlated with the length of time they remain in or on the plant. Thus, consider-

ing the effect of temperature on vapor pressure, it would be reasonable to expect a marked decrease in toxicity with a rise in temperature.

The viscosity of oil has an important influence on the speed of entrance into the plant. As the viscosity decreases, the rate of penetration increases, as does the speed at which visible injury symptoms develop. Vapor pressure and viscosity curves for *n*-decane are given in Figure 2. If the two are of equal importance in hydrocarbon penetration, they would approximately cancel each other. Such a cancellation may explain the lack of a marked change in hydrocarbon toxicity with variations in temperature.

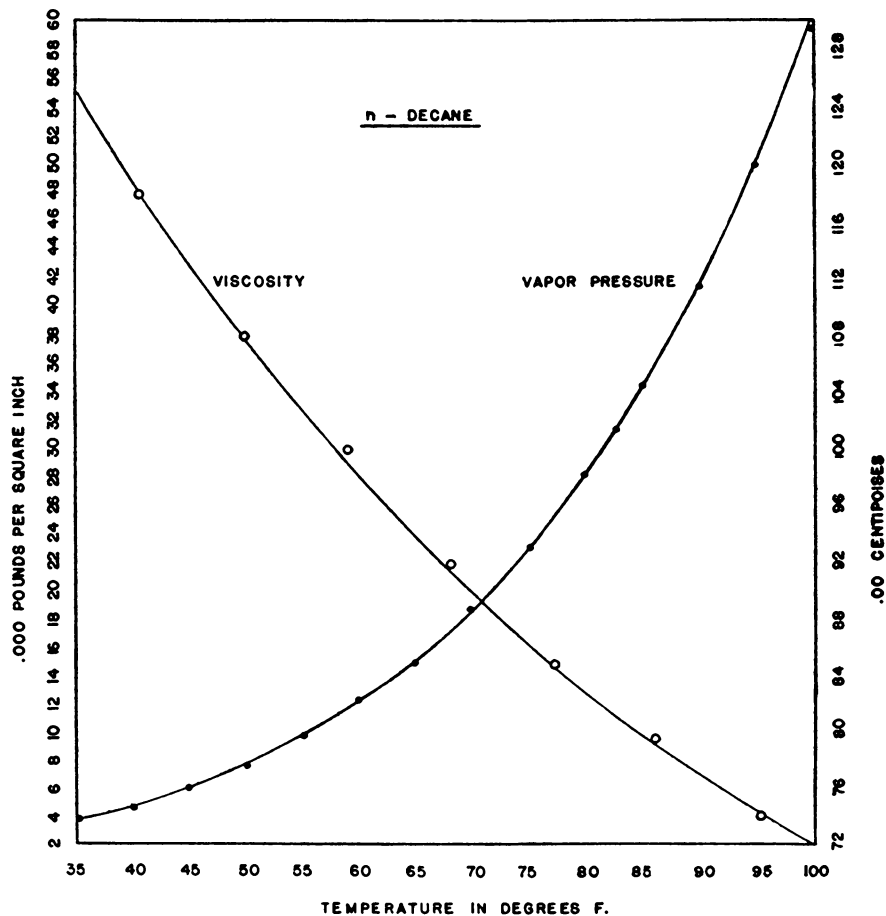


Figure 2. Effect of Temperature on Vapor Pressure and Viscosity of *n*-Decane

Formula and constants for calculation and a portion of the data from American Petroleum Institute (7)

Detailed studies of the influence of various environmental factors on oil toxicity are being continued.

Effect of Concentration on Selectivity

The test in which selective concentrations were used as a measure of toxicity indicated that most of the toxic hydrocarbons could be made selective by diluting them in a non-toxic oil. It was found in further tests with the aromatics diethylbenzene, tetrahydronaphthalene, and dimethylnaphthalene that the greenhouse results could be duplicated on field-grown carrots and weeds.

Studies were made of the relative importance of aromatic concentration and total volume of spray. Field plots were used for these tests, so that volume per acre rates could be accurately controlled. The selective concentration of dimethylnaphthalene was previously determined to be 12% in nontoxic oil when the total spray volume was 100 gallons per acre. In this test the 12% concentration of the aromatic was applied in volumes of 50, 100, and 200 gallons per acre. Additional treatments were applied in which the rate of the aromatic was kept at 12 gallons per acre, but the volume of spray was varied at 24, 50, and 200 gallons per acre. Both the 100- and 200-gallon-per-acre sprays which contained 12% dimethylnaphthalene gave excellent selective kill of weeds comparable to Stoddard solvent. The 12% 50-gallon spray caused slightly poorer weed kill, probably due to insufficient coverage. Sprays which contained less than 12% of the aromatic failed to kill weeds, and sprays which contained more than 12% of the aromatic killed the carrots, irrespective of volume per acre. Thus, the important factor in obtaining selectivity was the concentration of the aromatic in the spray. The amount of the aromatic or the total quantity of spray applied was relatively unimportant.

Emulsions

Stoddard solvent gives excellent selective kill of weeds in carrots when applied in pure form, but loses its selectivity when emulsified in water. The highly toxic aromatic hydrocarbons diethylbenzene, tetrahydronaphthalene, and methylnaphthalene gave excellent selective kill of weeds in carrots when mixed with nontoxic oil at the proper concentration. The same relative amounts of the aromatics applied emulsified in water, or pure, however, killed the carrots as well as the weeds. Attempts to obtain selective kill by reducing the quantity of the aromatic were unsuccessful.

There was some indication that the presence of nontoxic oil in the emulsion caused a tendency toward selectivity. For example, a 10% emulsion of either methylnaphthalene or dimethylnaphthalene killed the greenhouse test plants with no selectivity. The addition of 20% nontoxic oil, however, greatly reduced the carrot injury without an apparent reduction in toxicity to the other species. Tests were conducted with water emulsions of highly phytotoxic naphthas which contained 75 to 85% aromatics and had boiling ranges of 300° to 550° F. Excellent selectivity was obtained in some tests, but in other tests the emulsion gave severe injury to carrots. The results with emulsions of high aromatic naphthas were inconclusive.

It is difficult to explain why toxic hydrocarbons can be made selective to carrots by the addition of a nontoxic oil but not by the addition of water. Green (?) found some correlation between the toxicity of oils and their ability to emulsify. It is commonly found that high aromatic oils are easier to emulsify than are oils with low aromatic content. It is possible that some action between the aromatic hydrocarbons and the emulsifying agent results in increased toxicity. There is some evidence that the permeability of the protoplasmic membrane is the key to carrot resistance. If this is true, the presence of the emulsifier or the physical properties of the emulsion might increase the cell penetration of the hydrocarbons. Work is being continued along these lines and on the fundamental reasons for differential plant resistance to oils.

Acknowledgment

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Control of Weeds in Forest Nurseries with Mineral Spirits

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Petroleum naphthas, sometimes known as mineral spirits, are being successfully used in coniferous nurseries as selective herbicides at dosages of 14 to 75 gallons per acre, applied as a fine foliage spray at pressures of 50 to 100 pounds per square inch. The apparent safe and reasonably effective dosages are listed for over thirty species of conifers. They vary by age of trees, species, and geographic locality. Precautions in applying the mineral spirits are given. Equipment used in application is described. Estimated savings by control of weeds may range from 40 to 90%, compared with hand weeding of first-year seedbeds.

Hand weeding in forest nurseries is an expensive operation, and nurserymen are constantly on the lookout for cheaper methods of controlling weeds.

For several decades in our northern coniferous nurseries, sulfuric acid has been used as a fungicide to control damping off, and has proved to be of some benefit in keeping weeds under control during the germination period. In moderately acid, rather poorly buffered nursery soils, the sulfuric acid is usually applied at the rate of $\frac{1}{16}$ to 0.125 fluid ounce per square foot of seedbed, in a 2% solution immediately after seeding. It may reduce the weed stand as much as 60 to 80% in the 3-week period following treatment. The repeated use of sulfuric acid over a period of years has a tendency to create excessive acidity of the soil, adversely affecting growth of the trees.

Petroleum products such as stove oil were used as selective herbicides in fields of guayule—a rubber-bearing shrub—grown experimentally in California and the Southwest during World War II. Mineral spirits are used rather extensively for weed control in cranberry bogs in the lake states and in the Northwest.

Nursery Weed Control

Following the lead provided in 1942 and thereafter by truck gardeners in carrot (3) and parsnip (6) fields, investigations were started in nursery weed control, involving use of some of the more highly refined petroleum products known as mineral spirits or petroleum spirits. Their common industrial uses are as cleaning naphthas, paint thinners, and solvents. Among trade names of products successfully used in weed control in forest nurseries are Stoddard solvent, Sovasol No. 5, Varsol, Stanisol, Shell solvent, and Sohio weed killer.

The materials used by most nurserymen generally have an initial boiling point of around 300° to 320° F., a gravity (API) of 48 to 50, and aromatic hydrocarbon content in the range of 10 to 17%. They are applied full strength as a fine foliage spray at 14 to 75 gallons per acre and at a pressure of 50 to 100 pounds per square inch.

These materials seem best adapted for deweeding coniferous tree species, such as pines and junipers, which have considerable resistance to the oil sprays. Broadleaf species such as elm and walnut are seriously damaged or killed by moderate dosages of the oil sprays, and much research is needed to find if any of this group of plants are sufficiently resistant to warrant use of the mineral spirits as a selective herbicide.

The effect of the mineral spirits on weeds is very rapid. The leaves of small or oil-sensitive weeds droop within a few hours. After 24 hours they are completely dead and have turned grayish. In warm weather or with bright sunshine, the reaction is faster than on cool or cloudy days. Larger weeds may hang on for several days before they die. The oil-resistant weeds are only slightly affected and recover rather quickly.

Fairly strong applications may adversely affect conifers in several ways. The full effects may not be apparent until 7 to 10 or more days after treatment. Some first-year pines may, within a week or two, temporarily turn to a lighter shade of green or yellow-green, or the injury may show up as "oil-burn" spots at the ground line or on the stem, or as browning of the needles. Needles of second-year pines may develop reddish spots just above the base of the leaf sheath, while spruce may show bud injury or browning of the current growth of needles. Excessive dosages may cause mortality, especially if trees are less than 6 to 8 weeks old. Hence considerable care must be taken to select the proper level of treatment, to control the weeds but cause no appreciable injury to the trees.

Minshall and Helson (?) of the Dominion Department of Agriculture at Ottawa, Canada, have studied the physiological action of petroleum naphtha on carrots, parsnips, and several weeds including mustard. They used infrared absorption apparatus, and by means of readings taken at 10-second intervals following oil application, determined that photosynthesis ceased abruptly for all plants studied. With parsnips, photosynthesis was resumed within 30 minutes after application; it was one third of normal at the end of 3 hours, and at the end of 48 hours reached approximately the original rate before treatment. Parsnips did not wilt following treatment. The common mustard plant had a

Table 1. Apparent Safe Dosages of Mineral Spirits in Northern and Northeastern United States

Tree Species	Age			Nurserymen or Others Reporting Results
	4 to 6 weeks	6 weeks to 1 year	Over 1 year	
	Apparent Safe Dosage by Tree, Gallons per Acre			
Cedar				J. W. Augenstein, Montana
Eastern red	30	40	60	E. F. Biebesheimer, Wisconsin
Northern white	0	30?	40?	W. H. Brenner, Wisconsin
Rocky Mountain (juniper)	30	40	60	A. P. Chapman, Minnesota
Western red	25?	40	60	E. D. Clifford, Michigan
Fir				E. J. Eliason, New York
Balsam	30	40	50	A. E. Ferber, North Dakota
Douglas	0	40	50	J. M. Molberg, North Dakota
				D. A. Oliver, West Virginia
Larch				P. W. Robbins, Michigan
All species	0	0	0	J. H. Stoekeler, Wisconsin
Pine				H. B. Wycoff, Illinois
Austrian	40	50	60	
Eastern white	40	60	75	
Jack	50	60	75	
Mugho	40	50	60	
Ponderosa	40	60	75	
Red or Norway	50	60	75	
Scotch	40	50	60	
Western white	35	40	60	
Spruce				
Black	30	50	60	
Colorado blue	25	30	40	
Engelmann	30?	40	60	
Norway	25	40	60	
White	30	50	60	

First spraying of first-year beds should be done just as a few tree seedlings begin to emerge, or earlier if weeds have germinated. Thereafter, no spraying should be done from the time germination is complete, until 4 weeks thereafter.

Irrigation of beds with sprinkling system for 0.5 hour immediately before application of mineral spirits will minimize oil injury.

A fairly safe maximum for trees over 1 year old is about 80 gallons for pines and 60 gallons for spruces and firs in any single treatment.

The products reported used were Stoddard solvent, Sovasol No. 5, and Stanisol.

Table II. Apparent Safe Dosages of Mineral Spirits in Central Part of United States
(Including Indiana, Kansas, and Nebraska)

Tree Species	Age			Nurserymen or Others Reporting Results
	3 to 6 weeks	6 weeks to 1 year	Over 1 year	
Cedar				
Eastern red	25	30	40?	F. P. Eshbaugh, Kansas Geo. Hood, Nebraska C. C. Mony, Indiana
Rocky Mountain (juniper)	25	30	40?	
Pine				
Austrian	25	30	40	
Eastern white	25	30	40	
Pitch	25	30	?	
Ponderosa	25	30	40	
Red or Norway	25	30	40?	
Shortleaf	25	30	?	
Virginia	25	30	?	

A fairly safe maximum for trees 6 weeks to 1 year old is about 40 gallons, and over 1 year about 50 gallons per acre in any single treatment. No oil spraying should be done from time of germination until the great majority of the seedlings are about 3 weeks of age. Tree seedlings are especially susceptible to oil injury during the first 2 to 3 weeks following emergence.

The product reported used was Stanisol.

partial recovery of photosynthesis within 0.5 hour after treatment and continued in that stage for about 1 hour. Thereafter the leaves wilted and photosynthesis ceased completely.

The respiration rate of parsnip continued for at least 3 hours with little change after application, increased slightly thereafter for 5 days, and then returned to normal; in the oil-sensitive mustard, it continued for only 1 hour at the original rate, and thereafter tapered off gradually to zero some 2 hours after oil treatment, by which time the leaves were dead.

Crafts (2) in studies of the reaction of herbicidal oils on plants has suggested that the protoplasm of some plants is susceptible to oils and thereby destroyed, while others are resistant.

Gilgut (5) in 1945 noted that Stoddard solvent gave good control of weeds in beds of coniferous species, but that there was considerable variation in the oil resistance of the evergreens; the yews were sensitive to oil injury, while junipers were resistant.

Stanisol was successfully used by Robbins, Grigsby, and Churchill (8) at 87 gallons per acre to deweed one-year-old white pine seedlings, and also ponderosa pine seedlings which had just emerged from the soil and before they had shed their seed coats.

Cost of weed control in nurseries growing southern pines is reported by Cossitt (1) to have been reduced by 90% or more with mineral spirits. The species produced in this area include longleaf, loblolly, slash, and shortleaf pines.

In the New York state nurseries, Eliason (4) had used large scale spraying in 1947 to bring through 11,000 one-year seedbeds practically weed-free. The use of mineral spirits sprays is now a standard weeding practice in the Saratoga State Nursery.

In 1947, a weed kill of 91.2 and 90.8% was obtained in preliminary trials (11) with Stoddard solvent and Sovasol No. 5, applied at 70 to 80 gallons per acre in Hugo Sauer Nursery in northern Wisconsin. In this same series of tests, ordinary stove oil of higher boiling point than cleaning naphthas gave comparatively poor control of weeds.

Additional trials (9) in 1948 brought out the fact that first-year white spruce sprayed with 75 gallons per acre of mineral spirits on May 21, just as the trees were emerging from the soil, suffered considerable mortality, while similar sprayings made on June 24 when the trees were slightly larger caused little or no damage.

For sensitive tree species, it was found (10) that irrigation of the seedbeds with an overhead sprinkling system, just before spraying with mineral spirits, reduced injury to a minimum. The weed kill in watered plots was as good as on unwatered plots. Application of the oil sprays in the evening or on cool days also tended to lessen injury to conifers. Seed beds protected by half shade showed much less injury from oil sprays than those in full sunlight.

Mineral spirits can be used as a preseedling spray in late spring to kill weed seeds in the surface 0.25 to 0.5 inch, especially those with soft permeable seed coats, or those

which have partly germinated but have not yet emerged from the soil (12). Such pre-seeding treatments are effective only if the soil is fairly warm, which promotes permeability and sprouting of weed seeds, and if rather heavy treatments are applied, ranging from 75 to 100 or more gallons per acre. If mineral spirits are used as pre-seeding treatments, the beds must be completely leveled and readied for seeding, so that there is little or no soil disturbance after treatment. Otherwise weed seed below the depth of penetration of the solvent is brought to the surface, largely defeating the purpose of the spraying. If used as a pre-emergent spray and within 2 or 3 days after seeding of the conifer beds, dosages of 50 to 60 gallons per acre would probably be effective.

In an attempt to obtain a fairly good nation-wide picture of the present practices in regard to weed control in forest nurseries and methods of application of the herbicides, the author wrote to some 20 nurserymen and investigators, representing major geographic regions of the United States. The results of the survey are reported below.

Apparent Safe and Reasonably Effective Dosages of Mineral Spirits

One point of particular interest is the need for a somewhat closer knowledge of how many gallons per acre of mineral spirits to apply for different tree species, depending on age class, and varied to suit the geographic area. These data are summarized in Tables I, II, III and IV for the Northern and Northeastern Area, Central Region, Southern Region, and Pacific Northwest. In compilation of the tables it was sometimes necessary to arrive at a compromise because of a fairly wide range in experience as to safe and yet fairly effective treatments based on observations in a number of nurseries. Where there was rather scanty information, or considerable diversity of opinion on the sensitivity of a tree species of a given age to oil injury, a question mark has been used in the tables.

Table III. Apparent Safe Dosages of Mineral Spirits in Southern Part of United States, (Including Mississippi, Alabama, Tennessee, Texas, Oklahoma, Georgia, and Louisiana)

Tree Species	Age				Nurserymen or Others Reporting Results
	2 to 6 weeks	6 weeks to 3 months	3 to 5 months	Over 5 months	
	Apparent Safe Dosage by Tree, Gallons per Acre				
Cedar					
Atlantic white	20?	30	30	30	F. M. Cossitt, Georgia Albert Engstrom, Oklahoma G. F. Erambert, Mississippi C. F. Gouffon, Tennessee C. E. Kingsley, Louisiana G. T. Ratliffe, Louisiana
California incense	30	30	30	30	
Eastern red	20?	30	30	40	
Pine					
Aleppo	30	30	30	30	
Austrian	20?	30	30	40	
Loblolly	14	18	22	30	
Longleaf	14	18	22	30	
Ponderosa	20?	30	30	40	
Shortleaf	14	18	22	30	
Slash	14	18	22	30	

A fairly safe maximum for trees 3 to 5 months old is about 30 gallons per acre, and for those over 5 months old about 40 to 45 gallons per acre in any one treatment. No oil spraying should be done from time of germination until the great majority of the seedlings are 2 weeks or more of age. Tree seedlings are especially susceptible to oil injury during the first 10 days following emergence.

The products reported used were Varsol, Shell solvent, Anderson-Pritchard mineral spirits No. 10, and Stoddard solvent.

Somewhat heavier treatments have been used in the northern and northeastern zone of the United States than in the other three regions; one of the nurserymen, E. J. Eliason, had good success in 1949 at Saratoga State Nursery by treatments involving only 20 to 40 gallons per acre.

The tables indicate that younger trees are usually considered to be more sensitive to oil injury than the older age classes. In fact, the reports on the risk of damage on very young trees were so adverse that it was deemed wise to avoid any suggestion of large scale spraying of trees less than 2 to 4 weeks old (depending on growth rate and locality). More research, involving controlled experimental procedure, is required on this age class. There are some indications that very light applications of less than 20 gallons per acre may be safe in trees less than 2 to 4 weeks of age.

There is some opinion that mineral spirits with 15 to 17% or more of aromatic hydro-

carbons have greater weed-killing power per gallon than those in the range of 10 to 12%. This may explain why some nurserymen have obtained rather satisfactory weed control with as low as 20 to 40 gallons per acre while others have found that weed kill was not very good unless 50 to 60 gallons were applied per acre.

All observers agree that the mineral spirits are much more effective if applied when the weeds are only about 0.25 to 0.5 inch or less in height or in spread. When they have reached 3 to 6 inches in height, weeds tolerate two to three times as much spray material as when very small; furthermore, some of the larger weeds—for example, clover—tend to stool out from the ground line even though the foliage has been killed. Very small clover plants are killed outright by the oil spray.

Table IV. Apparent Safe Dosages of Mineral Spirits in Pacific Northwest

Tree Species	Age			Nurserymen or Others Reporting Results
	4 to 6 weeks	6 weeks to 1 year	Over 1 year	
Cedar Port Orford	30	40	40	F. W. Deffenbacher, Washington
Fir				
Douglas	30	40	40	
Noble	30	40	40?	
Silver	30	40	25?	
Hemlock Western	0	0	0	
Pine Ponderosa	30	40	25?	
Spruce Sitka	30	40	40	

First spraying of first-year beds should be done just as a few tree seedlings begin to emerge, or earlier if weeds have germinated. Thereafter, no spraying should be done from the time germination is complete, until 4 or 5 weeks thereafter.

Irrigation of beds with sprinkling system for about 1 hour immediately before and after application of mineral spirits will minimise oil injury.

The product reported used was Stoddard solvent.

The trend in forest nurseries now is to spray as often as four to six times during one growing season, using relatively light dosages per treatment and spraying at intervals as short as 2 to 3 weeks.

It has been rather generally observed in the lake states that oil injury to trees 1 year of age or older is more likely to occur when the new growth is very succulent as in late May or in June than later in the season when the needles have hardened up somewhat. Needles that are 1 year of age or older are more oil-resistant than succulent ones of the current season's growth.

Superintendent W. H. Brener of Griffith State Nursery, Wisconsin Rapids, Wis., noted that spring-sown red pine was much more susceptible than fall-sown beds, both sprayed on June 3, 1949, with 75 gallons per acre. Germination in the two lots occurred, respectively, around May 21 and May 1 to 7. His observations indicate that a 2- or 3-week difference in age was a considerable factor in relative oil-resistance.

Savings by Use of Mineral Spirits

Estimates in savings in weeding costs by use of mineral spirits instead of hand weeding usually range from 40 to 90% for first-year seedbeds. Savings are greatest in large nurseries, where the oil spraying can be highly mechanized so as to spray as many as three 4-foot-wide seedbeds simultaneously with a spray outfit moving from 2 to 5 miles per hour. Even in small nurseries, savings can be as much as 40 to 50% on first-year beds, using back-pack spray equipment, or the type mounted on a wheel barrow or light cart.

Spraying of first-year beds is likely to show the largest saving because of the difficulty of any mechanical cultivation of the very tiny seedlings which are so easily buried or damaged. Some nurseries broadcast seed their beds, making it necessary to rely entirely on hand weeding of seedling stock. The larger nurseries, however, have generally adopted a row spacing of 4.5 to 6.0 inches between seedling drills and 6.0 to 10.0 inches between

transplant rows. Hence, trees that are about 1 year old, or 1.5 to 2.0 inches high, can be rather successfully cultivated mechanically with power equipment at a cost low enough to put it into competition with oil sprays.

The mineral spirits in the lake states cost about 25 cents per gallon, or \$10 per acre with a 40-gallon treatment. The cost of application with power equipment ranges usually from \$2 to \$5 per acre, making a total cost of \$12 to \$15 per acre for one treatment. Some hand weeding is still necessary as a "mop-up" operation of oil-resistant weeds, but if spraying is properly timed, the additional labor cost is only about \$6 to \$8 per acre, bringing total cost per acre to a range of \$18 to \$23.

Among the oil-resistant weeds in northern nurseries are quack grass, mare's tail, ragweed, Canada thistle, clover plants over 3 inches in height, and red-top sorrel. In the southern portions of the United States oil-resistant weeds include sedge, crowfoot grass, rabbit tobacco, evening primrose, bitter weed, bitter sneeze weed, poor Joe, blue toad-flax, doll's daisy, Drummond pine weed, and hairy vetch.

Weeding done exclusively by hand often involves from 80 to 120 man-hours per acre. Current labor costs in our northern nurseries are at least 85 cents per hour. At 100 man-hours per acre, costs of hand weeding would be \$85 per acre, which is indeed a sharp contrast with the cost of weed elimination with mineral spirits, which can be done at only 21 to 27% or less of the cost of hand weeding.

Equipment Used

For large scale operations, some nurserymen mount a spray ring on a trailer, pulled by a light rubber-tired farm tractor. Others mount the entire outfit, including a 55-gallon drum, directly on the tractor with the spray boom set just forward of, and in full view of, the driver.

An outfit built by E. F. Biebesheimer, nursery superintendent at Hugo Sauer Nursery, Rhineland, Wis., consisted of a Meyers orchard sprayer mounted on a trailer with a tank of 100-gallon capacity. It has 12 Meyers fan-type nozzles spaced 18 inches apart, mounted on a three-section boom placed 20 inches above the ground. Each boom has a separate shut-off valve. The center boom is rigid, but the booms on either side are hinged so as to allow them to be swung to the rear in case only a single seedbed is to be treated. Oil-resistant hoses are used in all valves, gaskets, and tank-to-nozzle connections because ordinary rubber hoses deteriorate very rapidly when in contact with mineral spirits. Normally three beds, each 4 feet wide, are sprayed simultaneously.

A rather similar outfit with three 6-foot sections of boom is used in southern nurseries, with a low-pressure manifold, and using flat-spray pattern, 80° Teejet nozzles No. 8001 or 80015 manufactured by Spraying Systems Co., Bellwood, Ill. These are spaced 20 inches apart on the boom at a spraying height of 17 to 19 inches. Pressures used are usually 50 to 60 pounds.

Some spray-equipment manufacturers have prepared useful detailed tables showing rate of delivery in gallons per acre per nozzle at several nozzle spacings, at specific pressures, and at different tractor speeds in miles per hour.

In nurseries where the soil and moisture conditions are such that heavy equipment would be impractical, a very light hand-drawn outfit can be constructed similar to one made by Nursery Superintendent C. C. Momy of Vallonia, Ind.

The spray unit is a wheelbarrow-type garden sprayer with a 10- to 20-gallon supply with hand pump and a 3- to 5-gallon pressure tank with gage. The unit is placed on a light 2-inch angle iron frame mounted on four 20-inch bicycle forks and wheels, with the two front forks movable for steering by a single hand drawbar. In operation the rig straddles the seedbed. The spray boom is made of 0.25-inch galvanized pipe, about 5.5 feet long, to extend across a 4-foot-wide seedbed and into the paths on each side. There are six nozzle-equipped drops, four to spray the seedbed and one for each path. The drops over the paths have separate shut-off valves. The boom is constructed so that the nozzle height is adjustable for complete coverage without overlap, to heights of 10 to 16 inches, depending on pressure and wind conditions. The drops are fitted with

Monarch 80°, 0.032-inch weed nozzles with fan-shaped spray. At a speed of slightly under 2 miles per hour, the delivery is 50 gallons per acre.

With the above outfit, a three-man crew is able to spray a seedbed 450 feet long and 4 feet wide in 3 minutes. Its lightness and cheapness of construction should make it equally adaptable to rather small nurseries.

Other types of nozzles that have been used successfully are Mohawk Safeway No. 5, fan-type, and Monarch No. H-564, Size 28.

Spraying is most successful when done on days when there is little or no wind. In windy weather the spray drifts, and coverage is not uniform.

Adequate precautions must be taken to avoid danger of fire by smoking or other causes near spray rigs or at storage dumps. Carelessness in allowing the mineral spirits to drip onto the trees from leaky fittings or when spray rigs are standing still may result in tree damage or mortality.

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Nematocidal Action of Halogenated Hydrocarbons

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Soil fumigation is today a large industry, thanks to research in insecticidal activity, anthelmintics, and nematocidal physiology. Many halogenated hydrocarbons—chloropicrin, DD, ethylene dichloride, methyl bromide, ethylene dibromide, allyl bromide, ethylene chlorobromide, dichlorobutene, chlorobromopropane—have proved highly effective against nematodes. Research continues, with hundreds of people testing compounds. Highly toxic groups will be found, which may be used to step up old nematocides or bring new ones to the fore. Soil nematocides are contact killers and as such will be supplanted by chemotherapy, and after the day of chemotherapy physics may take over, with the use of ultrasonics and radioactive fertilizers. But soil fumigation is here to stay.

Although carbon disulfide is not a halogenated hydrocarbon, it would be remiss not to mention its early use as an insecticide and its introduction as a nematocide by Kühn (34) in 1881. This material was used against the root-knot nematodes by Bessey (3) in 1911. No practical development followed for many years. Mathews (40) in 1919 discovered nematocidal properties in chloropicrin and thereafter the chemical was developed by Johnson and Godfrey (32) in 1932 as a soil fumigant in Hawaii. Widespread commercial development of chloropicrin in this country followed and the search for more effective nematocides was begun. Screening activities were carried on by many organizations. Methods of field application were worked out by Neller and Allison (42) in 1935. Dose rate and spacing were worked out by Taylor (49) in 1939, range determinations by Chitwood (11) in 1939, soil profile diffusion by Thorne (50) in 1939, and temperature and moisture relations by McClellan, Christie, and Horn (39) in 1949. Carter (6) in 1943 was the fortunate individual who discovered the highly effective nematocide DD (dichloropropene-dichloropropane mixture). In the meantime ethylene dichloride, methyl bromide, and mixtures of halogenated and nitrohydrocarbons were being used by many workers. Since 1943 the search for other nematocides has proceeded with increased intensity. As a result, ethylene dibromide (14), allyl bromide (15), ethylene chlorobromide (15), dichlorobutene (37), and chlorobromopropane (33) have been introduced.

This development of soil fumigants has not been due to chance. The search has been guided by three major sources of information: insecticidal activity, anthelmintics, and nematocidal physiology. Basic research in each of these fields has contributed to our understanding. Insecticidal developments are widely known. Correlation of action of chemicals as insecticides and nematocides is poor. Many excellent insecticides are of little or no value as nematocides. Reasons for easier kill of insects are to be found in the breathing, motility, feeding, and ease of contacting these organisms.

Anthelmintic Contributions

An understanding of how to kill nematodes has come slowly. Some anthelmintics were developed in prehistoric days. Ancient anthelmintics were vegetable oils. No one asked why they worked; our ancestors merely accepted the fact that they were effective. In the latter part of the nineteenth and early part of the twentieth century oil of chenopodium, thymol, and chloroform came into use. Critical testing was begun by Hall in 1915 and through his searches the activity of carbon tetrachloride was brought to light in 1921; and Hall and Schillinger (29) in 1925 turned up tetrachloroethylene. Mueller (41) felt that these substances removed fat from the muscle cells of *Ascaris lumbricoides*. Wright and Schaffer (55, 56) and Wright *et al.* (57) reported on the action of halogenated hydrocarbons as anthelmintics, concluding that the efficacy depended on water solubility, position of the halogen, and length of the carbon chain. Similar work was done by Lamson (35, 36) in 1934 and 1935 on resorcinols, alkyl phenols, alkyl cresols, and more recently by Enzie (21, 22) on thymols and toluenes.

While none of these workers attempted to determine the mode of action, they did systematic screening from which an analyst can form certain concepts. In general, such substances must be of moderate aqueous solubility, 1:1250 to 1:5300. If more soluble than this, they are apt to be toxic to the host; if less soluble, they are apt to be present in too low a concentration to injure the nematode. Anthelmintics act at 37.5° C., hence the true solubility and concentration in the host's intestine are probably greater than indicated. Within the groups of compounds investigated, the author's observations show that the most effective anthelmintics—for example, tetrachloroethylene—are better cholesterol and wax solvents than the less effective ones. Trim (52) concluded in 1949 that *Ascaris lumbricoides* reacted to anthelmintics as though it were protected by a lipide membrane, though no such membrane was demonstrated.

Study of the results of all these workers, in the light of what is known about the permeability of nemic membranes, justifies certain observations. The introduction of a halogen into the molecule is not essential for action as an anthelmintic, but it does reduce the aqueous solubility and increase the boiling point and wax solvency or penetration. Bromine is more effective than chlorine in this respect. Dihalogens are more effective than monohalogens. Increase in length of the carbon chain also increases boiling point, reduces aqueous solubility, and increases lipide solvency. A double bond between the carbon atoms decreases boiling point and decreases aqueous solubility. Position of the halogen in the carbon chain also influences the aqueous solubility, boiling point, and lipide solvency. Within any given series of hydrocarbons, one finds a peak of anthelmintic action. This may or may not be the compound with the least damage to the host. Incidentally, toxicity to anthelmintics of the halogenated hydrocarbon group is manifested in the host primarily by fatty degeneration or fatty infiltration of the liver.

Nemic Physiology

On the basis of the work of Flury (28) in 1912, Fauré-Fremiet (23-25) in 1913, 1925, and 1936, Zawadowsky (58, 59) in 1914 and 1928, Schulz and Becker (44) in 1933, Schmidt (43) in 1936, Wottge (54) in 1937, Chitwood (8-12) in 1938, 1939, and 1940, Jacobs and Jones (31) in 1938, Fauré-Fremiet and Filhol (26) in 1937, von Brand and Winkeljohn (4) in 1945, Ellenby (19) in 1946, Trim (52) in 1949, and Brown (5), Timm (51), and Chitwood (13) in 1950, we can form certain generalizations relative to nemic membranes and lipides.

Cuticle. The cuticle of adult nematodes is relatively impermeable and is composed primarily of a complex of several proteins. These proteins include collagens, fibroids, elastoids, and keratoids, possibly hardened by tanning with polyphenols or quinones. Sometimes lipide materials are also present (8, 10, 52). When such lipide materials are present on the adult cuticle, they probably take the form of hydroxy fatty acids or esters of fatty acids with monohydroxy alcohols. Such materials may form ring compounds. Regardless of the exact chemical nature, the lipides are unquestionably one of the chief barriers to permeability. These materials are commonly difficult to demon-

strate as a structural entity, but were observed in *Ditylenchus* of narcissus by the writer (8, 10). Furthermore, nematode larvae immediately after hatching are much more permeable to all chemicals and much more readily killed than they are a few hours later. Von Brand has demonstrated fatty acids as the chief products of glycogen metabolism in nematodes. In the light of this information, it seems possible that the observation (7) of the excretion of acidic, viscid materials from the excretory pore and the spread of these materials as they slide down the body surface may have some bearing on the mechanism whereby larvae attain greater impermeability. Quinone tanning is also a possibility (5, 19).

Eggs. The eggs of nematodes are usually more resistant to adverse environmental conditions than are the adults (8, 10). The refractive shell is a chitinoïd and is permeable to water, gases, and chemicals (58). However, the egg shell is commonly covered by a mucoid which is hygroscopic. This material tends to prevent drying and reduce the penetration of many chemicals such as fat solvents. In the presence of oxygen this material commonly turns orange (possibly quinone tanning) on the surface and is thereafter less permeable to water. This tends to reduce evaporation. Certain stages of many nematodes are known to be capable of withstanding extremely dry conditions and remaining dormant in such a dried state for many years. However, we know nematode proteins are hygroscopic and the nematodes cannot withstand a complete absence of moisture. Mucoid materials, therefore, are thought to act in two ways, as a barrier to fat solvents, and as a means of preventing total dryness. Completely dry nematodes do not revive. A common example of such a mucoid is the so-called gelatinous mass surrounding the eggs of root-knot nematodes.

Inside the egg shell there is a well developed vitelline membrane, which is the chief protection of the nematode from chemicals in its environment (8, 10, 58, 59). Under some circumstances it gives some of the reactions of a sterol. For this reason (8, 10) cholesterol solvency was previously used as a means of selecting nematocides. The correlation of nematocidal action and cholesterol solvency was remarkable. Effective nematocides were found to dissolve cholesterol at the rates of 1 part of cholesterol to 10 to 35 parts of fumigant. Other characteristics of the best fumigants tested at that time were solubility in water at 20° C., 1:6 to 1:1150; boiling points, 75° to 128° C. Similar principles apply to fumigation of eggs of nematode parasites of vertebrates (38). It is known that the vitelline membrane is not cholesterol; it melts at 70° to 72° C., and will not give many of the reactions of cholesterol. Numerous formulas and characterizations of the "unsaponifiable fraction" of ascarids have been given.

These include a dipalmitate (28), ascarylic acid (Leroux, 26), and ascaryl alcohol according to Fauré-Fremiet, Schulz and Becker (44), and von Brand and Winkeljohn (4). A coprosterin and a cholesterol ester have also been suggested. In life the vitelline membrane is colorless and nonbirefringent unless under strain. In the latter case it appears birefringent. In widely diverse nematodes the vitelline membrane appears to melt at 70° to 73° C., indicating that it is probably a pure or nearly pure compound.

Timm (51) in 1950 extracted this material from eggs of *Ascaris lumbricoides* v. suis, obtaining a waxy material which melted at 69° to 72° C. Positive tests for a wax and for a monohydroxy alcohol were obtained. This material was fused with refined beeswax (melting point 66° C.) and the resultant mixture was found to have a melting point of 68° to 70° C.

Chitwood (13) observed crystallization of the vitelline membrane in the eggs of *Meloidogyne javanica*. These crystals were very similar in form and optical behavior to those produced by refined beeswax. Crystals of both origins became optically extinct and amorphous on standing. Ballantyne (2) in 1952 has found the vitelline membrane of *Heterodera schachtii* and *H. rostochiensis* also to be a waxy material. It appears that the vitelline membrane is similar to, if not identical with, the major ingredient of beeswax myricyl palmitate.

In Vitro Testing. Although it may seem out of keeping to take up in vitro testing of nematodes in miscellaneous reagents in this place, it is really germane to the issue. At one time the author ran tests on numerous types of organic compounds using the *Ditylenchus* of narcissus as test organism. Such tests were run on

a dilution basis, at two temperatures, 25° and 40° C., and at one duration, 2 hours. Among the alcohols tested amyl alcohol, hexanol, and ethyl alcohol were the most toxic, while methyl and butyl alcohols were least toxic. Since that time allyl alcohol has been found to be the alcohol most toxic to nematodes. If it were not highly soluble in water (1 to 36), it would probably be an outstanding soil fumigant. Uricchio (53) in 1951 found that among a number of chemicals tested as possible nematocides, amyl and allyl alcohol, cyclohexane, cyclohexyl chloride and bromide, and allyl acetone were the most toxic.

Among the aldehydes and ketones tested acetone was least toxic, formaldehyde, butyraldehyde, and crotonaldehyde next, and mesityl oxide most toxic. In this group of compounds temperature was a major factor, both formaldehyde and mesityl oxide being much more toxic at 40° than at 25° C. None were outstanding as cholesterol solvents, but mesityl oxide was the best; it penetrated nematodes the most easily and killed in the lowest concentrations.

Among the organic acids lactic acid was the least toxic, followed by propionic, oxalic, acetic, butyric, *n*-caproic, and formic in order of increasing toxicity with given per cent solutions of the acids. The single halogenated organic acid tested, monochloroacetic, was lethal in concentrations of 1 to 2000. It is also the best sterol solvent. Stephenson (47) in 1945, using 0.206 *N* solutions of inorganic and organic acids, found oxalic and formic acids the most toxic of the fatty acids he tested on the basis of gram molecular weight. According to this worker, none of the acids he tested showed activities not explainable upon the basis of pH (his pH ran from 1.35 to 2.0). Toxicity readings were based on time required to kill. Death followed cuticular inflation, which may well be interpreted as dissolution of the matrix layer of the cuticle. The finding that fatty acids are not themselves particularly toxic to nematodes is understandable, as they are known to be the chief product of glycogen metabolism in nematodes.

Other types of materials which are known to kill nematodes under certain conditions include calcium cyanide (50), ammonium and calcium chloroacetate (17, 45), sulfur dioxide (27), allyl and phenyl isothiocyanates (18, 46), urea—i.e., uramon (20)—and parathion (16, 48).

Basic Principles of Soil Fumigation

All the facts discussed have a distinct bearing on the principles of soil fumigation against nematodes. Plant parasites may be in the roots, loose in the soil, or in the form of eggs enclosed in a mucoid mass. In any case they are probably covered by a film of moisture. The fumigant must: (1) be dispersed through the soil, (2) penetrate all barriers, (3) kill, and (4) leave no phytotoxic residue.

Dispersion. This may be accomplished by thorough mixing (a questionable process), aqueous solution or emulsion (as a drench or in irrigation water), or by gaseous diffusion. The latter is the simplest process under most circumstances. In order to accomplish dispersion in open field fumigation, the vapor pressure must be neither so great as to force the gas out of the soil too readily, nor so little as to prevent adequate dispersion and leave phytotoxic materials in the soil. For this reason, one may conclude that the selection of proper fumigant at a given time and place should depend on temperature. Furthermore, if the gas is too soluble in water it is apt to be taken up before it reaches the nematode. Soil fumigants tend to saturate the soil moisture in their immediate vicinity before diffusing further to form unsaturated solutions. As a matter of fact, simple computations indicate that soil fumigants reach their maximum efficacy only when applied at a dose rate sufficient to saturate the moisture present in the particular soil at the time applied. Normal tillable soil may be considered as having a water content of not less than 9 pounds per cubic foot. A standard soil fumigant dose rate is 20 to 40 gallons per acre. This allows for 1.5 to 3 ml. of fumigant per cubic foot or 4100 ml. of water; concentrations of 1:1366 to 1:2700 are therefore provided for. Fumigants soluble in water to a greater extent would not be apt to disperse far. However, a higher water solubility than 1 to 1366 can be advantageous if mucoproteins must be penetrated before the chemical can reach the organism. Among the better nematocides ethylene dibromide appears inferior to dichloropropene in moist soils containing de-

composed roots but superior in soils containing rather fresh plant roots and egg masses; aqueous solubility is an adequate explanation. Boiling points of the most successful field nematocides have been between 70° and 140° C. Methyl bromide and carbon disulfide, though excellent as nematocides under restricted conditions, are much too volatile for large scale field work. Substances with boiling points in the lower portion of the acceptable range appear to be a bit more successful when they act during cool periods, while substances in the higher portion of the range seem to be more successful in regions of high soil temperatures. Logically, one would expect the perfect soil fumigant to have the same vapor pressure as water, so that it would diffuse through the soil in a permanent saturated aqueous solution. Materials with boiling points of over 140° C. have been very difficult to remove from soils, and considerable phytotoxicity is commonly encountered. Successful soil fumigants today have a range of water solubility of 1:200 to 1:3333.

Penetration of Barriers. These include soil particles, moisture, roots (if present), and nemic structures. The larval or adult nematode cuticle is essentially a complex of skeletoids which may or may not be tanned, and it may also be covered by a lipide substance. The egg may be enclosed within the tanned skin of the mother, it may be free, or it may be enclosed in a mucoid mass. In any case the chances are good that it is covered by some type of moisture film. Nemic mucoids being hygroscopic present a very real barrier. The egg shell proper, being chitinoid, is permeable and of little consequence from this standpoint. The vitelline membrane is waxy, and here is the greatest barrier of all. In order to reach this membrane the chemical must be soluble in water; yet the vitelline membrane is a chemical the very antithesis of water. Cholesterol solvency is a means of correlating nematocidal properties of chemicals. The most effective nematocides today will dissolve cholesterol at the rate of 1 part of cholesterol to 1 to 5 parts of fumigant at 20° C. Less successful materials require up to 25 to 50 parts to dissolve 1 part of cholesterol, and substances requiring over 50 parts to dissolve 1 part of cholesterol have been complete failures as field nematocides.

In general, solvency of beeswax is better correlated with nematocidal efficacy than is solvency of cholesterol. All outstanding nematocides dissolve or emulsify beeswax at 25° C. in proportions of 1:5 to 1:10. However, the action is not identical, though the minimum amount of solvent may be the same. Thus 1,3-dichloropropene, allyl bromide, and chloropicrin are emulsifiers, while carbon disulfide dissolves, forming a clear solution and ethylene bromide clears the beeswax as it dissolves. Herein may be the answer to divergent actions of compounds with similar constants. A small change in temperature causes 1,3-dichloropropene and allyl bromide to form clear solutions, which again become cloudy when the temperature is reduced.

Solvency or emulsification of beeswax, aqueous solubility, and vapor pressure are completely correlated with nematocidal efficacy as determined in laboratory tests. The correlation is not complete when field efficacy is considered. Thus carbon tetrachloride, benzene, and toluene should be good nematocides, but have not proved satisfactory in field tests. Likewise carbon disulfide, while a sound nematocide under optimum conditions, requires, for satisfactory nematode control, a greater quantity than would be expected on the basis of its solubilities and solvency. The answer may lie in the lack of polarity of these molecules.

Incomplete tables of the physical constants and efficacies of a large number of compounds have been prepared (Table I). However, investigations show that much more information is needed to give a complete understanding of soil fumigation. We need tables showing vapor pressure, aqueous solubility, solvency in or solubility of nemic waxes, and efficacy, for temperatures of 20°, 25°, 30°, 35°, and 40° C. Furthermore, efficacy should be expressed in relation to moisture content of soil and stage of nematode.

The Kill. This is a subject that can be studied only under the microscope. If a minute drop of water is placed in a B.P.I. watch crystal and the watch crystal is placed in a stender dish, free nematode larvae, free eggs, and a mucoid egg mass are added to the drop of water in the watch crystal, then a measured quantity of fumigant is added to the stender dish and the lid put down, the problems of a nematocide

can be simulated. First, it must vaporize; second, it must enter into aqueous solution; third, it must penetrate any nemic membranes; and fourth, it must kill. Free root-knot nematode larvae (*Meloidogyne javanica*) die first, then larvae in free eggs, much later larvae in eggs in the mucoid jelly, and finally immature eggs in this jelly. Death can be observed by mounting specimens at intervals. In the case of most soil fumigants a little cloudiness appears in the nerve ganglion area, followed by oil droplet coalescence in the intestinal region; then extraction of the oils begins (or is this hydrolysis—at any rate they diminish). The final step is complete disappearance of all oils. This step is not, however, a necessary prerequisite for death. Oil droplet coalescence itself is adequate to cause death. The vitelline membrane, which is the big problem in penetration, is not usually dissolved even by highly lethal gas concentrations. Hence action is through it.

Table I. Physical Constants of Hydrocarbons Tested for Nematocidal Efficacy

Chemical	B.P., ° C.	Aqueous Solubility	C.S. ^a	M.S. ^a	Nematocidal Rating
Ethylene dibromide	132	0.43	0.5	1.0	Good
1,3-Dichloropropene	75	0.03	..	0.7	Good
Chloropicrin	112	0.23	1.0	1.0	Good
Methyl bromide	3.6	0.09	0.5	..	Good, limited
Allyl bromide	71	Insoluble	0.5	0.75	Good
Dichlorobutene	132-145	?	1.0	1.0	Good ^b
1,2-Dichloropropene	97	0.27	..	2.0	Moderate
Carbon disulfide	46	0.22	0.25	0.5	Moderate, limited
1,3-Dichloropropane	125	0.29	..	4.0	Poor
1,1-Dichloro-1-nitroethane	122	0.5	9.0	7.0	Poor
Ethylene dichloride	83	0.87	10.0	4.0	
Propylene dichloride	97	0.27	
Benzene	80	0.08	0.5	0.5	
Toluene	111	0.05	0.5	0.5	
1,4-Dichlorobutane	155	4	
1,1-Dichloro-1-nitropropane	141	0.5	2.5	6	b
1-Chloro-1-nitropropane	139	0.8	4.0	10+	b
1-Chloro-1-nitroethane	122	0.4	8.0	10+	
1,3-Dibromopropane	167	0.17	
Ethylene chlorobromide	107	0.69	1.0	2.0	Moderate
Tetrachloroethylene	121	0.02	0.25	0.5	Poor
Xylene	139	0.09	0.75	2.0	Very poor
Nitromethane	101	9.5	20	10+	
Nitroethane	114	4.5	20	10+	
1-Nitropropane	132	1.4	13	10+	
2-Nitropropane	120	1.7	13	10+	
Carbon tetrachloride	76	0.08	0.5	1.0	
1,1,2-Trichloroethane	113	Insoluble	..	3.0	
Dichloropentane	178	Insoluble	..	3.0	

^a Ml. of chemical required to dissolve 100 mg. of cholesterol and beeswax, respectively, at 25° C.

^b Killed nematodes but left toxic residue.

Our evidence relative to the halogenated hydrocarbons is that both penetration and oil droplet coalescence are physical rather than chemical activities. Chitwood (13) found that the oil droplets coalesce at 53° to 54° C. This figure agrees nearly exactly with the point at which Hoshino and Godfrey (30) found a level place in the lethal temperature-duration curve. It is also suspiciously close to the temperature at which ascaridin (a nitrogenous compound) was found to be dissolved in water according to Fauré-Fremiet and Filhol (26). The oil droplets in question are a neutral unsaturated oil, solid at 0° C. They are apparently held in colloidal suspension and either temperature or soil fumigants cause an upset of the system. According to Ballantyne (2) these oils are probably mixed triglycerides of the linoleic, linolenic, and oleic groups.

We could theorize a great deal about toxic groups, but there is little evidence that we are dealing with any, except possibly when we have —NO₂ substituted compounds. Neither chlorine nor bromine showed any value as nematocides when tested in the field. Halogens reduce aqueous solubility and increase wax solvency; bromine is more effective in this regard than chlorine; the more halogens the more pronounced is this tendency, and the lower is the vapor pressure. Length of carbon chain increases boiling point, reduces aqueous solubility, and increases solvency of lipides. Double bonds and position of the halogens also affect solubilities and boiling points. No effects have been observed which could not be explained on the basis of one of these three factors. It would appear that a nitro group increases the toxicity of a halogenated hydrocarbon. However, in this case it would appear that the nitro group acts on nemic proteins chemically only after the

halogen has provided the mechanism of penetration into the organism. Lower nonhalogenated hydrocarbons, which are much too soluble in water and nowhere near as good cholesterol or beeswax solvents, are of little value as nematocides. The halogenated hydrocarbons all appear to kill nematodes in precisely the same way (as does carbon disulfide)—namely, through upset of the nemic colloid system. By this means proteins are precipitated, nerve endings blocked, nerve sheaths destroyed, and the cellular membranes made permeable so that osmotic pressure cannot be maintained. Death is a foregone conclusion. Incomplete action amounts to anesthesia.

This does not mean that toxic groups do not exist. The nitro group is undoubtedly toxic and other toxic groups exist—i.e., thio-, etc.—but only one compound containing one of these groups (chloropicrin) has been developed as a commercial soil fumigant. The halogenated hydrocarbons are nonspecifics, acting as lipide solvents, emulsifiers, or solutes. As a matter of fact the halogen is not necessary; it is a physical conditioner for the hydrocarbon.

The author was curious about all the discussion of inert ingredients, bulk of nematocides, and cost of diluents. Hence laboratory tests were conducted using benzene, toluene, xylene, kerosene, and crude oil as nematocides. Under the particular conditions of these tests, benzene and toluene gave all of the same results as the so-called nematocides; toluene may be a bit better than benzene; xylene not so good (boiling point too high); kerosene of less value; and crude oil killed only the nematodes in direct contact with it.

At the present time, it is not clear why benzene and toluene were unsuccessful as soil fumigants. Lack of polarity of these molecules or their size might be the explanation of why greater concentrations of these substances are required for kill than of substances of similar solubility, solvency, and vapor pressure. So far as can be seen from the data at hand, the same principles of nemic kill apply. Soil fumigants act in saturated or near saturated aqueous solution and must reach this solution by vapor pressure; after reaching it they must be able to penetrate a waxy membrane, and if they can do that they will be of such a character as to upset the colloidal system of the cells. Nematocides have improved during the past 10 years; the chief change in their physical characteristics has been a greater mean beeswax solvency and a more restricted range of aqueous solubility. The limit of boiling point is near 140° C. unless deliquescent substances are used. Halogenated hydrocarbons with more than four carbon atoms must be ring compounds or branched chains in order to have physical characteristics commensurate with their duties; highly unsaturated compounds and nitro groups are indicated.

Some caution is advised before discarding or adding materials as diluents. The spreaders and wetters of spray technology must not be overlooked. Soil fumigation with nematocides is spraying underground. On the basis of his observations, the author doubts that there is such a thing as an "inert ingredient." Everything present either helps or hurts in the undertaking at hand. Some inert ingredients may be or form polymers or break down in such a way that residues remain in the soil to the detriment of the plant (1). Others probably kill a few nematodes themselves and condition the soil moisture either to the benefit or the detriment of the so-called active ingredient.

Forecast

In 1942 the Government asked all its personnel to make suggestions as to proper procedure for the individual units during the war period. Remembering the development of chloropicrin during the first world war, cooperation with chemical companies was suggested, particularly the examination of by-products. The early development of dichloropropene was a result of just such alertness on the part of some individual. Today one sees a large industry of soil fumigants, with hundreds of people testing compounds empirically. There are unlimited numbers of organic compounds, among which are undoubtedly many as good as or better than any of those in use today. Intelligent study of basic principles will aid the investigation. The day will surely come when chemicals may be eliminated in the laboratory by merely testing their capacity to penetrate wax

membranes and making a few computations of solubilities and vapor pressures. This is not a dream.

Highly toxic groups will be found. They may be used to step up old nematocides or bring new ones to the fore. However, soil nematocides are contact killers and as such will be supplanted by chemotherapy. Plants will be fed materials toxic to the nematode. Such chemicals (stomach poisons) are already here, as indicated by sodium selenate. Plant parasitic nematodes can bathe in it, but unless it is absorbed by the plant and thus fed to the nematode, no injury is done. The mode of action of parathion is still uncertain. Plant parasitic nematodes placed in a saturated aqueous solution certainly survive for long periods, yet it has been found effective in the control of certain nematodes in living plants (16, 48). The next step is the introduction into the plant of nutriment to replace those taken from the plant by the nematode. The final step is the introduction into the plant of neutralizers of nemic enzymes. This may have already been done in the case of parathion, for it is said to inhibit cholinesterase formation in other animals. Chemotherapy will then have its day, but when that day is done physics may be expected to take over the burdens of the control of plant diseases. We can expect the use of ultrasonics and radioactive fertilizers.

Despite this brilliant future, soil fumigation will not disappear. It will merely become plebeian. Like the pick and shovel, it is here to stay.

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Petroleum-Derived Products in Agriculture Pest Control

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Inorganic chemicals are rapidly being replaced by organic chemicals in the field of agricultural pest control. Chemical products of the petroleum industry can be used, where economical, as the key material just as conveniently as chemicals from coal or vegetable matter to prepare such organic compounds for agriculture. Modern petroleum technology is making available not only improved products but new chemicals which make possible a better job of food production in this era of modern technology.

Products of the petroleum industry have been used in agriculture for the control of pests practically since the initial recovery of oil from the earth. The early uses were as dormant sprays for deciduous fruit trees and for weed control. The development and expansion of petroleum products and petroleum chemicals in agricultural pest control fields have closely paralleled the technological development of the petroleum industry.

The characteristic periods for use of petroleum products in this field have been from 1900 to 1915, from 1915 to 1925, from 1925 to 1935, and from 1935 to 1950. The first period, extending from 1900 to 1915, was characterized by the use of relatively simple products such as red oils, crude stove oils, and mixed mahogany soaps. The period 1915 to 1925 marked the improvement in the quality of the original petroleum products and also the beginning of agricultural usage for highly refined products—namely, white oils. The necessary characteristics for summer and winter spray oils were established and methods of use worked out thoroughly, thus opening a large market for white oils in agricultural pest control. The period 1925 to 1935 was characterized by the introduction of additional specialty products, petroleum chemicals, and specialized herbicides, and the extensive use of petroleum products as carriers for insecticides and fungicides. The last period has been especially characterized by the rapid expansion of petrochemicals and the transition of pest control from inorganic to organic chemicals, thus opening a vast market for the rapidly expanding petrochemical development.

The market for pest control chemicals in the United States has been estimated by various experts at from \$200,000,000 per year to twice that amount. Originally the market was essentially for inorganic chemicals, whereas today it is rapidly changing to a synthetic organic chemical field. The sources for these chemicals are coal, petroleum oil, and vegetable products. The ingenuity of the modern organic chemical firm is such that any one of these basic raw materials could supply all that the industry requires. Thus petroleum products are capable of serving as the raw material for practically all the organic chemicals required as products and chemicals for use as agricultural economic poisons. For economic reasons, it is impractical to draw on petroleum products for all these purposes, primarily because the agricultural market is not sufficiently large to justify large capital expenditures. For the most part the chemicals from petroleum used in agriculture have been justified for other primary markets, and the agricultural usage has

served as a supplement to the over-all demand rather than as a basic justification for the development.

Specialized Products

Weed-killing properties of petroleum oils have been known since the beginning of the petroleum industry. The recent developments in petroleum technology have permitted great specialization in herbicidal petroleum products, due primarily to refining technology and increased knowledge of herbicidal action by petroleum chemicals on weeds. There are available at this time selective weed killers for use in carrot fields, for example, which will kill the weeds and not affect the young carrots. Likewise, cotton can be sprayed for control of many weeds without damaging cotton, and yet another field of beets and certain other crops can be selectively sprayed for weed control without damaging the desired crop.

Other petroleum weed killers have been developed which are many times more effective against any type of plant growth than previously known natural petroleum products. These materials are applied either as pure oil or as emulsions in order to permit wider distribution of the active petroleum chemical, using water as the carrier. One of the most interesting developments in the field of petroleum weed killers is aquatic weed killers, to improve the flow of water through irrigation ditches and the like, reducing the cost of removing such weeds mechanically or by hand. The use of aquatic weed killers is a rapidly expanding market, and in this field the products are so specialized that the treated water may be used for irrigation and other purposes a few miles from the point of treatment without undue hazard.

The new and highly specialized petroleum products used as weed killers represent an application to agriculture of products developed by modern petroleum technology. Their increased usage is certain as these herbicides replace more costly means for weed control, in some cases reducing the cost to about one third that of previously known methods.

Quality control standards have been developed for the new petroleum weed killers and laboratory techniques have been worked out for testing and establishing the suitability of a given petroleum fraction for a specific herbicidal use. Although attempts to correlate herbicidal action with physical and chemical tests have not been entirely successful, the use of additional specific tests to determine the chemical composition of the fraction has served as an indicator of toxicity in the specific composition under study.

Spray Oils

Spray oils represent one of the most widely used petroleum products for pest control. Modern refining technology has made possible the production of both dormant spray oils and the highly refined summer spray oils of the white oil type to quality standards that were impossible in the earlier days of the petroleum industry. In the earlier days of spray oil usage in agriculture, the materials served primarily as a contact insecticide in themselves. Today these products are finding an increased market as a carrier or stabilizer for many of the newer organic chemicals. For example, a certain organic chemical may have a stability on plants of 24 hours if applied by itself, but if applied in combination with the proper type of petroleum oil, the residual life may be extended to say 4 days, thus greatly improving the efficiency of the compound.

Test methods have been developed for both dormant and summer spray oils to predict accurately the behavior of a given oil, from the viewpoint of both tree or plant response and efficiency against pests. In the earlier days of spray oils, it was difficult to predict the behavior of a given product without actual exhaustive field trials, but by making use of the experience and testing techniques that are now available, spray oils can be selected with definite knowledge as to their behavior under practical usage conditions in the field.

It seems likely that petroleum oils, both dormant and white oil summer types, will remain one of the most important petroleum products used in agricultural pest control for many years to come. These products have the advantage of comparatively low cost

coupled with high efficiency for a wide variety of uses, the latest of which is as a carrier and stabilizer for many of the newer organic chemicals.

Petroleum Sulfonates

One of the natural products of petroleum origin having broad usage throughout the years has been petroleum sulfonates. In more recent years these products have become more specialized, in that the sulfonate is made entirely from a petroleum fraction of a given control type and the product is purified and standardized for specific end uses. These products are of the anionic type and consist of from 20 to 60% petroleum sulfonates generally. The products are from dark to light brown colored, semifluid, water-soluble wetting agents and emulsifiers. The materials are generally composed of a more or less strongly hydrophobic hydrocarbon chain which is attached to a strongly hydrophilic solubilizing group. These materials are relatively stable in acid and alkaline solutions, and suitable for use with practically all pest control chemicals. For the most part, these materials have low surface and interfacial tensions and high wetting and penetration coefficients. One additional advantage is their stability in hard water generally encountered in many farming areas and also in water contaminated with clay, frequently found in irrigation districts using water from such sources as the Colorado River. The materials are also especially adapted for use in the preparing of fruit and vegetables for marketing and in particular for use in the rinse or wash water to remove dirt and other foreign bodies.

Sodium sulfonates of petroleum origin are also suitable for emulsifying spray oils, weed killers, and weed killer concentrates such as pentachlorophenol, and for use as auxiliary agents with other specialized emulsifiers using, for example, a higher percentage of the petroleum sodium sulfonate and a lower percentage of the more costly synthetic sulfonate.

Of the more modern detergents suitable for use in agricultural pest control, the alkyl aryl sulfonates represent the most modern and the preferred type, being superior to the natural petroleum sulfonates because of their product quality standardization, improved effectiveness in wetting and emulsifying, and reduced amount necessary for use in given formulations. These products are generally available as formulations containing 40% active agent, which is alkyl aryl sulfonate, and 60% sodium sulfate. They are also available as practically pure active agent, being relatively free from sodium sulfate. The material formulated as a 40% active agent is especially suitable for use in wettable powders, sulfurs, dusts, and other dry or powdered materials requiring wetting agent. The sodium sulfate-free material is especially suitable for use in emulsive liquid formulations such as petroleum oil sprays.

One of the defects of the synthetic material is its copious foaming power, which generally must be corrected by the use of antifoam agents. The foaming problem is especially important in soft water.

The alkyl aryl sulfonates are stable to the ordinary acid and alkaline pest control chemicals used by the industry. The materials are stable in either concentrated acid or concentrated alkali washes that might be used for removing residue or skins in processing fruit; being effective in such small quantities they afford one of the most practical means for cleaning and processing agricultural crops.

Petroleum xylene offers one of the most interesting petroleum chemicals both for use as a product and for use in synthesis.

The xylene serves as probably the preferred solvent for liquid emulsifiable concentrates containing such active agents as DDT, DDD, toxaphene, chlordan, aldrin, parathion, and certain other materials as typified by this class. The xylene has proved to be one of the finest solvents for these organic chemicals and also from the standpoint of emulsification in water, dispersion in water, and freedom from injury to the plants when applied at normal dilution levels.

The isomers of xylene offer one of the most practical starting points for organic synthesis for the preparation of valuable products for agricultural pest control. *o*-Xylene is a starting material in making dioctylphthalate, which is an important solvent for parathion. 3,6-Dinitro-*o*-xylene is also made from *o*-xylene. *m*-Xylene is the starting material

for *m*-xylyl chloride, a fumigant, for 2,4-dichloro-*m*-xylene, an insect repellent, and for certain other useful solvents.

Synthetic Polymers

Other interesting chemicals prepared from petroleum are the synthetic polymers obtained by the catalytic polymerization of normal and branched-chain butenes generally known as polybutenes. These chemically inert liquids are used as the basis for the manufacture of tree banding compounds to trap insects and also to make insect population counts by placing boards coated with these materials in orchards to determine insect flight, distribution, and population. Another use for these products is in the field of adhesives and depositors. Used in sprays and dusts, the materials impart high deposit of the solid particles and long residual properties. One of the interesting characteristics of these materials is their chemical inertness and safety to plants. They may be used at fairly high concentrations on plants during full growth with only moderate effect on plant growth. For this reason the materials are especially valuable as adhesives and depositors for powders applied to growing plants. The chemical stability, nonvolatility, and safety of the polybutenes should render these petroleum chemicals one of the more interesting for product development in the field of agricultural pest control.

Cresylic acid of petroleum origin has been produced for a number of years and following its initial production it found a ready acceptance in the agricultural field. The ease of oxidation of cresylic acids is such that they are capable of protecting other substances from oxidation and hence they are useful in stabilizing formulations containing readily oxidizable substances. As disinfectants petroleum cresylic acids also find a widely accepted usage in this field. The materials are especially used in sheep dips and in oil emulsions. The physical properties of cresylic acids of petroleum origin are essentially the same as those of coal-tar origin and currently a fairly wide range of petroleum cresylic acids are available to meet various requirements in product formulations.

The quaternary compounds of petroleum origin are among the most interesting materials useful to agriculture. These products are especially suitable for use in the dairy industry as sanitizers and in other food-handling and processing plants as germicides and sanitizers. They are also useful as wetting agents and auxiliary emulsifiers in various liquid product formulations. The chemical stability of the quaternary compounds renders these materials suitable for use in a wide range of products, their one limitation being incompatibility with soaps or other anionic surface active agents, and with certain other compounds. The quaternary compounds of petroleum origin will probably become one of the most widely used petroleum chemicals in agriculture, largely because of the safety and nontoxic nature of the compounds coupled with their extremely high bacteriological activity.

Naphthenic acid from petroleum continues to be of interest as a material for making copper naphthenate and wood preservatives for use in greenhouses and the like. Naphthenic acids occur naturally to the highest extent in naphthenic crude oils, certain of which are stated to contain over 1% total naphthenic acid. As yet these materials have not reached wide acceptance in agricultural pest control.

Elemental sulfur will probably rank as one of the heavy tonnage chemicals produced from petroleum in the not too distant future. The quality of elemental sulfur made from petroleum is excellent, the material comparing favorably with Texas crude sulfur.

Another group of chemicals being developed for agriculture is the nitroparaffin group, which is showing considerable promise as insecticides.

One of the new chemicals derived from petroleum is *n*-trichloromethylthiotetrahydrophthalimide. This product was tested as a fungicide by research institutions under the code SR-406. The material appears to be one of the most outstanding fungicides for use in agricultural pest control.

Vast quantities of petroleum benzene have been used in the manufacture of such widely used agricultural chemicals as benzene hexachloride and lindane, the essentially pure gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane.

The usage of paraffin wax as a coating on cartons for milk and other food products represents an expanding market for petroleum products.

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