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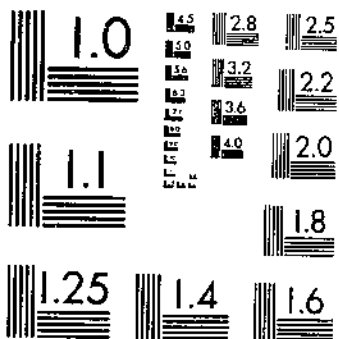
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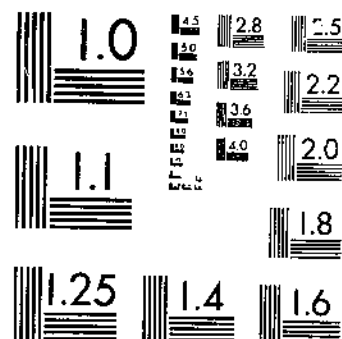
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MICROCOPY RESOLUTION TEST CHART
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TIB 253 (1931)

UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

PETROLEUM OILS AND OIL EMULSIONS AS
INSECTICIDES, AND THEIR USE AGAINST
THE SAN JOSE SCALE ON PEACH TREES
IN THE SOUTH

By H. S. SWINGLE,¹ *Assistant Entomologist*, and OLIVER I. SNAPP, *Entomologist*,
*Division of Deciduous Fruit Insects, Bureau of Entomology*²

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INTRODUCTION

The kerosene fraction of petroleum oils was apparently the first used for insecticidal purposes, probably because of its general availability. As early as 1871 a kerosene emulsion was recommended as an insecticide and was rapidly adopted for general use (95, 96).³ It

¹ Resigned June 30, 1929.

² Credit is due C. H. Alden, who conducted work on this project from 1922 to 1926. The results of a small portion of Mr. Alden's work are reported in this bulletin.

³ Italic numbers in parentheses refer to Literature Cited, p. 42.

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was later discovered, however, that the less volatile oils were considerably more toxic, and light to medium lubricating oils and crude petroleum oil were recommended by various workers from 1903 to 1910 (66, 67, 68, 87, 88). Volck (111, p. 6) stated in 1903 that oil distillates lying between the kerosene and the lubricating-oil groups were then commonly used in California.

The use of oil sprays against scale insects was checked during this period by the sudden popularity of lime-sulphur solution. This product was used as an insecticide in California as early as 1886, but was not tried out in the eastern part of the United States until 1893. The experiments at that time did not appear to be very successful, and lime-sulphur did not come into general use until about 1900. From then until 1922 it was the most popular spray for use against scale insects, and was considered very effective.

Jarvis (67), who worked upon oil sprays as early as 1907, stated that dissatisfaction with lime-sulphur was caused by its undesirable handling qualities rather than by the superiority of oil as an insecticide. Parrott, Hodgkiss, and Serrine (85) reported in 1906 that oil sprays were not so effective as the sulphur washes.

In 1910 Jones (68) reported that lubricating and crude-oil emulsions were much more effective than lime-sulphur against the European fruit lecanium and the pear scale. In 1911 Yothers (120) reported excellent results with similar oils against the white fly on citrus. Ackerman (3) reported in 1923 that the lubricating-oil emulsions as used by Yothers were much more effective than lime-sulphur for the control of the San Jose scale on apples. Other workers (4, 33, 55) immediately tried these emulsions and came to the same conclusion.

Oil sprays have now largely supplanted lime-sulphur as an insecticide for the dormant spray and have been recommended for the control of many other insects (16). In the last few years they have also been recommended as summer sprays for codling-moth eggs (92).

In view of the recent importance of oil sprays, a discussion of the chemical and physical properties of petroleum oils and of the principles of emulsification and the various factors influencing toxicity to insects and plants are given in this bulletin. The experimental work herein reported was conducted at the peach-insect laboratory of the Bureau of Entomology, Fort Valley, Ga., where work upon this project has been in progress since 1922. As a report was given in 1925 by Alden (4), this bulletin deals almost entirely with results obtained since that time.

CRUDE PETROLEUM OILS

ORIGIN OF PETROLEUM

Numerous theories have been advanced as to the origin of petroleum oils (47, 48). These may be roughly divided into inorganic and organic.

According to the inorganic theories, the various hydrocarbons in crude oils were formed by the action of water or superheated steam

¹LEBEY, R. W., and HARRIS, J. A. THE DORMANT SPRAY-OIL EMULSIONS AND SULPHUR SPRAYS. N. C. Agr. Expt. Sta. Div. Ent. Peach Insect Bul. 10. [mimeographed.]

upon various metallic carbides in the interior of the earth; or, by the action of carbonic acid upon various alkali metals, forming acetylene, which, by reduction and polymerization in the presence of metallic catalysts, led to the formation of the various hydrocarbons present in crude petroleum oils.

The organic theory is, briefly, that fats, waxes, and other stable fat-soluble materials have accumulated from plant and animal remains; and under the influence of pressure, heat, and various contact catalysts present in the earth these have been gradually transformed into petroleum oils. This theory best explains the nitrogen content of petroleum oils, their optical activity, and the fact that they are always found in sedimentary rock formations.

PRINCIPAL CONSTITUENTS AND GENERAL PROPERTIES OF CRUDE PETROLEUM OILS

Crude petroleum oils are complex mixtures of a large number of compounds (47, 48, 63, 72), principally hydrocarbons. The nature and relative quantities of the various compounds present vary greatly from one oil field to another and considerably between wells in the same field. In commercial practice crude oils are classified according to their bases as paraffin, asphaltic (or naphthene), or mixed if containing both asphalt and paraffin. This system is based upon the residue left after distillation (in the absence of cracking). From a chemical standpoint, only arbitrary classification is possible, owing to the complexity of the compounds present in any one crude oil. For practical purposes, however, the main constituents may be considered as hydrocarbons of the paraffin, naphthene, and aromatic series, unsaturated hydrocarbons, and asphaltic material.

Crude oils contain members of the above groups in varying quantities. Pennsylvania oils, usually classed as paraffin oils, contain both paraffin and naphthene hydrocarbons. Gulf coast oils, known commercially as asphaltic oils, contain naphthene hydrocarbons in addition to the asphaltic material. Mid-continental crudes containing paraffin, naphthene, and asphaltic groups are naturally classed as mixed-base oils in commercial practice.

GENERAL PROPERTIES OF GROUPS OF COMPOUNDS PRESENT IN PETROLEUM

THE HYDROCARBONS

UNSATURATED HYDROCARBONS

The compounds containing one or more double bonds between atoms are classed as unsaturated hydrocarbons. They consist largely of members of the olefine, acetylene, and partly hydrogenated cyclic hydrocarbon (e. g. terpene) groups. They are chemically active, forming additive compounds with halogens, and concentrated sulphuric acid; are easily oxidized; and have a tendency to polymerize, especially in the presence of various catalysts (e. g. sulphuric acid, aluminum chloride, fuller's earth, and also charcoal, and other porous substances).

In view of the activity of these compounds and their great tendency to polymerize, only very small quantities of unsaturated com-

pounds would be expected in crude petroleum since during its formation and accumulation conditions were favorable for long periods of time to polymerization and the formation of saturated groupings. Considerable chemical evidence is also available in support of the statement (47, p. 30) that only small quantities of unsaturated hydrocarbons are present in crude oils. Destructive distillation (cracking), however, results in the formation of a considerable quantity of these compounds.

AROMATIC HYDROCARBONS

Although double bonds are present in aromatic hydrocarbons, these compounds are classed separately from the above unsaturated compounds as they differ in chemical properties. They are usually present in only very small quantities, except in California crudes. Benzene, toluene, xylene, naphthalene, and others have been reported from various oils. It is unknown whether they occur as such in the crude oil or are split off from unstable compounds by mild cracking during distillation. They do not react with concentrated sulphuric acid but can be made to react with fuming sulphuric acid. They can be made to take up bromine and chlorine under proper conditions but do not take up iodine directly.

NAPHTHENE HYDROCARBONS

The naphthene hydrocarbons have the general formula C_nH_{2n} . They are ring compounds, behaving as saturated hydrocarbons and may be regarded as hydrides of the benzene series. They can be made to form substitution products, the halogens replacing hydrogen atoms, and may be nitrated or oxidized under proper conditions. They have higher viscosities and relatively low boiling points. They are not affected by concentrated sulphuric acid while cold; but when heated, or when fuming sulphuric acid is used, oxidation occurs.

PARAFFIN HYDROCARBONS

The paraffin hydrocarbons have the general formula C_nH_{2n+2} and belong to the methane series. The higher members of this series are solids and are known commercially as paraffin wax. They are saturated chain compounds and are practically chemically inert. They may be made to form substitution products with halogens under proper conditions and are not affected by either diluted or concentrated acids at ordinary temperatures. Sulphuric acid, while hot, exerts a charring action, and hot concentrated nitric acid slightly decomposes the molecules. Fuming sulphuric acid absorbs small quantities of the higher members of this series.

ORDER OF CHEMICAL ACTIVITY

In decreasing order of chemical activity, the foregoing hydrocarbon constituents are: "Unsaturateds," aromatics, naphthenes, and paraffins. The last three are much less active than the first, but increase in the size of the molecule, and the attachment of methyl groups and side chains greatly augments their capacity for reaction. Those of

high molecular weight, and especially those with long side chains, are easily nitrated, sulphonated, or oxidized.

OTHER COMPOUNDS

In addition to the hydrocarbons that have been discussed, other compounds and metallic salts are to be found in the crude petroleum oils. These will be considered under the headings of oxygen, sulphur, and nitrogen compounds and metallic salts.

OXYGEN COMPOUNDS

Among the oxygen compounds present are naphthenic acids. These are feebly acid and with alkalis form salts resembling those of fatty acids. These salts are good emulsifiers and are used to some extent in the manufacture of cheap soap. They are slightly soluble in concentrated sulphuric acid.

There are also present some asphaltic substances, which are oxygen-containing and sometimes sulphur-containing compounds. They have the property of drying readily and find use as road-surfacing materials. Resins are present in small quantities.

SULPHUR COMPOUNDS

The sulphur content of oils is usually small, and is retained largely in the higher distillates. Sulphur appears to be present as thiophenes and sulphides.

NITROGEN COMPOUNDS

The nitrogen content of oils is also small. It is present as basic compounds, probably tetrahydropyridine and quinoline derivatives. They are easily removed by diluted sulphuric acid.

METAL SALTS

A large number of metals have been found in traces in the ash of various crude petroleums. They occur principally as salts of the naphthenic acids.

LUBRICATING OILS

COMMERCIAL PREPARATION OF LUBRICATING OILS FROM CRUDE PETROLEUM

Commercial refining of crude oil for the production of various lubricating oils consists mainly in distillation for the removal of the more volatile compounds and subsequent chemical treatment to remove various other objectionable materials. These processes, which are treated fully in other works (47, 48, 63), will be only briefly described here.

DISTILLATION

The crude oil is allowed to stand in settling tanks to allow the water and other suspended matter to settle, often being slightly warmed to facilitate this. In case the water and oil have formed an emulsion, more drastic heating may be necessary. Separation may also be effected by centrifuging or by various electrical means.

The oil is then run into large stills and heated directly by fire, or by superheated steam, or both. The method most commonly employed is the application of direct heat to the exterior of the still and of superheated steam through perforated pipes in the bottom of the still. As the steam rises through the oil, it causes rapid evaporation and consequently distillation at a lower temperature than would be necessary with the use of direct heat alone. This largely prevents cracking, and produces a much better grade of oil. The temperature and quantity of steam are gradually increased during the course of distillation.

The various fractions are "cut" according to gravities. The first distillate is the naphtha or benzine. When the specific gravity reaches from 0.76 to 0.78, the distillate is deflected into the kerosene tank. The distillation is stopped when the gravity reaches from 0.84 to 0.85, or occasionally lower.

The thick, tarry residue is then treated for the production of lubricating oils. The whole is distilled, yielding a light distillate of low viscosity and leaving a residue of coke in the still.

This distillate is washed consecutively with acid and soda, chilled and pressed to remove the paraffin, and then fractionally distilled into heavy burning oils and various grades of lubricating oils.

CHEMICAL TREATMENT

ACID REFINING

Acid refining is carried on in large iron containers provided with conical bottoms to facilitate the drawing off of the acid sludge. The amount of concentrated (93-98 per cent) sulphuric acid required varies with different oils and with the degree of refining required in the finished oil. The acid and oil are vigorously mixed, usually by agitation with compressed air. After a sufficiently long reaction period, which is determined by trial, water is added and the sludge allowed to settle. The oil may then be again washed with acid, or treated with alkali.

ALKALI REFINING

Following the acid refining, the "sour" oil is drawn off into another agitator, and washed with alkali. A 10 to 25 per cent sodium hydroxide solution is usually used, the manner of application and the quantity varying greatly. The oil and alkali are generally heated by steam during treatment. The alkali wash water is then withdrawn, and the oil washed thoroughly with water and dried by blowing with air. The majority of red engine oils sold for use as insecticides receive no further treatment, although some are subjected to redistillation.

REFINING BY ADSORPTION

Of the compounds present in oils, the asphalts and resins, which give color to oils and are otherwise detrimental, are the most strongly adsorbed by various adsorbents; therefore adsorption is used in refining, especially in the production of white oils. Naphthenic acids, nitrogen and sulphur compounds, unsaturated hydrocarbons, aro-

matics, and naphthenes are adsorbed in decreasing order of rapidity. Paraffins are but feebly adsorbed. Molecular weight has great influence on this process; the higher the molecular weight, the more readily are the substances adsorbed.

The adsorbents used are fuller's earth, silica gel, and various charcoals. The oil may be allowed to filter slowly through beds of these materials, or the adsorbent may be added directly to the oil, and filtered off after agitation. This process is capable of completely decolorizing oils. It is usually customary, however, in the production of white or colorless oils to first drastically refine with sulphuric acid and then treat with adsorbents.

EFFECT OF VARIOUS REFINING METHODS UPON CRUDE OILS

EFFECT OF DISTILLATION

Distillation is always accompanied by more or less decomposition of the compounds of high molecular weight. The higher the temperature and the longer the time required for distillation, the greater the decomposition (or cracking). The use of steam greatly reduces this tendency to decompose by reducing the temperature necessary for distillation. Lubricating oils that have undergone such decomposition have lower viscosities and lower flash points. The larger and more complex the molecules, the more readily decomposition occurs.

The weight and complexity of the molecules in the distillate gradually increase with increase in temperature required for distillation. The lubricating fractions therefore contain mixtures of the more complex compounds of high molecular weight.

The paraffins are largely concentrated in the low-boiling fractions; with rising boiling point, the olefines, naphthenes, and aromatics begin to predominate. There is an increase in the quantity of olefines (unsaturated hydrocarbons) due to cracking during distillation.

EFFECT OF ACID REFINING

The action of concentrated sulphuric acid on petroleum distillates is very complicated and as yet imperfectly understood. Its effect upon the principal groups of compounds present will be briefly summarized:

Unsaturated hydrocarbons are attacked by sulphuric acid during refining, resulting in: (1) Formation of acid esters of sulphuric acid or of neutral esters by the addition of acid to the double linkage; (2) polymerization.

The acid and neutral esters pass mostly into the acid sludge, but a small portion of each remains dissolved in the refined oil. The tendency of olefines, which make up the greater part of the unsaturated hydrocarbons, to polymerize increases with increase in molecular weight. As these products of polymerization, although unsaturated, remain for the greater part in the oil, it is evident that a considerable portion of the olefines is not removed by sulphuric acid. In fact, it may be concluded (47, p. 123) that all but the olefines of low molecular weight remain chiefly in the oil either unattacked or as polymers.

Aromatic hydrocarbons, though not attacked at low temperatures, may be sulphonated and removed in the acid sludge if the temperature is allowed to rise.

A small portion of the naphthenic acids is removed by the acid, but the greater part remains in the oil. Sulphur compounds are partially removed, but other methods of refining are necessary for petroleum rich in sulphur. Nitrogen compounds pass completely into the acid sludge, as they are of basic nature.

Paraffins and naphthenes are not usually attacked at ordinary temperatures, but considerable quantities may be dissolved out by the acid sludge in some cases. As stated before, the high molecular members of even these groups of hydrocarbons may be sulphonated to some extent if combined with more reactive side chains.

Resins and asphaltic materials are polymerized by sulphuric acid and react with the acid, evolving sulphur dioxide, and are largely precipitated or dissolved.

EFFECT OF ALKALI REFINING

The sour oil from sulphuric acid refining contains, as detrimental impurities, the greater part of the original naphthenic acids, sulphuric acid esters, and sulphonic acids formed during acid treatment, as well as a considerable quantity of free acid in suspension. The oil is treated with caustic soda solution to remove these impurities, the organic acids being removed as sodium soaps. As these soaps are excellent emulsifiers, emulsions are often formed upon the addition of the soda wash. These are usually broken by prolonged steaming and settling.

COMPOSITION OF THE REFINED LUBRICATING OILS

Owing to their complexity and to the great number of different compounds present, comparatively little is definitely known as to the composition of lubricating oils. The mass of evidence (47, p. 258) tends to support the belief that the chief constituents of lubricating oils are saturated cyclic hydrocarbons of the naphthene and polynaphthene groups. A considerable quantity of paraffin may be present in oils from certain crudes. No evidence exists (47, p. 256) for the presence of aromatic hydrocarbons in lubricating fractions, although they may be present in small quantities or as side chains.

The quantity of olefines or unsaturated hydrocarbons present would appear to be small. Reports of the presence of large quantities are usually based upon iodine absorption, sulphuric acid absorption, or upon the formolite test. It has been shown that a large portion of the iodine forms substitution products with compounds other than olefines. The action of sulphuric acid has already been discussed, it being sufficient here to restate that, as has been stated by Gruse (47, p. 256), a large portion of the compounds absorbed by sulphuric acid from lubricating fractions are high-molecular branched-chain compounds and not necessarily olefines. The formolite test has been shown (48, p. 77) to be given only by aromatic hydrocarbons and therefore is not a measure of the unsaturated compounds present.

CHEMICAL AND PHYSICAL PROPERTIES OF LUBRICATING OILS.

The significance of the most important properties which are determined by analysis and the analytical methods used will be briefly described. More extended discussions will be found in the United States Government specifications for lubricating oils (109) and in the writings of Gruse (47), Gurwitsch (48), Haslam and Frölich (56), and Hurst (63).

OXIDATION

All lubricating oils are acted upon by the oxygen of the air, becoming yellow and turbid, depositing flocky precipitates, and acquiring an acid reaction. When these oils become completely oxidized by any means, the final products are carbon dioxide and water. The rate of oxidation is accelerated by sunlight, or the presence of charcoal, alkalis, or copper, and to some extent by other metals. Acid refining greatly decreases the rate of oxidation by removal of the more reactive compounds.

Oils are also oxidized by many bacteria. Söhngen (106) found that at 28° C. on exposed surfaces of 2 sq. m., an average of 15 mg. of kerosene and 8 mg. of paraffin were completely oxidized by bacteria in 24 hours. He stated that the intermediate products were probably fatty acids, the final products carbon dioxide and water.

De Ong (23) has suggested that the rate of oxidation of oils, with the production of acids, may be of importance in explaining foliage injury to citrus. He has suggested a modification of Sligh's method (105) for the evaluation of this factor. This consists of subjecting a definite weight of oil to the action of pure oxygen in a flask at 300° C. for a definite period. The acidity developed is measured by titration. The value of this character in oils is still unsettled.

UNSULPHONATED RESIDUE

A number of methods for the determination of the unsulphonated residue have been suggested (17, 40, 41). All consist essentially in shaking the oil with concentrated sulphuric acid and determining the volume which is not absorbed (unsulphonated) by the acid.

The exact nature of the compounds which are dissolved (or "sulphonated") is unknown. A number of writers state that the olefines or unsaturated hydrocarbons are the only compounds absorbed. As has been stated previously, a large portion of the compounds absorbed by concentrated sulphuric acid are high-molecular branched-chain compounds, not olefines; also, evidence exists indicating that only those olefines of low molecular weight are removed by acid, the higher members being polymerized and remaining in the oil.

It is probably more accurate merely to state that the sulphuric acid removes the most active compounds present. The unsulphonated residue gives a measure of the degree of refining which an oil has undergone; the higher the unsulphonated residue, the more drastic the refining. For ordinary red engine oils the unsulphonated residue usually ranges from 50 to 70 per cent; for white oils, from 95 to 98 per cent.

Graham's method (39) was used for the determinations of the unsulphonated residues listed in Table 1, which shows the results of analyses made by the Bureau of Chemistry and Soils of a large number of the more common lubricating oils used for the manufacture of emulsions. These are classified as paraffin, intermediate, or naphthene base crude oils.

TABLE 1.—Analyses¹ of a series of lubricating oils of the type used as insecticides

Oil No.	Viscosity (Saybolt, at 100° F.)	Density at 20° C.			Condition at -5° C.	Volatility (four hours at 105° C.)	Unsol. phonate residue	Flash point	Fire point
		Paraffin base	Intermediate base	Naphthene base					
	Seconds	Grams per cubic centimeter	Grams per cubic centimeter	Grams per cubic centimeter		Per cent	Per cent	° F.	° F.
1	47	0.847				4.18	74	276	300
2	76	.873			Solid	1.50	88.8	325	365
3	78		0.882			.04	64	345	395
4	79		.887		Liquid	.93	64	349	414
5	80		.879		Flows slowly	.92		326	378
6	85	.879			Liquid	.75	65	349	387
7	102			0.929		1.75	59	312	346
8	104.5	.883			Flows slowly	3.92		314.6	417
9	105	.884			Solid	.60	64.8	365	420
10	113		.886		do.	.57	63	374	428
11	116	.885			Does not flow	.40	64	345	395
12	124	.889			Solid	1.21	60	365	412
13	137			.924		.08	59	325	360
14	138			.922	Liquid	1.20	60.8	325	365
15	147	.890			Solid	.10	66	390	435
16	156		.894		do.	.20	61.2	380	435
17	158		.892		do.	.08	60	385	435
18	168		.895		do.	.60	61	404	451
19	186		.898		do.	.35	None.	387	449
20	187	.892			do.	.20	68	405	470
21	200	.895			do.	.22	62	422	474
22	216		.895		Flows slowly	.16		398	451
23	218		.921		do.	.09		313	285
24	220		.919		do.	.88		347	401
25	220		.920		Solid	.11	60	428	495
26	236		.921		Liquid	.09	53	360	403
27	237		.900		Solid	.05	65	405	475
28	239	.890			do.	.28	46	406	466
29	243		.890		Flows slowly	.11		270.6	470
30	270	.899			Solid	.09	58	428	493
31	272	.899			do.	.10	52	333	471
32	275		.902		do.	.12	59	430	406
33	308	.904			do.	.06	51	440	495

¹ Analyses were made by the U. S. Bureau of Chemistry and Soils.

DENSITY

Density here is expressed as the weight in grams of 1 cubic centimeter of oil, and was determined at 20° C. by use of a 50-cubic-centimeter pycnometer.

The densities of crude oils range from 0.65 to 1.06 gram per cubic centimeters. Lubricating-oil fractions have a minimum density of 0.84 or 0.85 gm. per cubic centimeter, lighter fractions falling into the kerosene group. The density, as a rule, rises with increase in molecular weight, boiling point, and viscosity; it also varies with the base of the crude from which the lubricating oil fraction was derived. (Table 1.) Comparing lubricating fractions of nearly the same viscosity, those from a naphthene-base crude are much denser than those from a paraffin crude. Aromatic hydrocarbons are denser than naphthenes, but occur in only small quantities in all except a few oils from the California field and occur there along with naphthenes. This offers a method for the separation of lubricating oils into classes based upon the crude oil from which they were derived.

VISCOSITY

Viscosity of a liquid may be defined as resistance to fluid motion. In the petroleum industry not absolute viscosity but a related property is measured (i. e. the time required for a definite volume of oil to flow through a standard opening under definite conditions). A number of different kinds of apparatus have been used for the determination of this factor. The values given by different instruments bear no simple relationship to each other or to true viscosity, and rather complicated conversion tables (59) must be used for the conversion of one into another. The values given in Table 1 were secured by the use of a Saybolt universal viscosimeter (109, p. 42) and are the time in seconds required for the delivery of 60 cubic centimeters of oil from the standard opening at a constant temperature of 100° F. Subsequent references to viscosity refer to that determined in this manner.

Viscosity decreases with increasing temperature and increases with increase in pressure. In a homologous series it increases with increase in molecular weight, boiling point, and density. Gruse (47, p. 260) concluded from a survey of the literature that it seemed likely that the viscous portions of petroleum oils are composed of hydrocarbons built up of five or six membered polymethylene rings (naphthenes), probably bearing many side chains, some of aromatic or unsaturated nature. Gurwitsch (48, p. 140) also concluded that the naphthenes are mainly responsible for the viscosity of a refined lubricating oil. The relative viscosities of the other groups are as follows, in decreasing order: Aromatics, paraffins, olefines, and diolefines.

FLASH POINT AND FIRE POINT

The flash point is the temperature at which an oil evaporates so intensively that its vapor, in an open cup of specified dimensions, or in a closed vessel to which air is admitted at specified intervals, forms an explosive mixture with air and ignites on the approach of a small flame.

The fire point is the temperature at which evaporation is such that the vapors not only flash, but continue to burn.

These two properties are more or less connected with the initial boiling point. In a general way, the flash and fire points increase with increase in viscosity, but numerous exceptions may be noted in Table 1. A low flash point is an indication of the presence of more volatile compounds in an oil. These tests are of value in determining the suitability of an oil for use in internal-combustion engines or where there is a fire hazard. They are of doubtful value in the evaluation of an oil for insecticidal use.

The flash and fire points (Table 1) were determined by means of the Cleveland open-cup method (109, p. 66).

VOLATILITY

Volatility, as reported in this bulletin, was determined according to the following method:

Place 20 grams of oil in a 3½-inch crystallizing dish, and heat at 105° C. for four hours in an electric oven. Reweigh, and report loss in weight as per cent volatility.

De Ong (23) has suggested a slightly different method for the determination of volatility. His method consists in placing a definite weight of oil upon asbestos strips and weighing periodically.

The first method, used by the United States Bureau of Chemistry and Soils, merely indicates the relative quantities of more volatile constituents present. The method of De Ong gives a more definite indication of the permanence of the oil film and is correlated with viscosity.

CONDITION AT -5° C.

The condition of an oil at -5° C. is a modification of the "cold test." A sample of oil is cooled to -5° C. and note made as to whether it is liquid, solid, or semisolid. Solidification is often taken as an indication that paraffin is present and that the oil is from a paraffin-base crude. If the oil is liquid, this may indicate that it is from a naphthene-base crude, or merely that the paraffin has been previously removed by chilling and pressing during refining. The value of this test for evaluation of an oil for insecticidal use is questionable.

COLOR

In general, the more highly refined the oil, the lighter the color. White oils are so highly refined as to lose entirely their red or brown color, but not their fluorescence.

EMULSIFICATION

HISTORY

Petroleum oils were originally applied undiluted to plants for the control of insects, but owing to the frequent severe injury following such applications, methods of applying them diluted with water were sought. As oil and water can not be mixed it was necessary to emulsify the oil in water, which consists essentially in dispersing it throughout water in the form of very small droplets.

The earliest emulsions were unstabilized mechanical mixtures produced either by the violent agitation of oil and water, or by forcing a small jet of oil and a large stream of water simultaneously through the spray nozzles. These methods were unsatisfactory owing to mechanical imperfections of the equipment used, and severe injury often resulted, which stimulated interest in the production of stabilized emulsions.

Soap, fresh milk, condensed milk (95, 96), lime, and flour (67) were among the first emulsifiers used in the preparation of stable emulsions. Emulsions of soap and kerosene, which were only temporary, were recommended as early as 1871 (95, p. 133), but a stable soap-oil emulsion was first prepared in 1882 (96). Milk as an emulsifier was first suggested in 1878 (95). These emulsions were usually prepared by pumping the oil, water, and emulsifier together under pressure through a spray nozzle.

THEORIES OF EMULSIFICATION

An emulsion consists essentially of a suspension of small droplets of one liquid in another. If a small quantity of oil and a slightly

larger quantity of water are shaken together in a test tube, a temporary emulsion is formed, consisting of relatively large globules of oil suspended in water. The oil droplets rapidly rise and coalesce, forming a layer above the water. If a small quantity of hydrated lime is added to the water before adding the oil and the mixture shaken moderately, large globules of oil are again suspended in the water. These rise to the surface; but now each globule may be observed to be surrounded by a film of hydrated lime, which keeps the droplets of oil from touching one another and coalescing. If the tube is now shaken very vigorously, the oil is found to be dispersed in rather fine globules, which remain suspended uniformly throughout the water for a long period; and occasional detached globules of oil may be seen on the sides of the tube above the emulsion, each surrounded by a white layer of lime.

This experiment demonstrates the essential features of the formation of oil-in-water emulsions. They consist merely in the breaking up of the oil into globules sufficiently small to remain suspended uniformly throughout the water for a reasonable time, and the addition of a stabilizer, or emulsifier, which forms a protective film around the dispersed oil droplets, thus preventing their coalescence. These oil droplets carry a negative electrical charge (46; 48, p. 147), and this is probably largely responsible for their remaining uniformly suspended throughout the emulsion.

With the use of a different stabilizer, an emulsion of water suspended in oil may be formed. A number of theories have been advanced to explain why some emulsifiers tend to cause the formation of oil-in-water emulsions, while others lead to the suspension of water in oil. These will be briefly mentioned.

"EASE OF WETTING" THEORY

According to Bancroft's rule, emulsifiers more easily wetted by water favor the formation of oil-in-water emulsions, whereas those more easily wetted by oil favor the formation of the water-in-oil type. To act as an emulsifier, the material must collect on the interface between the two liquids. This means that the material must be wetted by both liquids. The liquid having the greater affinity for the emulsifier and wetting it the more rapidly will therefore tend to form the outer or continuous phase of the emulsion (32).

ORIENTED-WEDGE THEORY

When a soap emulsifier is used, it has been believed that the soap forms a film approximately one molecule thick between the oil and water (43, 44). It has also been claimed that the molecules are definitely oriented, the hydrocarbon chain being turned toward the mineral oil and the metallic end of the soap molecule toward the water, the general rule being that each end of the molecule faces the liquid which it most closely resembles. As the cross section of the sodium or potassium atom of the soap is much greater than the cross section of the hydrocarbon chain, the geometric shape of the soap molecule approximates a wedge. Since the larger end (of soaps of monovalent metals) is the one soluble in water, oil would become the inner or dispersed phase, yielding an oil-in-water type of emulsion.

In the case of soaps of the bivalent metals, such as calcium or magnesium soaps, one atom of the metal is combined with two hydrocarbon chains. Consequently, in this case the hydrocarbon end of the wedge is the larger, and this would tend to the formation of a water-in-oil, or reversed type of emulsion (13, 32, 51, 60, 71).

This theory does not offer an explanation of those emulsions formed with inert emulsifiers such as kaolin, bentonite, and charcoal, and has been objected to upon other grounds (103, 107, 108). The "ease-of-wetting" theory offers a more generally applicable explanation. However, it may be well to recall here the fact, generally known to all those who have made or attempted to make emulsions, that the type of emulsion secured depends very largely upon the manipulation of the various ingredients. A potash fish-oil soap made by the cold-stirred method (93) may make an excellent reversed, or water-in-oil emulsion, unless directions are closely followed. The Missouri calcium-caseinate formula (7, 8), as many know, will give either type of emulsion, depending upon the sequence in which the ingredients are mixed.

It has been reported (100) that asphalt-base oils were more easily emulsified than those from a paraffin base. No such difference could be detected in the oils used in these experiments.

VARIOUS EMULSIFIERS USED

As the oil-in-water type of emulsion is the only kind used as an insecticide, subsequent references to emulsions will refer only to this type. A large number of emulsifiers have been used, and these will be briefly mentioned. For convenience these will be divided into soap and nonsoap emulsifiers.

SOAP EMULSIFIERS

As a general rule potassium soaps are used, as they form soft soaps that are easy to handle (18) and appear to make a more permanent emulsion. Sodium soaps are also used to some extent, especially as emulsifiers for miscible oils.

A number of animal oils have been reported in literature as suitable for the manufacture of soap emulsifiers. The most common, as well as the cheapest, is fish oil, which was recommended (86) as early as 1906. Red oil (86) and whale oil (120) were also recommended. Vegetable oils have been tried and were considered unsatisfactory by Penny (86), and satisfactory by Chandler, Flint, and Huber (9). Sodium and potassium salts of stearic, palmitic, linoleic, and linolenic acids (60, 65) have given good results.

During the course of the present investigation a number of vegetable oils were tested in the laboratory both in regard to their adaptability for soap making and to the emulsifying power of the soaps made with them. The saponification numbers of the oils were determined, and their soaps were prepared by boiling them with the required quantities of caustic potash.

The saponification numbers, that is the number of milligrams of potassium hydroxide required to saponify 1 gram of the oil, obtained by the official method of the Association of Official Agricultural Chemists for the oils used in the tests, are as follows:

Crude cottonseed oil.....	188.
Crude corn oil.....	188
Crude peanut oil.....	190
Crude soybean oil.....	190
Green olive-oil foots.....	191
Crude red oil.....	202
Crude palm oil.....	245
Crude Manila coconut oil.....	255

Coconut oil, peanut oil, soybean oil, corn oil, and, to a less extent, palm oil were hard to saponify completely, as they required long boiling. Coconut and palm oils have the additional disadvantage of being solid at ordinary temperatures and are therefore harder to handle.

Cottonseed oil, olive-oil foots, and red oil made good soaps. The cottonseed-oil soap proved to be the best emulsifier and was equal to fish-oil soap, both for use by the Government's standard boiled formula and for the making of cold-stirred emulsions. Its emulsifying power is reduced when a large excess of potassium hydroxide (more than 1 pound excess to 10 pounds of cottonseed oil) is used in the saponification. This soap was also tried out successfully on a commercial scale for the manufacture of emulsions according to the Government's standard boiled formula.

The red-oil boiled soap was only a fair emulsifier. It was found, however, that a soap which was an excellent emulsifier could be made by stirring this oil with potassium hydroxide without the use of heat. The use of an excess of potassium hydroxide and long-continued boiling practically destroyed its emulsifying power. This may have been due to the splitting of the molecule in the presence of alkali, as it is well known that oleic acid may be oxidized by fusion with caustic potash to palmitic and acetic acids, both of which are poor emulsifiers. Or it may have been due merely to the complete saponification of all the fatty acids present, as it has been shown that the presence of free fatty acids aids in emulsification (70). It may be well here to call attention to the observation of Mead and McCoy (73) that sodium-oleate solutions "age" markedly, and may then form a reversed, or water-in-oil emulsion, instead of the usual type. They believed the change due to reaction with some atmospheric constituent.

The soap from green olive-oil foots was inferior to fish-oil soap as an emulsifier, although it could be used. Probably other grades of this oil would prove much more satisfactory.

NONSOAP EMULSIFIERS

Salts of the naphthenic acids resemble soaps and make good emulsifiers (48, p. 146). Salts of the sulphonic acids and their derivatives are also good emulsifiers and are used to some extent for this purpose (60; 83, p. 769; 102).

Milk was used as an emulsifier as early as 1878 (94, 95). Lime, plaster of Paris, flour, precipitated chalk, silica, alumina, Bordeaux mixture, ferrous sulphate and lime mixture, glue, egg albumin, saponin, basic sulphates of iron, copper, and nickel, ferrous hydroxide, copper carbonate, calcium carbonate, calcium arsenate, lead arsenate, and fine clays were listed by Pickering (90) as early as 1907. Among the fine clays, kaolin (123) and fuller's earth have been spe-

cifically recommended, and bentonite (28) has been tested. A mixture of casein and lime, commonly called "calcium caseinate," was recommended (7, 8) in 1923, and has become probably the most widely used of any of the nonsoap emulsifiers.

TYPES OF EMULSIONS AND METHODS OF MANUFACTURE

For convenience in discussion, emulsions will be divided into groups based upon the method used in their manufacture. According to this scheme, they will be divided as follows: Hot-pumped, cold-stirred, and cold-pumped emulsions and miscible oils.

HOT-PUMPED, OR BOILED, EMULSIONS

Soap emulsifiers are used for making hot-pumped, or boiled, emulsions. The emulsion made by the standard Government formula is an example of this type. Practically all these formulae recommend the use of 1 pound of soap to each gallon of oil, but where the water to be used in spraying is very soft, half this quantity of soap is sufficient. The method of manufacture consists in mixing the oil with approximately half its volume of combined soap and water, bringing the mixture to a boil by the application of heat, and pumping it while still hot through fine nozzles at a pressure of from 200 to 400 pounds. The mixture is heated directly over the fire in the case of small batches, and by the use of steam in the case of large batches. The steam heat is applied either in closed coils around the jacketed cooking vessel or by allowing the live steam to rise through the mixture from perforated pipes in the bottom of the kettle. In the latter case less water is initially added to the batch.

These emulsions have the advantage of practically never failing to "make," and of remaining stable for relatively long periods (approximately one year). Their disadvantages lie in their higher cost due to the necessity of heating and to the higher price of the equipment necessary for their manufacture.

COLD-STIRRED EMULSIONS

Cold-stirred emulsions are also formed by using soap as an emulsifier. They differ from the hot-pumped emulsions only in the method of manufacture which requires neither unusual heat nor pumping. They were first used by Hubbard (95), and later described by Yothers (120). The method was recommended in a modified form by Whitcomb (115) and Richardson and Griffin (93).

The method of manufacture consists in repeatedly adding small quantities of oil to the soap, and thoroughly stirring in each addition of oil before the next is added.

After the required quantity of oil is thus worked in (usually 1 gallon of oil to each pound of soap), a stiff jellylike mixture is formed. Water is then slowly added, with constant stirring, till the finished emulsion contains 66 $\frac{2}{3}$ per cent of oil by volume. This is the standard oil content for commercial emulsions. If a good soap has been used, and the mixture thoroughly stirred, this emulsion is nearly as stable as one made by the hot-pumped formula.

Its advantages lie mainly in the cheapness of the equipment required for manufacture and in the fact that the use of heat may be practically dispensed with. There are, however, a number of disadvantages.

The dispersion of the oil droplets here depends upon the attraction between the soap and oil, and upon the shearing action due to stirring. This shearing action in turn depends upon the viscosity of the soap used. Too thin or too viscous a soap will not make this type of emulsion. Factors influencing the viscosity of the soap will therefore influence the quality of the emulsion secured. The main factors influencing the viscosity of the soap made from any one oil are the moisture content, the quantity and kind of caustic used to saponify the oil, and the temperature. These will be briefly discussed.

Soda soaps are as a rule too stiff to make this type of emulsion at all, though some make it very poorly. Potash soaps are used almost entirely. The use of an excess of caustic potash above that required for saponification results in a much stiffer soap, and in case such an excess is used the soap should have a higher moisture content. This is illustrated by the series of tests, reported in Table 2, with the use of a cold-stirred soap-oil emulsion (93). Results with a soap-cresol (93) emulsifier are also shown for comparison. A soap made with only a slight excess of caustic potash and having a moisture content of from 60 to 75 per cent was found to make the best emulsion. A very large excess of potassium hydroxide (2 pounds excess to 10 pounds oil) largely destroyed the emulsifying power of fish-oil soap for this type of emulsion.

TABLE 2.—Effects of moisture and excess potassium hydroxide in potash fish-oil soap upon its value for making cold-stirred emulsions. Temperature 50° F.

Emulsion	Type of emulsion secured when moisture content of soap was—					
	50 per cent		75 per cent		85 per cent	
	No excess of potassium hydroxide	Excess of potassium hydroxide ¹	No excess of potassium hydroxide	Excess of potassium hydroxide ¹	No excess of potassium hydroxide	Excess of potassium hydroxide ¹
Soap-oil.....	Very good emulsion.	Failed.....	Good emulsion.	Failed.....	Good emulsion.	Good emulsion.
Soap-cresol oil.....	do.	Very good emulsion.	do.	Very good emulsion.	Fair emulsion.	Do.

More than 1 pound excess potassium hydroxide to 10 pounds of fish oil.

Temperature has a great influence upon the viscosity of the soap, and a soap which will make an excellent cold-stirred emulsion at a temperature of 60° F. may be too stiff and fail completely at 40° or lower. A stiff soap may be made sufficiently fluid by the addition of small quantities of water or by heating. The addition of small quantities of water does no harm, but larger quantities result in the production of an unstable emulsion. Heating a stiff soap to approximately 125° was found to be the best method of rendering it sufficiently fluid readily to emulsify the oil.

Even with a fluid soap, difficulty was often experienced in making the emulsion at temperatures below 40°. Apparently the attraction between the oil and soap is insufficient at low temperatures for the soap to properly coat the oil particles. In such cases emulsions could be made after heating the soap to approximately 125°.

Very thorough stirring is essential to the production of a stable emulsion by this method, as is shown in Table 3.

TABLE 3.—Effect of stirring upon the size of oil droplets in a cold-stirred emulsion

Degree of stirring	Size of oil droplets			Stability
	Range	Mode	Average	
Oil completely stirred in after each addition.....	Microns 2 to 60	Microns 12	Microns 20	Unstable.
Oil completely stirred in and stirring continued until maximum stiffness was secured after each addition of oil.....	2 to 15	7	7	Stable.

Occasionally a cold-stirred emulsion will not only fail to "make," but will form a reversed emulsion. In such cases, Richardson and Griffin (93) state that it is necessary to start over again, using half the original quantity of emulsifier and stirring in the reversed emulsion in the same manner as the original oil.

With the use of the proper soap, and at temperatures between 50° and 80° F., very good cold-stirred emulsions may be manufactured. The use of "stabilizers" with the soap will greatly increase the stability of the resulting emulsion and the ease with which it can be made. These stabilizers are added directly to the soap, with constant stirrings, just before the oil is added; and appear to act by rendering the soap somewhat more fluid and to some extent as a mutual solvent for soap and oil, thus bringing the two into more intimate contact.

Amyl alcohol was recommended by Whitcomb (115) for this purpose and crude cresylic acid, cresol, and cyclohexanol by Richardson and Griffin (93).

The writers made a series of laboratory tests of alcohols, ethereal oils, fatty acids, phenols, and miscellaneous compounds as stabilizers. Of these, methyl and ethyl alcohol appeared of slight benefit for use with stiff soaps; butyl alcohol (both normal and tertiary) proved equal to either amyl alcohol or cresylic acid.

Oleic acid, or red oil, greatly improved the emulsion if the fish-oil soap contained an excess of caustic, but was worthless in the absence of free alkali. Other materials tested were of no value. Experiments with red oil indicated that this material acted by forming with the free alkali a cold-stirred potassium oleate soap. The fish-oil soap was therefore omitted, and the red oil added directly to a solution of caustic potash and stirred until a uniform consistency was obtained. The lubricating oil was then added, the mixture being stirred the meanwhile as described above. This was found to form a very good emulsion, approximately equal in stability to that made by the Government's standard boiled formula. Directions for making this emulsion are as follows:

Red-oil emulsion.—To 3 pints of water, add one-third pound of caustic potash. When dissolved, add 1 quart of red oil (oleic acid) and stir the mixture thoroughly until the soap formed is of uniform consistency. Add the lubricating oil slowly at intervals, until a total of 10 gallons has been emulsified, no addition being greater than one-third, and preferably only one-fourth, the volume of the mixture to which added. Stir thoroughly after each addition until maximum stiffness has been secured. After all the oil has been worked in, dilute slowly with water, stirring constantly, till the total volume equals 15 gallons.

The advantages of this emulsion are its cheapness and the fact that boiled soap is not required, thus doing away entirely with the need of heat for producing the emulsion. It has the same disadvantages as the other cold-stirred emulsions.

COLD-PUMPED EMULSIONS

As a rule, nonsoap emulsifiers are used in preparing cold-pumped emulsions, although soaps have been used (120). This method of making emulsions for insecticidal purposes is apparently among the earliest used (94). It consists simply of adding the emulsifier to the water, then adding the oil, and pumping the mixture under pressure out through a fine opening. It is usually repumped once or twice. The most common emulsifier used is calcium caseinate, the use of which has been noted by many writers (4, 7, 8, 9, 26, 57, 76)⁵; Bordeaux mixture (49) and kaolin (126) are also used to a lesser extent. Other emulsifiers have been previously listed (p. 15). These emulsions are cheap and are easily made on the farm with the ordinary power spray outfit. The mixture is emulsified by pumping three times through the spray rods at a pressure of from 150 to 275 pounds. This gives an emulsion which will hold up for from several days to several weeks, depending upon the pressure employed. By the use of higher pressures and the addition of a preservative, where protein or fermentable emulsifiers are used, emulsions may be produced equal in stability to the Government's standard boiled emulsion. Homogenizers using pressures of over 1,000 pounds per square inch, and colloid mills have also been employed for the commercial production of emulsions of this type.

The calcium caseinate emulsifier is formed by mixing casein and hydrated lime in the approximate proportion of 1 to 4. Casein is the active emulsifier, the lime being added merely to make the casein soluble in water, as it is soluble in an alkaline solution, but insoluble in a neutral one. Occasionally an old sample of calcium caseinate will fail to emulsify the oil. It has been found that this is because the lime has been converted into calcium carbonate by the carbon dioxide in the air, and its alkalinity thus destroyed. After the addition of fresh hydrated lime, no further difficulty is experienced.

MISCIBLE OILS

Miscible oils differ from the previously described emulsions in that the emulsifier is dissolved in the oil and that they contain only a relatively small quantity of water (usually less than 10 per cent). They have the appearance of a clear or slightly cloudy oil, but when water is added and the mixture agitated a white emulsion is formed.

⁵ LEBBY, R. W., and HARRIS, J. A. Op. cit. (See footnote 4.)

The active ingredient, as well as the principal one, in miscible oils is mineral oil. The following classes of emulsifiers may be used (5, 52):

- (1) Saponified rosin, oleic acid, or other fatty acids with more or less alcohol.
- (2) Sulphonated mineral oil with an alkali.
- (3) Sulphonated animal or vegetable oils and an alkali, with or without alcohol.
- (4) Soaps dissolved in phenols.

A small quantity of alcohol is usually added to make the hydrated soap dissolve readily in the oil. This usually results in a cloudy mixture, and just sufficient oleic acid is then added to clear the solution. Increasing beyond this the quantity of oleic acid decreases the stability of the emulsion which results upon dilution with water. It would appear likely that this method might be used to decrease the permanency of miscible-oil emulsions and thus increase their toxicity to insects.

The advantages of miscible oils are their low water content, which reduces freight and drayage charges, and their resistance to low temperatures. Their main disadvantage is their considerably higher cost as compared with oil emulsions, which is due to the kind and quantities of emulsifiers necessary for their production.

A large number of formulas for miscible oils (18, 66, 67, 74, 76, 86, 87, 88) and several general discussions of the principles involved in their manufacture (52, 73) have been published. A discussion of sulphonated oils has been given by Wennström (114).

METHODS OF ANALYSIS OF OIL EMULSIONS

As oil is the active ingredient in emulsions, methods for its determination are necessary for the proper evaluation of various commercial preparations. The oil content is expressed as the percentage of oil by volume. While no definite temperature has been adopted, this is generally supposed to be determined at room temperature (approximately 20° C.).

Methods for the determination of the oil content of emulsions have been suggested by Graham (39) and by Griffin and Richardson (45). The methods used were briefly as follows:

Water was removed and determined by distillation, the soap by extraction with alcohol, and the mineral oil found by difference. This was checked by recovery of the oil from an alcohol-ether extract.

The emulsions with soap emulsifiers were broken by shaking with dilute acid, and the separated oil measured directly.

Emulsions with gum emulsifiers were broken by shaking with alcohol and sodium carbonate.

As these methods are unsatisfactory for some types of emulsions, certain other methods which proved of value at this laboratory are given.

The calcium-caseinate emulsion may be analyzed for oil as follows: Add an equal volume of ether and approximately half that quantity of 20 per cent sodium hydroxide to 10 c. c. of the emulsion in a separatory funnel. Shake vigorously and allow to stand till the layers separate; the oil will be dissolved in the ether. Separate the layers and evaporate away the ether on a hot-water bath. Measure

the oil in a 10-c. c. graduate, having 0.1-c. c. subdivisions. Usually one extraction with ether is sufficient to remove all the oil.

Other emulsions may be broken by repeated ether extractions; by the application of heat, followed upon cooling by ether extraction; or by shaking with a combination of ether and acid or alkali. In the latter case, where acid is used, a correction must be applied for fatty acids if the emulsifier was a soap.

FREEZING POINTS OF OIL EMULSIONS

As has been stated, miscible oils are very resistant to freezing owing to the small quantity of water present. As ordinary oil emulsions contain over 30 per cent of water they are much more liable to injury by freezing. Apparently no data exist in the literature upon this subject, and statements as to the freezing point of the Government's standard formula emulsion vary from 15° F. (3, 63) to "only a little below that of water" (91). Experiments were conducted on a series of oil emulsions to determine the point to which they could be undercooled and also their true freezing points. All the ordinary precautions were observed which are used in freezing-point determinations. The undercooling point was taken as the lowest temperature to which the emulsion could be cooled, without stirring and in the absence of ice crystals, before freezing began. The true freezing point was determined upon new samples, crystallization being induced by seeding with an ice crystal at the approximate freezing point in one sample and by vigorous stirring in another.

The following list shows the true freezing points determined for a number of emulsions, all of which contained 66 $\frac{2}{3}$ per cent of oil by volume, all the soap used containing 67.07 per cent of moisture:

Type of emulsion	°F.
Commercial boiled emulsion, Government standard formula, sample No. 1.	31.3
Commercial boiled emulsion, Government standard formula, sample No. 2.	31.1
Cold-stirred emulsion, 1 pound soap to 1 gallon oil. Oil of 125 seconds viscosity	30.9
Cold-stirred emulsion, 1 pound soap to 1 gallon oil. Oil of 220 seconds viscosity	30.9
Cold-stirred emulsion, one-half pound soap to 1 gallon oil	31.5
Cold-stirred emulsion, 2 pounds soap to 1 gallon oil*	29.7
Cold-stirred soap-cresol (93)	30.4
Cold-stirred amyl alcohol-soap (115)*	30.0
Cold-stirred butyl alcohol-soap	29.5
Cold-stirred red-oil	31.8
Cold-pumped calcium-caseinate formula (7)	31.8
Soap solution; 1 pound soap diluted to one-half gallon with water	30.9
Water used in above emulsions	32.0

The true freezing point, as here shown, is the average of three determinations in none of which the emulsion was allowed to undercool more than 1° F. Apparently the ordinary oil emulsions can not be undercooled below 17° or 18° F. before freezing begins. The true freezing point is, as stated by Porter (91) only slightly below that of water. Apparently the freezing point of an emulsion depends entirely upon the kind of emulsifier used, and upon its concentration. The viscosity of the oil had no effect between the limits

* Could be undercooled to 17.6° F. Other emulsions could be undercooled only to 18.3° F.

ordinarily occurring in oils used in the making of lubricating-oil emulsions.

Samples of oil emulsions were frozen solid, without being stirred, and allowed to sit undisturbed till completely thawed out. The emulsions were not broken down or deteriorated in any manner by this treatment. If stirred vigorously while freezing or thawing, a considerable quantity of oil was freed. Apparently the best thing to do with a frozen emulsion is to leave it undisturbed until it is completely thawed out, as is ordinarily recommended.

EFFECT OF HARD WATERS ON VARIOUS EMULSIONS

The great majority of commercially manufactured emulsions contain a sodium or potassium soap as an emulsifier. These soaps react with calcium or magnesium in hard water, giving a calcium or magnesium soap which is insoluble in water, whereupon the emulsion may be broken down and the oil liberated. The liberated oil rises to the surface of the water in the spray tank, and the last trees sprayed are likely to receive an application of pure oil, causing severe injury, whereas other trees receive too little oil for effectiveness against insects.

Though few waters in central Georgia are sufficiently hard to break down an emulsion completely within the short time necessary to spray out the tank of diluted emulsion (approximately one and one-half to two hours), nevertheless considerable annoyance is caused by the insoluble soap plugging the nozzles. It was found that the violent agitation taking place in the spray tank speeded up the reaction between the hard water and soap and also by its churning action caused the insoluble soap particles to conglomerate into lumps. By removing the agitator chain on the spray outfit trouble of this kind was greatly reduced or entirely eliminated when the Government-formula soap-oil emulsion was used with water having a hardness equivalent to 175 or 180 parts of calcium carbonate per million parts of water. Sufficient agitation is secured from the vibration of the engine and pumps and from the movement of the spray outfit through the orchard to keep the ordinary diluted emulsion uniformly distributed throughout the spray tank. This was shown by testing the oil content of the spray collected from spray rods when the tank was full and again just before it was empty. The data of this test are given in Table 4.

TABLE 4.—Homogeneity of oil emulsion¹ spray in tank with and without the use of an agitator

Treatment of emulsion	Oil content of spray collected from spray rods—	
	When tank was full	When tank was nearly empty
With agitator running.....	Per cent by volume 3.15	Per cent by volume 3.17
Without agitator.....	3.10	3.30

¹ Government's standard boiled emulsion.

An emulsion resistant to hard water may be made by using an excess of soap (122), or a soap containing an excess of free alkali. This free alkali appears to act by reducing the ionization of the soap (43, 77), and probably also that of the calcium or magnesium salt contained in the hard water.

Yothers and Winston (125) recommend the use of the following materials for the stabilization of soap-oil emulsions mixed with hard water: Caustic soda, glue, milk, skim-milk powder, gelatin, corn meal, casein, wheat flour, cornstarch, and laundry starch. The last three should be boiled before being added to the emulsion. These stabilizers should be added to the concentrated emulsion, just before dilution in the spray tank, in the approximate proportion of 1 pound to each 3 gallons.

The nonsoap emulsifiers, with the possible exception of the sodium and potassium salts of the naphthenic and sulphonic acids and their derivatives, are generally considered resistant to hard waters. Where very hard waters must be used in spraying, the emulsifiers commonly used are calcium caseinate, kaolin, Bordeaux mixture, and starch or dextrin. The casein-lime mixture, or calcium caseinate, is the one most generally used.

In this connection Eyer and Robinson (31) have reported that the calcium-caseinate emulsion is unstable in the presence of magnesium sulphate and that oil may be freed.

The presence of sulphur (53) has been reported as preventing emulsification of an oil with Bordeaux mixture.

EFFECT OF MINERAL OILS UPON INSECTS

Considerable study has been made of the manner in which mineral oils kill insects, although most of it has been merely of a preliminary or fragmentary nature. A brief summary of this work will be given.

Scheifele (101) stated that it is known that oils do not act upon insects through the respiratory system. This conclusion is the direct opposite of that of all others whose work was reviewed.

Shafer (104) studied the action of kerosene and gasoline upon several insects and came to the conclusion that though both penetrated a short distance into the larger tracheae death was caused by the toxicity of their gases which apparently prevented the absorption of oxygen by the tissues. He decided, however, that death was not caused by suffocation, since the insects died more rapidly than when immersed in water or in an atmosphere of pure hydrogen. He also found that both oxygen and carbon dioxide could pass through a thin layer of kerosene.

Vickery (110) also concluded that the toxicity of petroleum oils was due to the vapor or gases given off. He reported that these vapors greatly stimulated the production of oxidizing enzymes by the oenocytes, which are ductless glands in contact with the tracheae, and that this increased the rate of oxidation within the insect to such an extent as to cause death.

Moore (78) immersed larvae of the wax moth in oils, and upon removal found that the tracheae were blocked and concluded that death resulted from suffocation. In another paper he and Graham

(80) concluded that lubricating oils penetrated the tracheae for short distances.

The effect of highly refined lubricating oil upon mealy bugs and scales was studied by De Ong, Knight, and Chamberlin (26). They found that oils and oil emulsions completely filled the tracheae when the insects were immersed in these fluids. Kerosenes penetrated the tracheae, but were sufficiently fluid to be expelled by the scale; and, after their expulsion, the insect was able to prevent further entrance for a considerable period. Lubricating oils were not expelled, probably owing to their higher viscosities. They also found that mealybugs died more rapidly when immersed in water than when immersed in oil. As a result of these studies they concluded that the death of scale insects through the action of at least refined lubricating oils was due to suffocation. English (29) also concluded that the lubricating oils produce death by suffocation.

Nelson (82) found that kerosene penetrated throughout the tracheal system; and, upon long exposures, into the muscles and nerve ganglia.

Parker (84) studied to a small extent the action of oils upon insect eggs and concluded that they caused gradual disintegration of the chitinous covering and coagulation of the embryonic protoplasm.

Oils have also been reported (53, 54, 98) to be of some value as repellents for certain insects, preventing egg deposition.

CHEMICAL AND PHYSICAL PROPERTIES REPORTED AS INFLUENCING THE TOXICITY OF OILS TO INSECTS

Viscosity has been considered probably the best index to toxicity of any of the properties of an oil (23, 25, 26, 29) by the majority, but not by all workers (42, 101) upon this subject.

Specific gravity has been reported as a fairly reliable index of toxicity (41).

Volatility (rate of evaporation) is considered of great importance as influencing the permanency of the oil film. This property is related inversely to viscosity.

The effect of the degree of refining, as measured by the sulphonation test, is unsettled. An oil with a low unsulphonated residue was considered somewhat more toxic to scales by De Ong, Knight, and Chamberlin (26) and English (29), while the latter considered it of minor importance in toxicity to aphids.

The nature of the crude-oil base from which the oil was derived was considered of importance by D. D. Penny (89), who found those from a paraffin base more toxic to leaf-roller eggs than those from an asphalt (naphthene) base. Green (42) and Neller (81) found those from both sources of equal toxicity to the San Jose scale and to leaf rollers.

DETERMINATION OF THE EFFECTIVENESS OF A SPRAY AGAINST THE SAN JOSE SCALE

The method most commonly employed in determining the toxicity of oil sprays to the San Jose scale is to compare the percentage dead upon a sprayed plat and an unsprayed check one month after treat-

ment of the former? Davis (14) and Abbott (2) have suggested that these results may be further checked by subsequent counts of the number of new scales on a given length of new twig growth the following spring, and of the number of infested fruits at harvest (14). By using these additional checks Abbott (2) concluded that mortality records made 30 days after treatment were accurate.

The interval of one month between the time of application and noting the results introduces more or less error into the method, owing to deaths from natural causes. Theoretically, this is taken care of by the use of unsprayed checks, but practically, it is usually not possible to have sufficiently large sprayed and check plats for the checks to represent accurately the sprayed plats. The error introduced, however, is apparently not large.

SELECTION OF PLATS AND TREES AND METHODS OF MAKING THE TESTS

A brief description will be given of the methods used in this study for the selection of plats and count trees, and those used in taking the results.

Peach orchards throughout the central Georgia peach belt were inspected for the presence of San Jose scale, and one was selected for use which had an average of at least 1 tree in every 10 heavily infested. As a rule, trees sufficiently infested for use as count trees are not more common than this. It was necessary, therefore, to use approximately 50 trees for each plat. Heavily encrusted or otherwise severely devitalized trees were not used, as they were likely to die before the close of the experiment. The block of trees selected was gone over, each tree examined and mapped, and those with sufficient infestation to be used as count trees indicated. This map was then divided into plats, each plat containing at least 5, or possibly more, infested trees. Five trees in each plat having the heaviest infestation of live scales were then selected as count trees from which records were to be taken.

Samples of infested twigs, each about 1 foot long, were then taken from the count trees. These were tagged with their respective numbers and taken into the laboratory, where counts were made. Unsprayed check trees were located at random throughout the plats.

All counts, both before and after spraying, were made by the same man to eliminate the personal equation. Two hundred scales were counted at random upon each twig over a linear distance of approximately 8 inches where possible. Care was taken to see that the twigs and scales were dry before being examined (61). These counts were made under a binocular, each scale covering being removed and those dead recorded. This gave a total of 1,000 scales examined for each plat.

All count trees upon which less than 40 or 50 per cent of the scales were alive were discarded as record trees and others substituted where possible. This was done since, if only a small number of scales are alive at the beginning of the experiment, undue weight will be given in percentage control because of the few which, owing

¹ LEIBY, R. W., and HARRIS, J. A. Op. cit. (See footnote 4.)

to resistance to, or protection from, the spray applied, remain alive through the treatment.

All trees in each plat, with the exception of the checks, were thoroughly sprayed the day following that upon which these counts were finished. One month later samples were again taken from the same trees, and counts made exactly as before.

METHODS USED IN COMPUTATION OF PERCENTAGE CONTROL

The following formula was recommended by Abbott (1) for the computation of percentage control:

$$\text{Percentage control} = \frac{x-y}{x} \times 100.$$

when x = percentage living in the check.

y = percentage living in the treated plat.

This formula is rather generally used, but is objectionable for the reason that it is practically impossible under ordinary conditions to have plats large enough for the checks to represent accurately conditions throughout the experimental plats. Great variation also in the percentage alive occurs from tree to tree and from plat to plat at the beginning of the experiment.

In some cases the following formula gives more accurate results, as it compensates for this variation:

$$\text{Percentage control} = \frac{x-z}{x} \times 100.$$

when x = percentage alive in the plat before treatment.

z = percentage alive in the plat after treatment.

In the case of scale experiments, however, where the percentage alive is determined one month after treatment, this second formula often does not give accurate results because of a high natural mortality due to predators, parasites, low temperatures, and other factors, and because of the production of young scales by any females left alive.

To compensate for heterogeneity, for natural mortality, and for natural increase, the following formula has been adopted:

$$\text{Percentage control} = \frac{ax-z}{ax} \times 100.$$

where a = percentage alive in checks at the close of the experiment divided by percentage alive in checks at the beginning of the experiment.

x = percentage alive in plats before treatment.

z = percentage alive in plats after treatment.

This would perhaps tend to give a low value, as the number of scales killed by predators is probably larger on the unsprayed checks than on the treated plats. It is believed, however, that the last formula should be the most accurate of those given, and by its use closely agreeing results were secured in spray experiments over a 3-year period. In its application the probable error was determined by the Bessel formula.

RESULTS OF FIELD EXPERIMENTS AGAINST THE SAN JOSE SCALE

TYPE OF EMULSION USED IN EXPERIMENTS

The Richardson-Griffin (93) cold-stirred soap-oil emulsion was used throughout these tests, as this type is easily made up in small batches and is practically identical with the Government's standard formula for boiled emulsions. One pound of potash fish-oil soap with moisture content of 67 per cent was used as an emulsifier to each gallon of oil. By stirring after each addition of oil until maximum stiffness was attained, fairly uniform emulsions were secured throughout the range of viscosities used. The size of the droplets ranged from 1 to 17 μ , with modes of from 6 to 7, and averages of from 4 to 6 μ .

RELATION OF PHYSICAL AND CHEMICAL PROPERTIES OF OILS TO TOXICITY

Analyses of various oils and the results of field tests over a 3-year period are given in Table 5.

TABLE 5.—Experiments on the toxicity of various oils¹ to the San Jose scale on peach trees, Fort Valley, Ga., 1926-1929

Oil No.	Viscosity (Saybolt, at 100° F.)	Density at 20° C.	Flash point	Fire point	Un-sulpho-nated residue	Volatility (four hours at 105° C.)	Apparent base	Per cent control obtained by dilutions of—			Season of experiment
								1 per cent	2 per cent	3 per cent	
	<i>Secs.</i>	<i>Gram per cubic centimeter</i>	<i>° F.</i>	<i>° F.</i>	<i>P. c.</i>	<i>P. ct.</i>					
1	47	0.847	276	300	74.0	4.18	Paraffin			0.0	1927-28
2	76	.873	325	365	68.8	1.50	do			96.33±0.52	1926-27
3	78	.882	345	395	64.0	.04	Intermediate			98.11±3.3	1927-28
4	79	.887	349	414	62.0	.93	do		91.4±2.7		1928-29
7	102	.920	312	346	52.0	1.75	Naphthene			97.16±0.95	1927-28
9	105	.884	365	420	64.8	.80	Paraffin			99.88±1.84	1926-27
16	113	.886	374	428	63.0	.57	Intermediate		92.2±2.4		1928-29
12	124	.889	365	412	60.0	1.21	Paraffin		93.8±1.0		1926-27
13	137	.924	325	360	59.0	.08	Naphthene			99.25±0.40	1928-29
15	147	.890	300	435	66.0	.10	Paraffin	74.94±1.29		99.12±0.34	1927-28
18	168	.895	404	451	61.0	.60	Intermediate			99.40±0.2	1926-27
19	196	.898	387	449	60.0	.35	do		94.57±3.2		1928-29
20	187	.892	405	450	68.0	.20	Paraffin		96.50±1.0		1928-29
21	200	.895	422	474	62.0	.22	do			99.26±0.24	1926-27
25	220	.920	428	495	60.0	.11	Intermediate			97.70±0.3	1928-29
33	308	.904	440	495	51.0	.06	Paraffin			94.06±0.9	1928-29
										99.55±0.22	1926-27

¹ All analyses of these oils were made by the U. S. Bureau of Chemistry and Soils.

The viscosity of an oil appears to be the most accurate measure of its toxicity when used as a dormant spray for the control of the San Jose scale. When used at a per cent strength, the coefficient of correlation between viscosity and toxicity is +0.929 for a range in viscosity of from 79 to 220 seconds. At a 3 per cent strength, in the range of 76 to 124 seconds, the coefficient of correlation is +0.974; but oils of higher viscosity showed no further increase in toxicity within the range of from 124 to 308 seconds. An oil of 47 seconds' viscosity gave no control.

For commercial spraying, where 3 per cent spray is ordinarily used, an oil having a viscosity (Saybolt at 100° F.) of less than approximately 125 seconds is therefore not recommended. It will be noted (53, 91) that workers farther north have found oils with viscosities as low as 90 seconds quite effective. As viscosity decreases with increase in temperature, the warmer winter climate in middle Georgia may be responsible for the higher viscosity required here. The dormant spraying is usually done here during December and January. The average of the mean monthly temperatures of these months, for the 3-year period during which these investigations were conducted, was 49.3° F.

Volatility (loss during four hours at 105° C.) up to 1.75 per cent is apparently no measure of toxicity when oils of sufficiently high viscosity are used. (Table 6.) Oils of low viscosity (below 50 seconds) are more highly volatile and are less toxic.

The unsulphonated residue may vary widely without indicating differences in toxicity, as is shown in Table 7. The same control was given by oils having no unsulphonated residues and those with residues of 68 per cent.

The base from which the crude oil was derived apparently has no value as a measure of toxicity, as is shown in Table 8. Flash and fire points also offer no indication as to toxicity. Density can not be used as a measure of toxicity; however, the density of oils of the same base appears to give some indication of toxicity.

TABLE 6.—Relation of volatility of oils to control of the San Jose scale on peach trees at Fort Valley, Ga.

Oil No.	Volatility (4 hours at 105° C.)	Viscosity (Saybolt, at 100° F.)	Strength of dilu- tion	Control
	Per cent	Seconds	Per cent	Per cent
2.....	1.60	76	3	95.3±0.5
3.....	.94	75	3	96.1±3.3
7.....	1.75	102	3	97.2±0.9
9.....	.60	105	3	99.0±1.8
12.....	1.21	124	3	99.2±0.4
13.....	.08	137	3	99.1±0.3

TABLE 7.—Relation of unsulphonated residue of oils to control of the San Jose scale on peach trees at Fort Valley, Ga.

Oil No.	Unsul- phonated residue	Viscosity (Saybolt, at 100° F.)	Dilution of spray	Control
	Per cent	Seconds	Per cent	Per cent
19.....	0.0	180	3	99.3±0.2
33.....	51.0	368	3	99.5±.2
13.....	59.0	137	3	99.1±.3
7.....	59.0	102	3	97.2±.0
21.....	62.0	200	2	97.7±.5
4.....	62.0	70	2	91.4±2.7
20.....	68.0	137	3	99.3±.2
2.....	68.8	76	3	98.3±.5

TABLE 8.—Relation between base of crude oil and control of San Jose scale on peach trees at Fort Valley, Ga.

Oil No.	Base of crude oil	Viscosity (Saybolt at 100° F.)	Control
7	Naphthene or asphalt.....	Seconds	Per cent
13	do.....	102	97.2±0.9
9	Paraffin.....	137	99.1±.3
12	do.....	105	96.9±1.8
15	do.....	124	96.3±.4
	do.....	147	99.4±.2

CONCENTRATION OF OIL REQUIRED FOR THE CONTROL OF THE SAN JOSE SCALE

Tests with various concentrations of oil emulsions have been conducted at the Fort Valley, Ga., laboratory on a semicommercial scale since 1922. The average of four years' results against the San Jose scale are given below. All oils used had a viscosity of over 175 seconds.

Oil in emulsion	Per cent control
1 per cent.....	91.0
1½ per cent.....	96.9
2 per cent.....	96.1
3 per cent.....	99.1

Owing to the rapid reproduction of the San Jose scale in the South severe injury may result to the tree and fruit unless practically 100 per cent control is obtained. For this reason, only the 3 per cent dilution is recommended for commercial use. When the trees are heavily encrusted, two applications of a 3 per cent oil spray are usually necessary to clean up the infestation successfully. As a few scales always escape destruction, peach trees, especially those under 6 years of age, should be sprayed yearly as insurance against severe injury.

Old orchards adjoining young orchards must also be sprayed as a protection to the latter. The necessity for this is shown by the following experience gained in 1927: Each tree in a 2-year-old orchard adjoining an old unsprayed orchard was thoroughly examined for scale in the fall, and none could be found. Neither orchard was sprayed that winter. Before the following fall the young trees became heavily encrusted, and 25 per cent of them were entirely killed, apparently having become infested from the old orchard adjoining.

Unfavorable results occasionally followed the use of an oil emulsion in Georgia within the first few years after it was recommended to growers. The main reason for this was found to lie in the fact that many commercially manufactured emulsions contained considerably less oil than was implied by the label. The directions given usually stated that 9 gallons of the concentrated emulsion should be added to 121 gallons of water to secure a 3 per cent spray. To give this strength at this dilution, the stock emulsion must contain 66½ per cent of oil by volume.

Tests made of numerous brands in 1926 showed that the oil content of the stock emulsions ranged from 40.4 to 67.2 per cent, the average being approximately 60 per cent. This resulted in the use of sprays usually containing too little oil for effective results. The oil content of emulsions used in Georgia has now been officially set at not less than 66 per cent oil by volume.

It has been reported by Frost (34) that if the same strength spray was used, a heavy application gave good, and lighter application poorer control of aphid eggs. This undoubtedly also holds good for other insects; and as the application usually made by experimental workers may safely be classed as heavy, whereas those made by growers are generally much lighter, this may also explain why poorer control is often secured by the latter.

EFFECT OF RAIN AFTER APPLICATION

Jarvis (57) stated that if rain occurred before the water in the emulsion on the trees evaporated, respraying would be necessary.

In 1926, 0.76 inch of rain fell less than six hours after the spraying was completed, but no reduction in the control resulted. Practically the same conditions were experienced on several other occasions. After the water has evaporated and the oil has been deposited upon the tree, subsequent rains appear to be without influence upon toxicity, and respraying is then apparently unnecessary.

QUICK-BREAKING VERSUS PERMANENT EMULSIONS

The first emulsions used were mechanical mixtures made by discharging a stream of oil and a stream of water simultaneously through the same nozzle. As these often injured the trees, "permanent" oil emulsions were devised (66, 67, 86, 96), and these have proven the most satisfactory up to the present time.

In 1903 Volck (111) stated that mechanical mixtures of oil and water were replacing the permanent emulsions in California. He claimed that as the former gave up their oil quickly upon reaching the tree they were much more effective and seemed to spread out over a relatively greater surface. He also reported trying out the application of oil by the use of an air blast.

In 1909 Jones (68) used a mechanical or "quick-breaking" emulsion, temporarily emulsified with caustic soda, upon several scale insects and found that it gave poorer control than the more permanent emulsion made with fish-oil soap.

In 1927 De Ong, Knight, and Chamberlain (26) recommended the use of a quick-breaking emulsion made with a casein-lime emulsifier. They made the same claims for it as Volck had previously made for the quick-breaking type, and were able to show that more oil was retained by trees when sprayed with this type of emulsion than when sprayed with the more stable emulsions ordinarily used. By the use of this type of emulsion a lower oil content could be used in the spray with equal effectiveness. They recommended a 2 per cent strength.

An unstable or quick-breaking emulsion differs from the more stable types in that less emulsifier is used, the oil droplets are much

larger, and oil separates from the emulsion much more readily. The emulsion theoretically "breaks" and frees the oil immediately upon being applied to the trees. As oil is the active principle in an emulsion, it therefore becomes immediately available as an insecticide. This, and the fact that much less oil is lost in the drip, or "run-off," from trees is supposed to make this type of emulsion much more effective.

Griffin, Richardson, and Burdette (46) concluded that the size of the oil droplets in an emulsion influenced toxicity to aphids, those with the larger droplets being more toxic. They also found that more oil was retained by plants when the oil droplets were large than when they were small. This they explained by the assumption that plant surfaces tend to repel oil droplets, as both have a negative electrical charge; for, since electrical charge is a surface phenomenon, a small droplet carries a greater charge than a large droplet in comparison to its volume, and the latter would consequently have a much greater chance of adhering to the plant.

English (29) also claimed that a quick-breaking emulsion was the more toxic and that large droplets are an indication of an unstable emulsion, and small droplets of a stable emulsion.

Ginsburg (36) reported that emulsions and miscible oils which, when diluted, gradually liberated oil upon the surface of the liquid, were the most toxic to red-mite eggs. Permanent emulsions gave poorer control, whereas those releasing oil quickly upon dilution were least toxic.

Quick-breaking emulsions can be made, using smaller quantities of any of the previously mentioned emulsifiers than are ordinarily used, this resulting in a less stable emulsion with larger oil droplets.

As the size of the oil globules in various emulsions is considered of some importance, this was measured in the more common types. (Table 9.)

Davey (12) has suggested that the average size of the oil droplets in a permanent emulsion can be measured by the area spread upon the surface of clean water in a manner similar to that used by Langmuir in measuring molecular dimensions. This method would be accurate only upon the assumption that all droplets remained upon the surface of the water in a layer only one droplet deep.

Griffin (44), and Griffin, Richardson, and Burdette (46) measured the droplets directly upon a slide under a microscope. This method was adopted by the present writers because it was simple and reasonably accurate. Each emulsion was diluted to spray strength, mixed thoroughly, a sample placed in a drop of water upon a slide, and spread out into a thin film. Fifty droplets were measured under a microscope upon various portions of the slide and their sizes recorded. Each emulsion was again shaken and a sample taken. This was repeated until a total of 200 droplets had been measured for each emulsion. The sizes of the oil droplets in various types of emulsions and miscible oils are given in Table 9.

TABLE 9.—Size of oil droplets in various emulsions and miscible oils

Type of emulsion	Diameter of oil droplets			
	Maximum	Minimum	Average	Mode
	<i>Microns</i>	<i>Microns</i>	<i>Microns</i>	<i>Microns</i>
Government standard boiled soap-oil emulsion, sample 1.....	8	2	4	4
Government standard boiled soap-oil emulsion, sample 2.....	9	2	3	2
Government standard boiled soap-oil emulsion, sample 3.....	11	2	5	5
Cold-stirred, 1 pound of soap to 1 gallon of oil (125 seconds viscosity).....	17	1	4	6
Cold-stirred, 1 pound of soap to 1 gallon of oil (220 seconds viscosity).....	17	1	6	7
Cold-stirred, ½ pound of soap to 1 gallon of oil (125 seconds viscosity).....	25	1	5	10
Cold-stirred, 2 pounds of soap to 1 gallon of oil (125 seconds viscosity).....	13	1	4	6
Cold-stirred cresol-soap emulsion.....	4	1	1	1
Cold-stirred amyl alcohol-soap emulsion.....	5	(¹)	(²)	(³)
Cold-stirred butyl alcohol-soap emulsion.....	5	1	2	2
Cold-stirred red oil emulsion.....	15	1	2	2
Cold-pumped calcium caseinate (Missouri formula).....	22	3	9	11
Commercial miscible oil, sample 1.....	7	(¹)	2.5	1.5
Commercial miscible oil, sample 2.....	3	(¹)	1	1
California "quick-breaking" emulsion*.....	70	2.5	15	20

¹ Too small for measurement under high power of microscope.

² Less than 1 μ .

* Sample taken as it left the spray rods.

For the cold-stirred emulsions a good soap was used, and they were stirred very thoroughly. This procedure gave approximately the smallest droplets that could be secured in cold-stirred emulsions. The use of a poor soap or less stirring resulted in less stable emulsions with larger droplets. Samples 1 and 3 of the Government's standard emulsion were pumped at a pressure of from 300 to 325 pounds, whereas sample 2 was pumped at a pressure of 350 to 375 pounds. The Missouri emulsion was made at the pressure ordinarily used of 175 to 200 pounds.

The viscosity of the oil apparently may range from 125 to 220 seconds practically without influence upon the size of the oil droplets. According to Huber (62) a reduction in the quantity of emulsifier increases the size of the oil droplets and decreases the stability of the emulsion.

When cresol or amyl or butyl alcohols are used with soap in the production of cold-stirred emulsions, the size of the oil particles is approximately the same as that of miscible oils.

RESULTS OF TESTS WITH QUICK-BREAKING AND PERMANENT EMULSIONS

In Table 10 are given the results of tests with a number of emulsions having oil droplets of varying sizes. Emulsions the average sizes of whose oil droplets ranged from 1 μ to 9 μ showed little difference in toxicity in field tests. A quick-breaking type of emulsion where the oil droplets had an average size of 15 μ was somewhat more effective than the much more stable red-oil emulsion.

TABLE 10.—Size of oil globules in various emulsions and efficiency in control

Type of emulsion	Emulsifier	Diameter of oil droplets		Viscosity of oil (Saybolt at 100° F.)	Control obtained at 2 per cent strength
		Range	Average		
Government standard	Potash fish-oil soap	Microns	Microns	Seconds	Per cent
Cold-stirred	Crosol-soap	2 - 8	4	220	93.7±1.3
Missouri cold-pumped	Casein-lime	1 - 4	1	220	93.7±1.5
Cold-stirred	Red oil-potassium hydroxide	3 - 20	9	200	94.9±.4
Quick-breaking	Casein-lime ¹	1 - 15	2	137	92.2±2.7
Cold-stirred	Potash fish-oil soap	2.5-40	15	137	96.7±1.3
California quick-breaking	Casein-lime ¹	1 - 17	6	186	96.5±1.0
		(?)	20	186	89.2±2.5

¹ Used in the proportion of 4 ounces per gallon of oil.

² Used in the proportion of 1.5 ounces per gallon of oil.

³ Ranges from droplets 2 μ in diameter to quantities of free oil present due to inefficient agitator on spray outfit.

The California quick-breaking emulsion (26) was tested, but was found to be insufficiently stable for use with the ordinary spray outfit, the amount of agitation being insufficient to keep the oil emulsified. As a result, trees sprayed while the tank was full received too dilute a spray, whereas those sprayed when the tank was nearly empty received too much oil.

The oil content of the spray from a quick-breaking emulsion, taken from the spray rods of an outfit having as efficient an agitator as any outfit used in central Georgia, was tested at intervals and the results are given in Table 11. The maximum quantity of casein-lime recommended (26) was used as the emulsifier. Apparently an insufficient quantity of emulsifier was recommended for use with the ordinary type of outfit; for when the tank was full the concentration of oil applied was too low for efficient results, whereas the last material to pass through the spray rods contained sufficient oil to injure even dormant trees. Where outfits with less efficient agitators were used, results were even worse. In one case about half the oil remained unemulsified and would have caused severe injury if the tank had been completely sprayed out. In the table there is also shown for comparison the oil content of the spray at the same points from the Government standard boiled emulsion.

TABLE 11.—Oil content of spray delivered from spray rods by an outfit having a very efficient agitator, with two types of emulsions each containing 2 per cent of oil by volume, Fort Valley, Ga.

Type of emulsion	Oil in spray ¹ when tank contained—			Oil in last material to come through rods
	200 gallons	20 gallons	5 gallons	
California quick-breaking emulsion ²	Per cent	Per cent	Per cent	Per cent
Government standard boiled emulsion	1.3	1.4	4.4	64.0
	1.9	2.0	2.0	2.0

¹ Samples collected from spray rods.

² Emulsified with casein-lime used in the proportion of 1.5 ounces per gallon of oil.

The control secured with a quick-breaking emulsion was slightly better than that secured with emulsions of the very stable type, but no better than the average results obtained over a 7-year period with the Government standard boiled emulsion of the same oil concentration.

SUMMER VERSUS WINTER APPLICATIONS FOR SAN JOSE SCALE CONTROL

Summer applications of oil emulsions upon deciduous trees for the control of the San Jose scale have been tried by a number of workers (3, 4, 15). They have proven uniformly much less successful than the winter applications and have not been recommended (124) except in cases where it is necessary to hold the scale in check till the dormant treatment can be applied. This reduction of effectiveness is apparently due to the too rapid evaporation of the oil at summer temperature, and to the presence of foliage which makes it much more difficult to secure uniform coverage of the tree with the spray. On citrus trees, better results are reported (118) from fall than from spring spraying with oil emulsions.

USE OF VARIOUS MATERIALS TO INCREASE THE TOXICITY OF OIL EMULSIONS

As it has been shown that oils, free, and in the form of emulsions, penetrate the tracheae of insects, they would appear as ideal vehicles for the carrying of respiratory poisons into the tracheae where they would be most effective. As early as 1891, Gillette (35) found that dry pyrethrum added directly to a kerosene emulsion greatly increased the toxicity of the latter to various insects. In 1928, De Ong (21, 22, 24) recommended that free nicotine be dissolved in oil and then emulsified, claiming that toxicity to insects was greatly increased thereby. Hammond (50) has reported that nicotine sulphate added to the diluted emulsion did not increase toxicity to aphids.

The writers have tried an emulsion made from a lubricating oil in which paradichlorobenzene was dissolved, with somewhat promising results against the San Jose scale.

The most promising field for the use of this type of oil insecticide would appear to be against various feeding and sucking insects during the summer, as temperatures are then sufficiently high for rapid volatilization of the active material incorporated in the oil.

EFFECT OF MINERAL OILS UPON PLANTS

EFFECT OF FREEZING TEMPERATURES AFTER SPRAYING

Oil sprays have been widely used for a number of years upon dormant fruit trees without injury excepting under certain conditions. Wakeland (112) reported that injury occurred upon his experimental plats when the temperature fell to 18° F. on the day following the application of the oil spray. Porter (91) cited a case in which injury occurred when the oil sprays were applied during a snowstorm. Others (30, 121) have also stated that oil sprays were

likely to injure dormant trees if freezing temperatures followed immediately after the application, although Isely (64) and others (124) have reported that no injury occurred to deciduous trees under these conditions when a 2 to 4 per cent spray was used. It is, however, apparently safer to follow the commonly recommended practice of spraying only when the temperature is above 40° F.

EFFECT OF SUMMER APPLICATIONS

Summer applications of oil sprays are much more likely to cause injury, especially to the foliage and fruit. Volck (111, p. 15) found that toxicity to plants increased with increase in specific gravity. Gray and De Ong (41) also found this to be the case, but De Ong, with Knight and Chamberlain (26), later reported that toxicity was more nearly related to viscosity than to specific gravity. English (29) stated that the higher the viscosity and the lower the volatility, the more likely an oil is to injure plants. Moore and Graham (79) found the oils with lower boiling points more toxic to plants than high-boiling oils.

Gray and De Ong (41), and De Ong (19) found that the degree of refining of an oil, as measured by the sulphonation test, greatly influenced the toxicity of an oil to foliage; the higher the unsulphonated residue, the safer the oil was for use on plants. This conclusion has also been reached by others (23, 29, 36). This factor has been reported to be without influence upon toxicity to dormant trees (29).

The ease of oxidation of an oil (23) has also been suggested as a factor influencing injury.

Even when highly refined oils are used upon trees or plants during their active season, considerable injury has been reported to result. Through the use of oil sprays blossoming may be delayed, or occasionally advanced (6, 58); premature dropping of leaves and fruit may occur (4, 26, 27, 36, 116); coloration and ripening of fruit may be retarded (6, 26, 116, 117, 122); and the greasy residue left may occasionally be objectionable on ornamentals (113). Lack of sunlight seemed to have influenced the amount of injury caused by an oil spray on certain ornamental plants (10).

A staining method for the study of the penetration of oil sprays into plant tissue has been described by Knight (69).

EFFECT OF OIL EMULSIONS UPON PEACH TREES

CONCENTRATION OF LUBRICATING OIL TOXIC TO PEACH TREES

Oil sprays applied to peach trees practically never contain over 3 per cent of oil by volume. No case of injury to the trees by this strength has been observed by or reported to the writers over the 10-year period in which oil emulsions have been used as a dormant spray in Georgia. In several instances an oil spray of 9 per cent strength has been used commercially without injury. A series of sprays ranging in oil content from 3 to 66 $\frac{2}{3}$ per cent were applied to the same peach trees each year for three years, starting when the trees were 1 year old. When applied while the trees were dormant no injury

was caused by concentrations below 25 per cent. The 25 per cent spray killed the tips of a few twigs, the 40 per cent spray killed the young twigs down to the main branch, and the 66 $\frac{2}{3}$ per cent spray killed twigs and branches down to the trunk. Entire trees were not killed by any of these concentrations. The unsulphonated content of an oil up to 95.2 per cent did not influence the toxicity to dormant trees.

When the oil sprays were applied after the buds had burst and the blossoms and leaves had started growth, the 3 per cent and 6 per cent spray burned leaves and blossoms slightly; the 12 per cent spray killed practically all the buds which had burst; and the 25 per cent and 40 per cent sprays killed the tips of the twigs. A white oil (plate 1) caused much less injury when applied at this stage than did a red oil. (Plate 2.) Apparently a high unsulphonated residue indicates low toxicity to leaves and blossoms.

Red lubricating oils caused severe defoliation and twig injury at a concentration as low as 1.5 per cent when used as a summer spray. White oils caused only slight injury to leaves at 3 per cent strength. These results agree with those previously reported (36, 37, 41).

DESCRIPTION OF INJURY

Twigs injured by oil sprays applied during the winter begin to die from the tips downward. The bark and cambium present a brown, water-soaked appearance and have a sour smell. The twig later shrivels and dries up. Small, round, brown spots bordered with red are formed upon green growing twigs and leaves by the application of red lubricating oil sprays during the summer. These spots resemble arsenical injury but are usually smaller and more numerous.

EFFECT OF TIME OF APPLICATION UPON BLOOMING PERIOD

The blooming period of fruit trees has been reported to be both delayed and advanced by the use of oil sprays (6, 53). De Ong (20) reported that spraying while the tree was entirely dormant was without effect; whereas applications made either just before dormancy began in the fall, or just after it was broken in the spring, retarded blossoming. While no such effects had been noticed by the writers in Georgia peach orchards over a series of years, the following experiments were conducted to secure more accurate data upon this point.

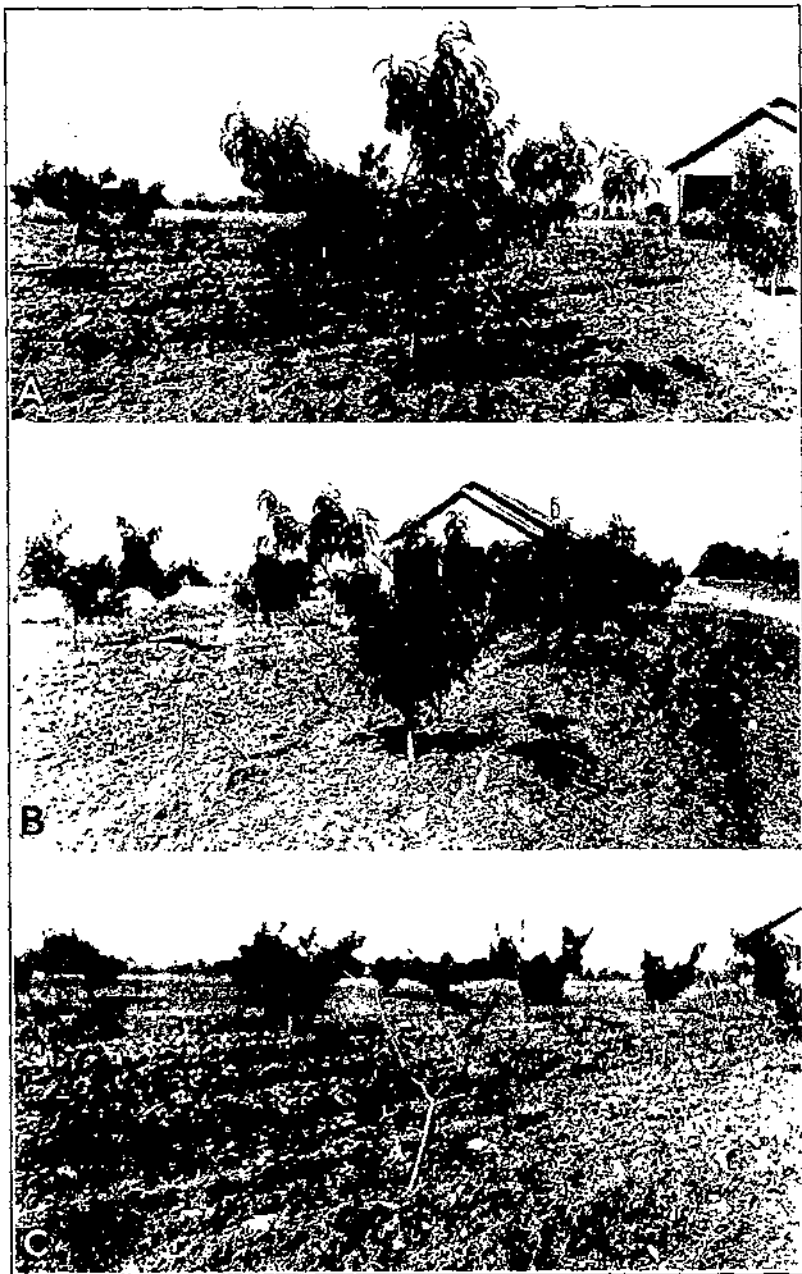
Three blocks of Elberta trees were sprayed with a 3 per cent oil to determine the effect of time of application upon blooming. One block was sprayed in November while a few green leaves still remained upon the trees, another was sprayed in the middle of December when the trees were entirely dormant, and the third was sprayed in February just after the buds had begun to break. The trees in all three blocks bloomed at the same time, and no differences could be detected.

No evidences of later blossoming have been observed even when a 25 per cent spray was applied while trees were dormant. The only time oil-sprayed trees were found to bloom later than unsprayed trees was when 12, 25, and 40 per cent oil sprays were applied when the earliest buds were in the pink stage. These early buds were



EFFECT OF OIL-EMULSION SPRAYS ON PEACH TREES

These trees were sprayed with emulsions of a white oil (unsulphonated residue 95.2 per cent) after the buds had begun to burst. A, At 12 per cent strength; B, at 25 per cent strength; and C, at 40 per cent.



EFFECT OF OIL-EMULSION SPRAYS ON PEACH TREES

These trees were sprayed with emulsions of red engine oil (unsulphonated residue 50 per cent) after the buds had begun to burst. A, At 12 per cent strength; B, at 25 per cent strength; and C, at 40 per cent.

killed by the oil, and consequently the trees appeared to bloom slightly later than unsprayed ones.

CUMULATIVE INJURY

As has been pointed out previously, lubricating oils are oxidized rather readily by the oxygen of the air, and rapidly by microorganisms, with the final production of water-soluble acids or of carbon dioxide and water. Since the oil is spread out in a very thin layer over the surface of the tree, conditions would be very favorable for such oxidation, and an oil film would hardly be expected to remain upon a tree for any great length of time. Cumulative injury would therefore not ordinarily be expected to occur.

Since practically no data were available upon this point, the results of the following experiments conducted by the writers are given. All sprays were applied while the trees were dormant:

Two hundred peach trees were sprayed each year for eight years with a 3 per cent oil spray. No injury to the trees could be detected.

Trees sprayed for three years with a 12 per cent oil spray were uninjured.

Trees sprayed for three years with a 25 per cent oil spray showed no greater injury the third year than they did the first.

It may be concluded from the foregoing experiments that there is practically no danger from cumulative injury when the oil applications are made approximately one year apart.

There is, however, possibility of danger from more frequent applications. Two or more applications of a 3 per cent oil spray are often necessary for the proper control of scales upon encrusted trees, and these must be applied within the dormant period of approximately three months. Table 12 gives the results of a number of experiments made to determine the effect of repeated applications of oil sprays of different strength.

TABLE 12.—Tests for cumulative injury from oil sprays on dormant peach trees, Fort Valley, Ga., 1928

Oil content of spray (per cent)	Applica- tions	Interval between applications	Injury
	Number		
3	2	1 month	None.
6	1		Do.
6	2	1 week	Do.
6	3	do	Do.
6	4	do	Killed tips of one twig. ¹ No other injury.
6	5	do	No injury.
6	16	do	Killed tips of several twigs. No other injury.

¹ Tree 1 year old; 3-year-old trees were uninjured.
² All trees sprayed 5 and 6 times were 3 years old.

Three weekly applications of oil spray containing 6 per cent oil were made without injury to trees only 1 year old; and five weekly applications were made to 3-year-old trees without causing injury. It is evident from these results that there is little danger of injury from several applications of a 3 per cent oil spray during one season.

THE WETTING OR SPREADING POWER OF SPRAYS AND THE RELATIVE COVERING POWER OF VARIOUS DORMANT SPRAYS

Considerable attention has been given by a number of workers to methods of comparing the "spreading" or "wetting" power of various spray materials.

Moore and Graham (80) stated that the degree of spreading of a spray upon a surface depended upon the relative strengths of the forces of adhesion and of cohesion (and consequently of surface tension). They suggested that the distance a spray penetrated into the tracheae of an insect should be taken as a measure of its spreading power on chitin.

Robinson (97), while agreeing that low surface tension was an indication of good spreading power, was unable to establish any proportional relationship between the two. Cooper and Nuttall (11) concluded that the interfacial tension between the liquid and the solid upon which it spread was a better indication of its spreading power than surface tension. As the interfacial tension between a liquid and solid can not be readily measured, and as leaves, fruit, and young twigs are usually covered with a waxy material, they determined the interfacial tension between the spray solution and paraffin oil.

Woodman (119) determined the weight of a spray solution which would cling to a glass slide or leaf under definite conditions and found this somewhat related to spreading.

English (29) tried measuring the angle of contact (11; 48, p. 439, footnote; 119) between a drop of spray and the plant surface and adopted a modification of this method as an indication of the spreading power of a liquid spray. He found that emulsifiers of high wetting ability produced emulsions of greatest toxicity to aphids, other things being equal, but was unable to find any correlation between this factor and toxicity to scale insects.

It would appear that a spray with high spreading power should cover a greater surface than one with much less spreading power. On the basis of this reasoning Jarvis (66) stated that 1 gallon of an oil spray would cover as much tree surface as 1½ gallons of lime-sulphur. Experimental workers in general have accepted this as true. Chandler, Flint, and Huber (9) reported, however, that 1 gallon of lime-sulphur covered as much tree surface as 1½ gallons of oil spray. Since their experiments were published numerous conflicting claims have been made as to the covering power of the various dormant sprays.

In Table 13 is given the number of gallons of various dormant sprays required to cover 100 trees. These figures are based upon the results from spraying approximately 3,000 trees with oil emulsions, 700 with lime-sulphur, and 500 with miscible oils.

TABLE 13.—Relative covering power of various dormant sprays as tested in experiments at Fort Valley, Ga.

Year	Series of experiments: No.	Quantity required to cover 100 trees					
		Oil emulsion with soap emulsifier		Oil emulsion with casein-lime emulsifier		Lime-sulphur (1-8)	Miscible oils (1-15)
		2 per cent oil	3 per cent oil	2 per cent oil	3 per cent oil		
		Gallons	Gallons	Gallons	Gallons	Gallons	Gallons
1922	1	98	93			96	
1923	1		100			247	288
	2	145	132	194	194	172	203
1924	1	238	245		232		
	2	132	133	134	143	163	
1925	1	172	152	141	127	153	
	2		78				83
1929	1		125				119
	3		147				139

¹ Trees were fairly uniform in size throughout the plots within each series, but varied greatly from series to series.

Small variations in Table 13 are of no significance as the total surface of the different series of trees varied considerably. It is evident that there is no practical difference between the covering power of oil emulsions, lime-sulphur, and miscible oils; none between oil emulsions with soap for an emulsifier and those with calcium caseinate for an emulsifier; and none between oil sprays containing 2 per cent and those containing 3 per cent of oil.

The covering power of a spray under orchard conditions, when applied with a pressure of 250 pounds or more, seems to depend largely upon the size of the disk opening used in the spray rods. The quantity of spray required may be reduced one-fourth or more by the use of disks with very small openings, and this also usually results in better covering.

It is of course possible that the effectiveness of oil emulsions might be increased by the addition of materials to cause better spreading and penetration (38), although Melander (75) noted that a caseinate spreader decreased the effectiveness of oil sprays for the San Jose scale and for leaf-roller eggs.

COMPATIBILITY OF OIL EMULSIONS WITH VARIOUS INSECTICIDES AND FUNGICIDES

Emulsions made with soaps of monovalent alkali metals are not compatible with lead arsenate, and probably not with the fluosilicates, as these chemicals decompose in an alkaline solution. They also are not compatible with arsenates of calcium, magnesium, or barium or lime-sulphur, as these compounds will react to form insoluble soaps, thus freeing the oil; but by the addition to these emulsions of various stabilizers, as recommended by Yothers and Winston (125), these reactions may often be retarded sufficiently to enable a combination of oil emulsion and lime-sulphur to be applied without injury to the plant. Such emulsions are compatible with Bordeaux mixture, the latter also often being added to hard water to stabilize them (55).

The inert emulsifiers without soap are, as a rule, compatible with practically all insecticides or fungicides, although the casein-lime emulsion has been shown to be somewhat unstable in solutions containing magnesium sulphate (31). Where emulsions must be used with various insecticides or fungicides it is generally much safer to use one of the inert emulsifiers that does not contain soap.

SUMMARY

In this bulletin crude petroleum oils are discussed with regard to their origin, principal constituents, and chemical and physical properties.

The various methods used in the production of lubricating oils from crude oils are given. The composition and chemical and physical properties of the oils have been briefly reviewed and their significance indicated. The methods of analysis ordinarily used in the evaluation of oils have been mentioned, various theories of emulsification have been discussed, and a list of emulsifiers which have previously been used or recommended is given.

A number of vegetable oils were tested for the production of soap emulsifiers, cottonseed oil proving as effective as fish oil for this purpose. Red oil, or oleic acid (an animal product), was found to make a good cold-stirred soap. The saponification numbers of the oils tested are given.

The principles involved in the manufacture of various types of emulsions and miscible oils are discussed and the advantages of each type given.

The manufacture of both the boiled and cold-stirred types of emulsion was studied, and the results are reported. The viscosity of the soap was found to influence greatly the quality of the emulsion obtained by the cold-stirred method of manufacture. This was in turn found to depend upon the moisture content, the kind and quantity of caustic used in its production, and the temperature. A soap made with only a slight excess of caustic potash and having a moisture content of from 60 to 75 per cent was found to make the best emulsion. If the temperature of the oil and soap was below 40° F. it was found preferable to first heat the soap to approximately 125° before stirring in the oil. The oil must be added slowly and very thoroughly stirred in to secure a stable emulsion by this method. Butyl alcohol was found of value as a stabilizer for these emulsions, being approximately as good as the amyl alcohol or cresylic acid previously recommended. A cold-stirred red oil, or oleic acid, soap proved a good emulsifier for cold-stirred emulsions, and a formula for this is given.

It was found that old casein-lime mixtures which failed to emulsify oils could be made to do so by the addition of fresh hydrated lime.

Methods of analysis of oil emulsions previously described, and those used at the Fort Valley, Ga., laboratory are briefly mentioned.

The freezing points of the more common emulsions were determined and are found to range from 29.7° to 31.8° F. The emulsions, however, could be undercooled for short periods to 17° or 18° before freezing began if undisturbed. If stirred while either freezing or

thawing, the emulsions were broken down, whereas if left undisturbed, they practically always thawed out without breaking.

It was found that much of the trouble from the use of soap-oil emulsions with moderately hard water could be eliminated by disconnecting the agitator upon the spray outfit.

Previous work on the effect of mineral oils upon insects is reviewed, the evidence indicating that the death of scale insects from the action of lubricating oils is due to suffocation.

The methods employed in testing the toxicity of oil sprays in the field against the San Jose scale and a revised method for the computation of percentage of control and compensating for heterogeneity have been described. Viscosity, density, volatility, and the degree of refining, as measured by the sulphonation test, are discussed as influencing toxicity to insects.

From the results of field tests, viscosity appeared to give the best indication of the toxicity of an oil as a dormant spray for the San Jose scale. Density was a considerably poorer indication. For most effective results in the South a mineral oil should have a viscosity (Saybolt, at 100° F.) of not less than 125 seconds and a volatility (loss for four hours at 105° C.) of not more than 1.75 per cent, and should be used at a 3 per cent strength. Volatility had no weakening effect up to 1.75 per cent when oils of sufficiently high viscosity were used. One oil tested which had a viscosity below 50 seconds was more highly volatile, and showed no toxicity at a 3 per cent concentration. The unsulphonated residue, the nature of the base of the crude oil, and the flash and fire points were apparently without effect upon toxicity.

The average percentages of control of the San Jose scale given by oil sprays over a 4-year period were as follows: A 1 per cent spray gave 91.0 per cent control, 1½ per cent gave 96.9 per cent, 2 per cent gave 96.1 per cent, and 3 per cent gave 99.1 per cent control. Only a 3 per cent spray is recommended for commercial use.

Rain falling after the water in the oil spray on the trees has evaporated does not affect the toxicity of the spray.

The sizes of the oil droplets in the more common emulsions were measured, and the diameters are given in Table 9.

At a 2 per cent strength, the more unstable emulsions were found to be slightly more toxic than the more permanent ones. The difference, however, was slight. The California "quick-breaking" emulsion, when emulsified according to directions, was found to be insufficiently stable for use with the ordinary spray outfit.

The effect of mineral oils upon plants is discussed. Oil sprays containing 25 per cent, or more, of oil injured dormant peach trees. Lower concentrations were without effect. The percentage of unsulphonated residue of an oil did not affect the toxicity of the oil to the trees when used as a dormant spray, but a high unsulphonated residue indicates that the oil is safer for use on peach trees in foliage than an oil with a low residue. Oil sprays did not retard or advance the blooming period of peaches. No evidence of cumulative injury could be detected from the use of yearly applications of oil sprays. When applied weekly, three applications of a 6 per cent oil spray could be made upon one-year-old dormant peach trees without injury. Older trees were able to stand even more applications.

No differences could be detected in the covering power of lime-sulphur, oil-emulsion, and miscible-oil sprays under orchard conditions; also none between oil emulsions having soap and casein-lime as emulsifiers, and none between oil sprays containing 2 and 3 per cent of oil.

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