Petroleum-derived spray oils: chemistry, history, refining and formulation

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Abstract

Modern use of petroleum-derived oils as agricultural crop protectants dates back to the 1800s, but it was not until the latter half of the 20th century that advances in petroleum chemistry allowed substantial modification and diversification in their commercial applicability. In the 1880s, a kerosene–soap emulsion was used with some success against scales and aphids in citrus trees. The search for something more effective led to the use of emulsified crude petroleum sprays, but these were too phytotoxic. Eventually, researchers concentrated on distillates in the range between kerosene and lubricating oils. Three basic classes of carbon structures present in petroleum oils are paraffins, aromatics and naphthenes. In 1915, E. de Ong showed that tree injury was caused by substances (aromatics and other unsaturated components) in oils that were removable with sulfuric acid; the remainder is the unsulfonated residue, or UR. In 1929, this principle became the basis for W. Volck's patents on low-unsaturate oils having a high level of non-reactivity to sulfuric acid. A few years later, R. Smith noted the relationship between pesticidal efficiency, phytotoxicity and oil heaviness; he recommended distillation as a preferred basis for grading spray oils for heaviness in terms of average molecular weight. Viscosity and boiling-range measurements ultimately became the most useful data for indicating performance rankings among oils of common origin and manufacture. The importance of the emulsifier used with the oil was determined to be in its influence on spray deposit, which affects its pest control efficacy. Modern refining improvements after distillation progressed from solvent extraction (1950s) to hydrogenation and dewaxing to increase the UR value (1960s), and hydrocracking, which replaced solvent extraction for the production of high-UR oils (late 1960s). The past 10 years have seen processes such as iso-dewaxing to further enhance the paraffinic content of oils, although increased difficulty in emulsification could compromise the pesticidal efficacy of these products.

Introduction

Petroleum oils have been in use as crop protectants for over a hundred years, and their history has covered a remarkably broad range of developments concerning every aspect from geographic origin and chemical purification to techniques of emulsification and combination with other crop spray materials. Advances in petroleum chemistry over the past 40 years have minimised the importance of the source of the crude and the influence this once had on its gross composition or base, the relative quantities of the various compounds present, and certain of its resulting chemical and physical properties such as viscosity and boiling point.

Current methods that allow the blending, purification and synthesis of different types of petroleum oils have resulted in the ability to virtually custom-manufacture effective oil products for specific uses. Although oils were once limited to early-season or dormant sprays in the interest of avoiding oil injury to green plant tissue, newer, highly refined horticultural mineral oils (HMOs; also called petroleum spray oils) and agricultural mineral oils (AMOs; broad-range petroleum spray oils) are seeing more recognition of their usefulness in and compatibility with modern pest management approaches. Most agricultural oils now in use are still petroleum distillates, but there is a growing trend to examine the applicability of vegetable and animal oils to certain crop protection needs.

The diversity of oil products and the terminology associated with them over the years has sometimes contributed to confusion and misunderstanding of how best to exploit the strengths of petroleum products as crop protectants. Nevertheless, increased interest in this area by both refiners and agriculturists is responsible for a renewed examination of the oils' advantages and applications. Although oils are some of the oldest pesticides still in use, the prospect of their continued development and modification for future agricultural purposes seems more certain now than ever.

Chemistry of petroleum oils

Origin

The origin of petroleum has been the subject of a number of theories, which may be thought of as being either inorganic or organic in perspective. The principal tenet of the inorganic theories is that diverse hydrocarbon compounds found in crude oils were the result of the action of water or steam on various metallic carbides inside the Earth, or of carbonic acid on alkaline-earth metals to form acetylene (ethyne, C_2H_2). Through chemical reduction and polymerisation in the presence of metallic catalysts, these became hydrocarbons that are now found in crude petroleum. According to the organic theory, years of plant and animal remains have resulted in the accumulation of fats, waxes and other stable, fat-soluble materials in the Earth's crust. The constant effects of pressure, heat and contact catalysts present in the Earth have gradually transformed these substances into petroleum oils. Although less specific chemically, this theory best accounts for the nitrogen content of petroleum oils, their optical activity (indicating a lack of molecular symmetry) and the fact that they are always found in sedimentary rock formations (Swingle & Snapp 1931).

Composition

Although crude petroleum oils are complex mixtures of a large number of compounds, they consist primarily of hydrocarbons. The type, proportion and specific composition of compounds present in a given crude generally vary from one oil field to the next, and even among wells within the same field. These crudes are classified in commercial practice according to their bases being either paraffinic, asphaltic (often erroneously called naphthenic), or, if they contain both classes of compounds, mixed; this nomenclature derives from the type of residue left after distillation. Because of the complexity of compounds present in any specific crude oil, only arbitrary chemical classification of these mixtures is possible, but for practical purposes the main components can be categorised as paraffin chains (straight or branched), naphthene rings, aromatic rings, unsaturated hydrocarbons, or asphaltic material. Traditionally, crude oils from different regions have been classed according to the relative amounts of these materials they contain. For instance, oils from Pennsylvania in the eastern USA, usually described as paraffinic oils, contain both paraffinic and naphthenic hydrocarbons. US Gulf Coast oils, known commercially as asphaltic oils, contain naphthenes in addition to the asphaltic material. Mid-continent US crudes, classed as mixed-base oils, are composed of paraffins, naphthenes and asphaltic groups (Ebeling 1950, Chapman et al. 1952, Davidson et al. 1991).

Unsaturated hydrocarbons

It is useful to distinguish the principal chemical groups present by their general properties. The unsaturated hydrocarbons contain one or more double bonds between carbon atoms; these consist mainly of the open-chain alkenes (sometimes called olefins), acetylene, and partly hydrogenated cyclic hydrocarbons, such as terpenes. These are chemically active compounds that form additively with halogens and concentrated sulfuric acid; they are easily oxidised and have a tendency to polymerise, particularly in the presence of catalysts such as aluminium chloride, charcoal and other porous substances. Because of their high reactivity and tendency to polymerise, unsaturated compounds generally would not be expected to be present in large quantities in crude petroleum, as the time during which the petroleum would have formed and accumulated provided very favourable conditions for the chemical reactions needed to form saturated groupings.

Aromatic hydrocarbons

These can be considered separately from the unsaturated hydrocarbons, despite the occurrence of double bonds, because of the distinctions that exist in their chemical properties. They are also usually present only at very low levels, with the exception of crudes from certain regions (such as California in the western USA), and include such

compounds as benzene, toluene, xylene and naphthalene. They may occur initially as components of the crude oil, or they may be derived from unstable compounds produced by mild cracking during the distilling process. These components do not undergo reactions with concentrated sulfuric acid (although they may be made to react with fuming sulfuric acid); they can also be made to combine with bromine and chlorine under the proper conditions.

Naphthenic hydrocarbons

These are ring compounds with the general formula C_nH_{2n} that act chemically like saturated hydrocarbons, and can be considered as hydrides of the benzene series. They form substitution products with halogens, and under suitable conditions can be oxidised or nitrated. Their viscosities are higher than the aromatics', but they have relatively low boiling points. Like the paraffinics, they resist reacting with concentrated sulfuric acid, but only when cold; at higher temperatures (or with fuming sulfuric acid), they undergo oxidation.

Paraffinic hydrocarbons

Now generally known as alkanes, these compounds belong to the methane series, and have the general formula C_nH_{2n+2}. Larger members of this series (those with 16 or more carbon atoms) are solids at room temperature and are classed commercially as paraffin waxes. These saturated chain compounds are practically inert chemically; the name 'paraffin' is derived from the Latin words *parum affinis* ('with little affinity'), which attests to their low level of reactivity. They form substitution products with halogens under the proper conditions, but are unaffected by dilute or concentrated acids at room temperature. However, they may be charred by hot sulfuric acid, and hot concentrated nitric acid causes slight molecular decomposition.

These four broad categories are listed in descending order of chemical reactivity, although the latter three are significantly less active than the unsaturated hydrocarbons. For each group, an increase in molecular size or in the degree of methyl group attachment is correlated with greater reactivity. Compounds of higher molecular weight, and particularly those possessing long side chains, are more prone to being nitrated, sulfonated, or oxidised.

Other compounds

Crude petroleum may also contain metallic salts, oxygen, nitrogen and sulfur. Among the oxygen-containing compounds are naphthenic acids. These weakly acidic substances form salts with alkali metals similar to those of fatty acids. Such chemicals are good emulsifiers and have found some use in soap production. Also present as resins are some asphaltic substances, which contain oxygen or sometimes sulfur. As materials that dry readily, they are used as bonding agents in road surfacing materials. Sulfur is usually a minor component in the higher distilled products, generally in the form of thiophenes and sulfides. The nitrogen content of oils is also small. Nitrogen is usually present in basic compounds such as quinoline derivatives and is easily removed by sulfuric acid.

Chemical and physical properties

Investigation of the so-called 'higher boiling fractions' of petroleum falling in the lubricating oil range (the fractions from which crop spray oils are derived) started from the observation that they consisted of a mixture of paraffinic, naphthenic and aromatic hydrocarbons in various proportions, contaminated perhaps with small amounts of sulfur and nitrogen derivatives and products of hydrocarbon oxidation. It has been evident to petroleum researchers from the start that the chemical structure of the components of an oil exerts a significant influence on its chemical and physical characteristics. The specific effects of any given structural trait were the subject of numerous diverse opinions held by early workers in this field. In time, the focus of technical investigations came to rest on the matter of hydrogen deficiency of comparative fractions of oils as an underlying basis of differences in oil properties; more specifically, the relationship of this attribute to the nature and extent of ring structures present was considered to be most consequential (Mikeska 1936).

A series of specific properties determined by analytical methods is routinely used to characterise a petroleum oil with regard to its ring structures, which relates to its degree of hydrogenation and paraffinicity and, thus, its suitability for controlling plant pests and diseases. Among the most common of these properties are viscosity, molecular weight, boiling point and boiling range data, unsulfonated residue, aniline point, pour point and gravity. Specific protocols for carrying out the tests of these values have been established

by the American Society for Testing and Materials (ASTM), an organisation that promotes and standardises specifications and methods for describing or identifying petroleum products. The methods, denoted as ASTM followed by a letter and number, are described in relevant ASTM publications.

Viscosity

The viscosity of a liquid can be defined as its resistance to fluid motion. In petroleum industry terminology, a related property is expressed, that being the time required for a given volume of oil to flow through a standard opening under specific temperature and pressure conditions. The apparatus used to measure this property is known as a Saybolt viscosimeter (Frear 1942). ASTM D 446 defines how the viscosimeter is used. The viscosity is expressed in Saybolt Universal Seconds (SUS). The viscosity of most spray oils tends to fall in the range 60–100 s at 37.8℃ (Davidson et al. 1991), with the optimum range between 63 and 75 s for 60- and 70-s oils (Chapman 1967b). An early discovery was that viscosity of an oil of a given molecular weight increases with a decrease in hydrogen content, and that viscosity can give some information about molecular size of an oil. Generally, oils with a higher viscosity are thought of as having greater pesticidal efficacy (Pearce et al. 1942). However, flow rate through a viscosimeter is affected by both molecular size and shape. This derives from the fact that, although flow rate decreases with an increase in molecular size, rate is also affected by the shape of the molecules. Therefore, viscosity alone is not sufficient to characterise an oil's suitability as a pest control agent.

Viscosity measurements are useful in indicating heaviness ranges among oils of common origin and manufacture. For example, a highly paraffinic oil with a viscosity of 50 s may be more effective than an extremely naphthenic oil with a viscosity of 125 s. For this reason, the viscosity measurement currently has come to be less important as an explicit specification for an HMO or AMO, owing to the greater role played by an oil's paraffinicity in this regard.

A related trait is viscosity index (VI), which indicates the effect of temperature change on the viscosity of an oil. Liquids become less viscous as temperature increases; the higher the VI of an oil, the lower its tendency to change viscosity with temperature. The VI of paraffinic oils is inherently high, but is low in naphthenic oils and even lower in aromatic oils. The VI has been found to be a good indication of the relative proportions of the hydrocarbon molecules

in ring structures or paraffinic side chains (Davis & McAllister 1930).

Molecular weight

The molecular weight of an oil is directly related to its heaviness, and therefore the size of the molecules it comprises, as reflected in the fact that the lighter or lower-molecular-weight fractions come off earlier (at lower temperatures) in the distillation process than those that are heavier and of higher molecular weight. Although mineral spray oils typically are composed of molecules containing anywhere from 16 to 32 carbon atoms, with corresponding differences in molecular weight (e.g. 226 to > 400), the peak of maximum efficiency varies according to the chemical composition of the components. For a more naphthenic oil, this point would occur at a molecular weight of approximately 287, whereas the optimum molecular weight for a paraffinic oil has been found to be as high as 354 in some studies in which pesticidal efficacy has been determined (Riehl & LaDue 1952). Paraffinic oils may be more efficient pesticides than naphthenic oils by virtue of the shape of the hydrocarbon molecules, implying an interaction between viscosity and molecular size (Riehl & LaDue 1952). Tests on mite and insect eggs showed little pesticidal advantage in the use of oils above a molecular weight of 300 (Pearce & Chapman 1952; Chapman 1967b). This guideline is less applicable in the case of motile forms, such as scale crawlers and aphids (Ebeling 1950; Phillips & Smith 1963; Trammel & Simanton 1966).

Boiling point and boiling range

A distillation test is the method for determining the full range of volatility characteristics of a petroleum oil by progressively boiling off a sample under controlled heating. The mid boiling point, or 50% distillation temperature, is the temperature at which 50% of the liquid has collected in a container after condensing in a chamber connected to the distillation vessel, and the boiling range (10%–90% distillation range) is the temperature spread between the 10% and 90% boiling points. If the boiling range is small, the oil is said to be 'narrow-cut' or 'narrow-range' (NR), and composed of components with similar volatilities; if it is wide, the oil is termed 'wide-cut' or 'broad-range'. In this way, boiling point data are directly related to the molecular size of the compounds in the oil. The boiling range is additionally used as a criterion for selecting from among oils having a similar mid boiling point; a wider range is evidence of a

less uniform composition. Boiling points of petroleum fractions increase as the number of carbon atoms per molecule increases. Spray oils are taken from the oil fraction that distils off at temperatures between 315.6° and 482.2°C at atmospheric pressure (760 mm Hg or 101.3 kPa; ASTM D 447) or between 190.6° and 273.9°C under a vacuum of 10 mm Hg (1.33 kPa; ASTM D 1160). This latter had been the principal method used for distillation until problems with reproducibility and precision motivated the search for a more reliable alternative. As a result, analysis of candidate petroleum oils using high-resolution gas–liquid chromatography (simulated distillation: ASTM D 2887) has now largely supplanted reduced-pressure distillation as a tool for specifying physical and chemical properties of oil (Furness et al. 1987), although the 10 mm Hg distillation method is still used for quality control purposes in the USA, as dictated by current registration guidelines.

However, strict comparison of boiling points among different oils does not necessarily give specific information about their structural similarity, as boiling point depends on the length, branching and number of side chains, the presence of paraffinics and aromatic or naphthenic rings, the occurrence of side chains on these components, and the degree of saturation (Fenske & Hersh 1941). For example, the normal paraffins generally have higher boiling points than the corresponding naphthene derivatives. Oils currently recommended for verdant use are those that are classified as narrow-range, because they exhibit both pesticidal efficacy and safety to the plant. The optimum boiling range for a 60-s oil has been recommended to be no more than 44°C (with a 50% point of 211° ± 5°C), and for a 70-s oil to be 52.8°C (with a 50% point of 224° ± 5°C) (Chapman 1967a). (The ± 5°C variation refers to the sensitivity of the analytical method used to calculate the midpoint, not to the variability of the oil specimen.) The mid boiling point is useful because it gives an indication of oil volatility from the plant surface; products with a lower mid boiling point (e.g. 211°C at 1.33 kPa) volatilise more quickly after after application than oils with a higher mid boiling point (e.g. 224° or 235°C) (see Knight et al. 1929, Riehl 1969, Briggs & Bromilow 1994). This has consequences not only for pesticidal efficacy, but also for plant safety, as less volatile oils can—depending on UR values and quantities of oil deposited—be more prone to injuring plant tissue. Too high a volatility in an oil would lead to evaporation before penetration into the pest's body could take place, and a product that was excessively non-

volatile could sit on the surface of an arthropod cuticle indefinitely without effect. Expressed in other terms, if the boiling range is too wide, the lighter fraction provides little in the way of pesticidal action, and the heavier fraction poses a danger of phytotoxicity.

The median equivalent *n*-paraffin carbon number of a contemporary HMO (PSO) has become an increasingly important specification in some markets, particularly Australia. It gives information about the oil's molecular weight. For instance, Exxon's Orchex® 796 is an *n*C23 product. This indicates that its 50% distillation temperature is equivalent to the boiling point of a normal (*n*) straight-chain paraffin (alkane) with 23 carbon atoms. Its adoption, based on gas chromatographic distillation (ASTM D 2887), will help overcome confusion that has arisen through the use of specifications based on different temperature scales and pressures (see Kuhlmann & Jacques 2002).

Unsulfonated residue

The unsulfonated residue, or UR, value is a measure of the degree of refinement of an oil and an indication of the amount of phytotoxic materials remaining after the distillation and refining process. The method used to determine this value (ASTM D 483) involves shaking the oil several times while it is hot with a mixture of concentrated fuming sulfuric acid. The most active compounds present, including unsaturated hydrocarbons such as open-branched alkenes and high-molecular weight branched-chain compounds, are absorbed by the acid. The percentage of oil not absorbed is the UR (Swingle & Snapp 1931; Simanton & Trammel 1966; Davidson et al. 1991). An oil with a high UR (≥ 92) contains a high percentage of stable hydrocarbons and is free of most reactive impurities. Although the UR does not indicate the form of the hydrocarbons present and is not directly correlated with pesticidal efficacy, it is a good measure of overall quality and is directly related to the physiological effect of the oil on plant tissue. Below the 92 UR value, an oil is potentially more phytotoxic.

A related property is oil composition, often designated as percentage C_P, C_N and C_A, for the percentage of carbon atoms in paraffinic, naphthenic and aromatic structures, respectively. A value higher than 60% C_P designates a paraffinic oil; one higher than 35% C_N a naphthenic oil; and one higher than 35% C_A an aromatic. Generally, the more paraffinic an oil, the less likely it is to contain phytotoxic aromatic compounds. The more paraffinic oils possess bet-

ter spreading characteristics on tree bark, which translates into better control of sessile forms such as arthropod eggs (Pearce & Chapman 1952).

Aniline point

This test (ASTM D 611) gives the lowest temperature at which a specified quantity of oil is soluble in an equal amount of aniline (a benzene derivative), and therefore gives an empirical measurement of the solvent power of the hydrocarbons present. The lower the aniline point, the greater the solvency, or reactivity, of the oil, which in turn gives an indication of the oil's aromaticity. Paraffinic hydrocarbons have higher aniline points than aromatic types (Mair & Willingham 1936; Rossini 1937). For instance, for an aromatic oil with a 75% aromatic content, the aniline point would be between 32.2° and 48.9°C; for a naphthenic type containing 40% aromatic structures, it would be between 65.6° and 76.7°C; and for a paraffinic oil with a 15% aromatic content it would be between 93.3° and 126.7°C (Vlugter et al. 1935).

Pour point

This is defined as the temperature 3°C above that temperature at which oil will not flow from a jar held horizontally for 5 seconds (ASTM D 97). This value is applied to a petroleum oil to evaluate its ability to remain in a liquid state at cold temperatures, as a guide to storage, handling, spraying and formulation procedures. It is also used to ascertain that the oil does not contain excessive amounts of paraffin waxes (alkanes with 16 or more carbon atoms), which are pesticidally less desirable and can leave a whitish residue on the plant surface. Such substances not only dilute the more suitable hydrocarbons in the oil, they can also disrupt the plant's transpiration. Suitable pour point values range between –20.5° and –6.6°C; highly paraffinic oils tend to have unacceptably high pour points, which are readily lowered to appropriate levels by dewaxing (Simanton & Trammel 1966; Davidson et al. 1991). Naphthenic oils have pour points over a wider range, from –45.6° to –6.6°C.

Gravity

The specific gravity of a petroleum product is the ratio of a given volume of the product to that of an equal volume of water. This value is determined by ASTM D 1298; the standard reference temperature is 15.6°C. The higher the specific gravity, the heavier the product. Petroleum products may also be defined in terms of API (American Petroleum Institute) gravity (ASTM D 287), according to a formula that uses an inverse ratio of conversion. Therefore, the higher the API gravity value, the *lighter* the material, or the lower its specific gravity. For spray oils, a higher API gravity for a given distillation range indicates a higher proportion of paraffin-type compounds and fewer naphthenic and aromatic types (Simanton & Trammel 1966). Typical measurements of API gravity (in degrees) for paraffinic oils are 27°–37°; for naphthenic oils, the range is 17°–27°. It is currently more common to use ASTM D 2140 to calculate the hydrocarbon type, for the relative proportion of paraffinics, naphthenics and aromatics in an oil, without relying on the API gravity.

History of petroleum oils

Pre-20th-century work

It is clear from a reading of early literature that knowledge of petroleum's existence as a substance from the Earth dates back at least to the 1st century AD. The writings of Pliny the Elder (Plinius 77) make mention of petroleum as an inflammable mud from a marsh in Samosata, on the west bank of the Euphrates River in south-western Turkey. He reported that 'When this touches anything solid it sticks to it.' There is also a passage regarding naphtha as being a similar substance that flows out like 'liquid bitumen'. Although he gives no direct evidence of being aware of its value as a pest control substance, there are indications that Roman citizens of his time were on this track in their early efforts to eliminate pests of the home orchard, vineyard and garden. Insects reportedly affecting fruit trees and vines included worm-disease, wood-maggots, horned insects and leaf-rolling caterpillars. One remedy was to boil down two gallons of the lees of olive oil and mix it with a third part of bitumen and a quarter part of sulfur. This, it was cautioned, must be done in the open air because the mixture could catch fire indoors. The preparation was to be smeared around the bases and under the arms of the vines, which would 'prevent the caterpillar'. Ants were kept away from trees by smearing the trunks with a mixture of red earth and tar. From these recommendations, it is apparent that the protective qualities of complex hydrocarbons were already being examined nearly 2000 years ago. However, it must also be noted that this was an era of certain pest-mitigating tactics that relied more on traditional lore than empirical proof. To protect the

tops of the trees against caterpillars and pests that produce decay, Pliny advised touching them with the gall of a green lizard. It was also said that caterpillars could be totally exterminated in gardens by fixing up on a stake the skull of a female animal of the horse class, or a river crab hung up in the middle of the garden (Plinius 77).

Oils used as insecticides were first mentioned in the literature by Goeze (1787), but it was not until about 1865 that a petroleum distillate (kerosene) was first used against scale insects on orange (*Citrus sinensis* (L.) Osbeck [Sapindales: Rutaceae]) trees, probably because of its general availability 6 years after the first petroleum well was drilled. It was employed as a soap emulsion by Cook in 1877 (Cook 1890). Riley and Hubbard also tested kerosene applied on citrus in aqueous emulsions (Riley 1892); because they found this treatment to be not completely satisfactory, they assessed unrefined distillates in the range between kerosene and the lubricating oil fractions (Riehl & LaDue 1952). In 1880, kerosene became a standard treatment as a 10% emulsion for the control of aphids and other soft-bodied citrus insects, and at 25% for more resistant scale insects. Near the turn of the century, the pest activities of San José scale (*Quadraspidiotus perniciosus* (Comstock) [Hemiptera: Diaspididae]) generated interest in other distillates and even crude petroleum (Lodeman 1896; Ebeling 1950; Chapman 1967a). Crude oil was apparently used first by Smith in 1897 (Smith 1899), who applied a 25% emulsion as both a dormant spray and a summer spray. It was emulsified by mechanically mixing a hot soap solution with the oil. Later, 'miscible oils' were developed, in which the emulsifier was dissolved in the oil by using phenol, cresylic acid, or naphthalene. These had the obvious advantage of being concentrated and were therefore easily diluted to the required strength for application. However, product variability made them difficult to use, and impurities present often caused severe damage to plants. This was a primary consideration that led to their eventual replacement by the more refined lubricating oils (Frear 1942).

Progress in the development of petroleum-derived spray oils was temporarily slowed around 1900 by the introduction of lime-sulfur for scale insects (Smith 1952). However, by 1905, safer spray oils started to become available for use against these pests, in the form of emulsions or emulsifiable oils (Parrott et al. 1906). Yothers and McBride (Yothers 1918) first tried a heavier petroleum component, an engine lubricating oil, on citrus in Florida in 1906. The use of cuts of

petroleum in the light lubricating oil range was evidently not readily accepted at this time. There was some continued experimentation with distillates, but they caused unacceptable tree and fruit damage.

Development of modern petroleum-derived spray oils

In 1923, an important transition event was Ackerman's (1923) success with a 2% light lubricating oil against San José scale that had not been controlled with lime-sulfur. This was the same oil previously developed by Yothers (1918) for Florida citrus. The results contributed to a renewed interest in petroleum-derived spray oils and the supplanting of oil over lime-sulfur as a scalicide. From this point on, petroleum oils eventually became the principal dormant or semi-dormant treatment in deciduous fruit orchards, encouraged by the increased incidence of fruit tree leafroller (*Archips argyrospila* (Walker) [Lepidoptera: Tortricidae]), the eggs of which could be killed with oil. Further support came from de Ong et al. (1927), who reported that the quick-breaking emulsion concept improved oil's insecticidal efficacy against citrus pests.

After the impetus provided by Ackerman's work, it is possible to identify four major developments that were responsible for the kinds of petroleum fractions ultimately used in contemporary HMOs and AMOs (Chapman 1967b):

- The discovery that the hydrocarbons that cause acute leaf injury are the aromatic and other unsaturated compounds
- The finding that both chronic phytotoxicity (such as yellowing and dropping of leaves and growth retardation) and pesticidal efficacy are related to oil 'heaviness', or average molecular weight
- The recognition that pest control and plant safety objectives in selecting a spray oil should be based on the pest being treated and the amount actually deposited on the plant
- The discovery that pesticidal efficacy is related to the dominant basic structural composition of the hydrocarbons present.

Effects of aromatics

In the period 1914–16, some breakthrough experiments by Gray & de Ong (1926) established the relationship between oil unsaturates and plant damage by showing that the ob-

served injury was caused by substances in the oil that were removable with sulfuric acid. In 1924, Volck (1929) filed patent claims based on this principle for a series of plant spray oils of low-unsaturate content, claimed for products having a UR of > 85. That same year, he marketed a premixed emulsion of a highly refined heavy petroleum for California citrus. This was probably the first high-UR oil available commercially; it was a so-called mayonnaise type, owing to its appearance, and was recommended at a rate of 10%–13%.

Influence of molecular size

Smith (1932) conducted intensive studies of factors involved in the effects of oils used against red scale (*Aonidiella aurantii* (Maskell) [Hemiptera: Diaspididae]) and other pests in citrus. He found that the so-called 'weight' of the spray oil accounted for both its insecticidal efficacy and its potentially deleterious effects on the plants. He saw these properties as being related to the oil's distillation range and recommended distillation to provide a better basis for classifying and grading petroleum spray oils than viscosity. There was confusion during this period regarding the selection of petroleum spray oil for a given use, because some were labelled according to viscosity and others according to distillation range. The California Department of Agriculture (CDA) (Marshall 1932) recognised the need for standardisation, and used this work as a basis for establishing a series of grades of 'summer or foliage'-type oils. This classification into five grades—light, light-medium, medium, heavy-medium and heavy—used a minimum UR of 91%–94% and the percentage of oil that distilled at 335.6°C and 101.33 kPa, which was arbitrarily judged to be a good pre-cracking point. The minimum required standards for each grade are given in Table 1 (Chapman et al. 1952; Davidson et al. 1991).

Table 1. California grade standards for distinguishing types of petroleum spray oils based on unsulfonated residue (UR) and distillation properties, 1932.

Grade	Minimum UR (%) (ASTM D 483)	% Distilled at 335.6° C (ASTM D 447)	Viscosity (SUS) at 37.8° C (ASTM D 446)
Light	90	64–79	55–65
Light-medium	92	52–61	60–75
Medium	92	40–49	70–85
Heavy-medium	92	28–37	80–95
Heavy	94	10–25	90–105

The standards established by California were the first using distillation properties in official specifications for spray oils and were judged to be so suitable that they were used virtually unchanged for more than 30 years (Anonymous 1966). These oils, which have been replaced by contemporary HMOs and AMOs, are no longer recommended for use.

In 1938, the CDA enacted provisions specifically directed toward the regulation of dormant spray oils (Cox 1938), which at the time consisted of products with a UR of about 70% and in the viscosity range of 100–135 s. Dormant oils used in the western USA were manufactured from asphaltic or naphthenic base crudes from California; in the east, the oils included both naphthenic and paraffinic class products (Chapman et al. 1941). Chapman et al. (1942) recommended in their dormant oils specifications that the oil be a relatively narrow-boiling-distillate portion of the petroleum. Pearce & Chapman (1952) concluded that there was no pesticidal advantage in oils greater than a certain median molecular weight (approx. 310), particularly for non-motile forms such as eggs and sessile scale stages. But they did identify a plant safety advantage in using the least persistent product possible; this led to the adoption of 60–70-s oils instead of 100-s so-called 'superior' oils. Chapman (1959) tightened the specifications by including a 50% distillation temperature and a 10%–90% range, using gas chromatography to define its chemical characteristics.

Role of oil deposit

Besides the UR and distillation characteristics, a third factor of primary importance to the effect of oil is the amount deposited. Ebeling (1932) showed that control of red scale was directly related to the amount of oil deposited; heavier oils gave better results, and UR apparently was not a factor. There may be a quite narrow range in the amount deposited between an effective dose and a phytotoxic dose, especially for plants in leaf (Smith 1932). Among the factors affecting the oil deposition rate are the oil's concentration in the spray; the kind and amount of emulsifying agent; the kind of equipment used to apply the spray; the quantity of spray applied per tree; and the nature of the plant surface treated. Deposition is often measured by the addition of dye and the use of spectrophotometry (Pearce et al. 1948). This parameter can become the best basis for conducting dosage–response studies, as pesticidal efficacy is directly related to how much oil is present.

Structural composition

Pearce et al. (1942) showed the relationship between the paraffinicity and pesticidal efficacy of an oil; this was later corroborated by several other workers, including Riehl & LaDue (1952). These observations led to the first recommendations for paraffinic oil to control orchard pests. In 1947 (Chapman 1967b), specifications were issued for a more highly refined, paraffinic oil, a 'superior type'. By 1959, the viscosity rating was linked to the terminology (e.g. '100-s superior oils'). In the 1960s, there were two weights (or viscosities) of spray oil recommended, a 60-s and a 70-s oil. These differed in molecular weight, viscosity and distillation temperatures. More recently, technical advances in the distillation and refining process have made it unnecessary to include a specification for viscosity, as is covered in the next section; however, spray oils meeting contemporary specifications would generally be expected to fall in the 60–70-s range.

Criteria for selecting plant spray oils

By the mid 1960s, it was clear that modern plant spray oils needed quite specialised traits to be acceptable for use in diverse pest control situations. Chapman (1967b) summed up the major criteria resulting from the previous decades of research, coming up with a profile of what became known as NR oils.

Chemical considerations:

- Aromatics and other unsaturated hydrocarbons contribute little to the pesticidal action of petroleum-derived spray oils; moreover, they are phytotoxic and should be reduced to levels as low as possible (preferably < 8%).

- An oil's mechanism of action in killing pests directly is physical; it interferes in the normal gaseous exchange of the pest's respiration.

- Once the first two considerations are satisfied, the desired average molecular weight of the product and the structural composition of saturated hydrocarbons present can be considered. Pesticidal efficacy starts to decline below an average molecular weight of approximately 310, regardless of the structural composition, and rises as paraffinicity increases. Suitable verdant plant oils can be selected from fractions having an average molecular weight of approximately 290–330, with those on the lighter end better suited for use on more sensitive plant species.

Physical and chemical considerations:

- Recommended oils are characterised principally by their viscosity, gravity, UR, pour point and distillation temperature (50% and 10%–90% range). Use of these characteristics would allow the recommending of products deriving from substantially different crudes; e.g. a 'better' naphthenic oil (containing > 60% paraffinic structures) might be just as acceptable as a highly paraffinic oil.

- Narrow-distillation-range products are desirable for both plant safety and pesticidal efficiency. Wider cuts will contain at one end portions that are too light to contribute any pesticidal activity, and at the other end components that could injure the plant.

- Gas chromatography (ASTM D 2887) should be used to improve the precision of older ASTM distillation methods which allow tolerance limits in the distillation that are too wide.

Overall, selection of HMOs and AMOs is simplified by specifying those that are paraffinic in composition. This allows more efficient use of properties such as viscosity, gravity and density for evaluation of candidate oils. The major limitation of verdant-type spray oils is the potential for phytotoxicity. The use of high-UR oils solves many of the plant injury problems, but complications arise with the combination of oils and other pesticides, owing to an oil's solvent and leaf-penetrating abilities. The small likelihood of completely avoiding all potentially unfavourable tank-mix combinations was a principal reason why the use of oil in New York was previously limited to the period ending just before the bloom stage of orchard crops until the more recent development of such verdant HMOs as nC21 Sunspray® Ultra-Fine®, nC23 Orchex® 796 and Stylet-Oil®, and the AMO nC25 Volck® Supreme, among others (Table 2). Traditional use of products to kill pests also limits verdant use. However, growing interest in the effects of oil deposits on arthropod behaviour (e.g. oviposition and feeding) suggests that the range of pests susceptible to control through this mode of action is much greater than the range susceptible to mortality. This change of emphasis is unlikely to change the criteria for products, as the major limitation is the risk of phytotoxicity.

The way in which spray oils work as pesticides has been the subject of considerable debate and conjecture over the years. In 1952, Smith summarised most of the current theories regarding oil's mode of action, which he categorised

Table 2. Optimum properties of 6 'narrow-range' oils manufactured and used in the USA in 1990 (based on Davidson et al. 1991).[1]

Specification	Orchex®796 [2]	Sunspray® Ultra-Fine [2]	NR 415 [2]	NR 440 [2]	Volck® Supreme [3]	Gavicide® Super 90 [4]
Distillation temperature (°C at 1.33 kPa) ASTM D 1160						
50%	226.7	212.2	212.8	226.7	246.7	226.7
10%–90% range	37.8	36.1	33.3	44.5	47.2	30.5
UR (% min.) ASTM D 483	92	92	92	92	99	93
API gravity ASTM D 4052	35.1	32.0	32.0	31.0	34.8	33.0
Viscosity SUS (s at 37.8°C) ASTM D 446	74	68	70	100	105	86
Pour point (°C) ASTM D 97	−14.4	−12.2	−6.6	−6.6	−12.2	−15

1. Davidson et al. (1991) used the term 'narrow-range' to refer to both (a) paraffinic oils with ≥ 92% UR and 10% to 90% distillation ranges (ASTM D 1160) of ≤ 44°C at 1.33 kPa and (b) then-recently formulated 'supreme oils'. They regarded the latter to be as safe as 'narrow-range' products for use on plants, but stated that the oils may pose more of a phytotoxicity problem on water-stressed plants because of their greater persistence. Furness et al. (1987) used the term 'narrow-range' when referring to paraffinic nC21 and nC23 products with ≥ 92% UR, with respective 10% to 90% distillation ranges of ≤ 44°C (ASTM D 1160) / nC6 (ASTM D 2887), and 52.8°C / nC7. Furness et al. (1987) also considered nC21 and nC23 oils with these properties as equivalent to California NR 415 and NR 440 oils respectively. A product with a distillation range of nC7 is now commonly considered 'broad-range' and, on the basis of the work of Kuhlmann & Jacques (2002), would be classed as an AMO. The term 'supreme oil' is now widely recognised as meaning a paraffinic product that would now be classified as an AMO. Some of these products, and some HMOs, have very high UR values (99.9%) that meet criteria required for US Food and Drug Administration classification as food-grade medicinal (pharmaceutical) paraffins.

2. On the basis of ASTM D 2887, these narrow-range products were or are HMOs.

3. The distillation properties of Volck Supreme given by Davidson et al. (1991) and available elsewhere suggest that it would now be classed as a > nC25 AMO according to ASTM D 2887-based criteria proposed by Kuhlmann & Jacques (2002).

4. According to Jacques & Kuhlmann (2002), Gavicide Super 90 is a naphthenic product with a higher average molecular weight than found in HMOs as defined by them.

according to whether it was being applied to eggs or motile forms. He proposed that when used as ovicides, oils may act by:

- preventing the normal exchange of gases through the outer coating
- hardening the outer covering so as to prevent hatching
- interfering with the water balance of the egg
- softening or dissolving the outer covering of the egg, through interference with normal embryonic development
- penetrating the egg and coagulating the protoplasm or interfering with enzyme or hormone activity
- exerting a negative effect on the insect's delicate integument.

When used against motile arthropods as insecticides and acaricides, oils were thought to act by:

- blocking spiracles, thus leading to suffocation
- penetrating the tissue in the liquid phase and 'corroding' it by breaking down tissue structure
- containing volatile components that are toxic and act as fumigants.

Smith & Pearce (1948) had studied the respiratory effects of oils on eggs of the oriental fruit moth (*Grapholita molesta* (Busck) [Lepidoptera: Tortricidae]) and found them to be responsible for decreased respiration rate, presumably

through mechanical interference with normal gaseous exchange. They further concluded that the less-reactive paraffinic oils showed greater ovicidal efficacy than the more-reactive unsaturated oils.

The modes of action of HMOs and AMOs on arthropod behaviour are not known or are poorly understood. They represent significant opportunities for future research.

Refining and formulation of petroleum oils

Fractionation processes

Selection of crude oil is the first step in the manufacture of petroleum spray oils. There are variations in crude type and quality, so proper selection is important to the economical production of these compounds. Paraffinic base oils, including HMOs and AMOs, are ideally produced from a paraffinic-type crude oil that yields an acceptable volume of base oils without the need for extensive processing. Kerosene can also be obtained from this same crude oil, and the white oils (highly refined straight mineral oils used for food, medicinal and cosmetic applications) can be produced by further processing the base oils.

The process of refining a crude oil for the production of various products, including the lubricant and spray oil fractions, essentially involves distillation to remove the more volatile compounds followed by chemical treatment to remove various other undesirable materials. The best practical methods of achieving a complete separation of hydrocarbon oils are fractional distillation and selective solvent extraction. Distillation separates petroleum hydrocarbons according to their molecular size, as expressed by their relative boiling points, and selective extraction separates according to the relative solubility or type of compounds present in the oil (Fenske & Hersh 1941). Using the proper combination of these processes can give an end product or 'fraction' that contains molecules of similar size and type. Commercial fractionating processes typically consist of a technically extensive series of intermediate steps (not discussed in detail here), the fundamental sequence of which has historically relied on distillation, crystallisation, extraction and adsorption.

Distillation

The primary refining step is atmospheric distillation or fractionation, in which crude is separated into fractions, or components, in a distillation tower. Heat, usually applied at the bottom of the tower, causes the oil vapours to rise through progressively cooler levels of the tower, where they condense onto plates and are drawn off in order of their respective condensation temperatures, or boiling points. The lighter-weight, lower-boiling-point fractions exit higher in the tower. The primary fractions, from low to high boiling point, are hydrocarbon gases (such as ethane and propane); naphtha (a collection of light petroleum distillates including gasoline blending stocks, mineral spirits and various petroleum solvents); kerosene; diesel fuel and heating oil; and heavy gas oil for use in cracking (decomposition) procedures. Next come the reduced crude or lubricants fractions, which under vacuum distillation yield the naphthenic lubrication oils, paraffinic lubrication oils and waxes. Heavy materials remaining are called the bottoms and include such components as heavy fuel oil and asphaltic substances. Those fractions taken in liquid form from any level other than the very top or bottom are called sidestream products. A product removed in vapour form from the top of the distillation tower, such as propane, is called overhead product. Distillation may take place in two stages: first, the lighter fractions—gases, naphtha and kerosene—are recov-

ered at essentially atmospheric pressure; next, the remaining crude is distilled at reduced pressure in a vacuum tower, which causes the heavy lubrication fractions to distil at much lower temperatures than possible at atmospheric pressure, thus permitting more lubrication oil to be distilled without the molecular cracking that can occur at excessively high temperatures (Exxon 1980).

Straight distillation at a fixed pressure is usually the best fractionating process to apply first to a crude mixture to separate it into a series of constant-boiling fractions, each of which is essentially a pure substance or a solution of compounds having practically the same boiling point. These constant-boiling mixtures may then be subjected to one or more of the other fractionating methods. The bottoms from the atmospheric distillation tower would crack or break down into smaller molecules if distillation was done at atmospheric pressure. Therefore, distillation at a reduced pressure (vacuum distillation) separates the base oil fractions by boiling point; this is especially useful for separating hydrocarbons of different types that have the same boiling point at atmospheric pressure but that have differences in relative partial pressures (Rossini 1937).

Crystallisation

Crystallisation by simple refrigeration is particularly useful in separating a component that is present in a large amount (such as a normal paraffin that has previously been concentrated by distillation) from a mixture of other components that crystallises when cooled. One method of achieving this result, termed equilibrium melting, entails first solidifying the entire mixture and then gradually raising the temperature while removing the liquid impurities by centrifugation, repeating the process so to leave the desired hydrocarbon in essentially pure form. For mixtures of a more complex composition, this technique can be modified by using a solvent to dissolve the wanted component and then crystallising from the solvent, which is removed by a method such as evaporation.

Extraction

Fractionation by extraction is accomplished by using an appropriate liquid solvent in which the constituents of the mixture distribute themselves in different proportions from what they had in the original mixture. Commonly used agents are furfural (an aldehyde derived from corn cobs and oat hulls), N-methylpyrrolidone (NMP), phenol, liquid

sulfur dioxide and nitrobenzene. The oil and solvent are mixed in an extraction tower, which results in the formation of two liquid phases: a heavy phase consisting of the undesirable components (generally unsaturates such as aromatics) dissolved in the solvent, and a light phase consisting of high-quality oil containing some solvent.

The phases are separated and the solvent is recovered from each by distillation.

Solvent dewaxing

For the base oil to be fluid at low temperatures, the paraffin waxes must be removed. In this process, the solvents methyl ethyl ketone (MEK) and toluene are mixed with the base oil and then chilled to a low temperature, typically around –18℃. The MEK dissolves the wax, and the toluene dissolves the oil. The wax is precipitated, and the desired liquid phase, now a base oil with a pour point of approximately –18℃, is filtered out.

White oil acid treating

HMOs and AMOs are 'finished' after the dewaxing step to produce white oils; the conventional method uses fuming sulfuric acid, which reacts with the aromatics to form sulfonic acids. Those that are insoluble can be removed by settling, but the sulfonic acids that are soluble in the base oil must be converted to sulfonates and extracted with alcohol.

Adsorption

Bringing an oil into contact with a substance such as activated clay causes some compounds contained in the oil to adhere to the solid, which can effectively separate classes of compounds and improve the oil's colour. By means of adsorption with silica gel, aromatic hydrocarbons can be removed from a mixture of paraffinic and naphthenic hydrocarbons. Similarly, the naphthenes can also be separated from the paraffins. Using Fuller's earth or bauxite, minute solids can be adsorbed from lubricating oil, along with traces of water, acids and polar compounds. Materials most prone to adsorption in the manufacture of petroleum spray oils include nitrogen and sulfur compounds. Molecular weight has a major influence on this process, those substances of higher molecular weight adsorbing more readily. It is customary in the production of white or colourless oils to first refine with sulfuric acid and then treat with adsorbents (Swingle & Snapp 1931).

Recent technical advances

Hydrogenation

By the late 1950s and early 1960s, hydrogenation began to be used after the solvent extraction step of the refining process to make a white oil. This is the chemical addition of hydrogen to a hydrocarbon in the presence of a catalyst, such as nickel–molybdenum or nickel–cobalt. In destructive hydrogenation, hydrocarbon chains are ruptured (cracked), and hydrogen is added where the breaks have occurred. In non-destructive hydrogenation, hydrogen is added to a molecule that is unsaturated. This process involves high temperatures (260°–315℃) and pressures (5500–13 800 kPa), and achieves a moderate amount of saturation by removing some impurities such as sulfur (to produce hydrogen sulfide), nitrogen (as ammonia), or oxygen (as water). By providing a few more UR points, this process gave refiners more flexibility with their source crudes.

Hydrocracking

This replacement for the solvent extraction process is a newer method for reducing the aromatic content of a base oil. Its use started in the late 1960s and early 1970s. In this process, the oil is subjected to extreme conditions (427℃ and 20 700 kPa) in the presence of a metallic catalyst and hydrogen. Under these conditions, the aromatic rings are broken and saturated with hydrogen, thereby converting them to paraffins. This enables refiners to produce high-UR, low-phytotoxicity spray oils from essentially any crude oil (pers. comm. J. Nutter, Sun Oil Company, Philadelphia, Pennsylvania, USA).

Iso-dewaxing

Implemented only during the past 10 years, this process converts a by-product wax (such as a 30-carbon hydrocarbon compound) into a pure paraffin by attaching a methyl group at each end. This method is commonly used in combination with hydrocracking to increase a base oil's paraffinicity.

Formulation of petroleum oils

Emulsification

Early Work

Initially, petroleum oils were used for insect control by simply applying them undiluted to plants, but this led to such severe injury that the natural consequence was to search for practical methods of diluting them in water (Swingle & Snapp 1931). Because the physical nature of an oil prevents its forming a solution in water, it is necessary to emulsify it, which entails dispersing it throughout the water in the form of minute droplets. The earliest attempts at emulsification were mechanically produced mixtures, either through vigorous agitation of the two ingredients or by simultaneously forcing streams of each through the spray nozzle under pressure; no agents were added to stabilise the emulsion. Because of inadequacies in the equipment used for this process, the emulsion often failed, and severe plant injury was commonplace (Swingle & Snapp 1931).

The search for materials to stabilise the emulsions turned up a range of candidates, among them soap, fresh or condensed milk, lime and flour (Riley 1891, 1892). A kerosene–soap emulsion, which did not hold the emulsion stable for a practical period of time, was recommended as early as 1871, but a more stable soap–oil emulsion was used in 1882 (Riley 1892). Such emulsions were normally prepared by pumping all the ingredients—oil, soap and water—together through the spray nozzle.

Theories of emulsification

An emulsion consists essentially of small droplets of one liquid suspended in another. Simple agitation of water with a small quantity of oil will result in the formation of globules of the oil that eventually rise to the surface of the mixture and re-coalesce into a uniform layer. However, the addition of a small amount of a stabiliser such as hydrated lime will prevent or at least greatly delay this coalescence by forming a thin barrier around the oil droplets. These droplets also carry a negative charge, which contributes to their tendency to disperse evenly throughout the emulsion (Richardson & Burdette 1927). Use of different stabilisers can result in an emulsion of water droplets in oil, known as an 'invert' emulsion. Explanation of the type of emulsion formed has been attempted by several theories:

'Ease of wetting' theory. Those emulsifiers more easily wetted by water tend to result in standard oil-in-water emulsions, whereas those more easily wetted by oil tend to form invert emulsions. The material must collect on the interface between the two liquids to act as an emulsifier, so it must be wettable by both liquids. The liquid with the higher affinity for the emulsifier (i.e. more readily able to wet it) will tend to form the continuous phase of the emulsion (Finkle et al. 1923).

'Oriented wedge' theory. The molecules of a soap emulsifier assume a specific orientation in the thin film that they produce between the oil and the water. According to this theory, the soap's hydrocarbon chain is directed toward the oil side of the interface, and the metallic salt end of the soap molecule is oriented toward the water, according to the rule that each end aligns with the liquid it most resembles. The geometric shape of this molecule is said to resemble a wedge, as the sodium or potassium end is larger in cross-section than the hydrocarbon end. Because the larger end is the one soluble in water, the oil would become the inner or dispersed phase, producing an oil-in-water type of emulsion. For soaps made with bivalent metals such as calcium or magnesium, one atom of the metal combines with two hydrocarbon chains. Therefore, the larger end of the wedge is the hydrocarbon, which would yield a water-in-oil, or invert, emulsion.

These theories do not adequately explain those emulsions formed with inert substances such as kaolin, bentonite and charcoal (Seifriz 1925). However, the types of emulsions formed in any given case can often depend to a large degree on such factors as the method of handling, the mixing procedure used, and even the mixing sequence.

Types of emulsifiers

In the case of soap emulsifiers, potassium soaps have been used preferentially in the past, because of their ease of handling and the greater permanence of their emulsions. Sodium soaps have also been used, principally as emulsifiers for miscible oils. Animal oils have been recommended extensively in the literature, especially fish oil, which was inexpensive, and whale oil (Penny 1906; Yothers 1911). Vegetable oils have been tried with mixed results; some of the more satisfactory types were cottonseed oil from *Gossypium hirsutum* L. [Malvales: Malvaceae], olive oil from *Olea europeae* L. [Scrophulariales: Oleaceae] and Turkey red oil (sulf-

ated castor oil) from *Ricinus communis* L. [Euphorbiales: Euphorbiaceae] (Swingle & Snapp 1931).

A host of non-soap emulsifiers has been tested, including (besides milk, lime and flour) plaster of Paris, chalk, silica, alumina, Bordeaux mixture, glue, egg albumin, metal sulfates, and calcium and lead arsenates. Among the fine clays, kaolin, bentonite and Fuller's earth have been recommended (English 1925; Yothers 1925; Frear 1942).

Types of emulsions

Hot-pumped (or boiled) emulsions. Soap emulsifiers were used for making the hot-pumped emulsions. In this method, the oil was mixed with soap combined with water, and the mixture was heated to boiling and pumped through fine nozzles while still hot. Advantages of these emulsions were their reliability of formation and stability over relatively long periods of time. Unfortunately, they were expensive to prepare because of the heating process and the equipment needed for producing them (Swingle & Snapp 1931).

Cold-stirred emulsions. These were also made by using soap as the emulsifier, but differed from the hot emulsions by not requiring heat or pumping (Yothers 1911). With this method, small quantities of oil were repeatedly added to the soap and thoroughly stirred after each addition. Their advantages were in the low cost of equipment needed and the virtual elimination of the need for a heating source. However, the dispersion of the oil droplets depends on the attraction between the soap and the oil, which in turn depends on the viscosity of the soap used. This can be a difficult parameter to control, as it is influenced by the soap's moisture content, the nature of the caustic agent used to saponify the oil, and the temperature.

Cold-pumped emulsions. These were generally prepared with non-soap emulsifiers and were some of the earliest mixtures used. The method consisted of simply adding emulsifier to the water, followed by the oil, and pumping the mixture out through a fine opening under pressure. The most commonly used emulsifier was calcium caseinate; Bordeaux and kaolin have also been used (Hammond 1926). These emulsions were cheap and easy to make on the farm, so they found favour with a large number of growers.

Miscible oils. These differed from the emulsions noted above because the emulsifier was dissolved in the oil, and the emulsion contained a relatively small quantity of water (usually < 10%). They appeared clear or slightly cloudy, but formed a white emulsion when water was added and agitated; the active ingredient in miscible oils was mineral oil. The advantages of these emulsions were their low water content, which added to their ease of handling, and their stability at low temperatures. Their main disadvantage was their higher cost compared with oil emulsions (Swingle & Snapp 1931).

Later experience with emulsifiers

In 1927, de Ong et al. reported that the 'quick-breaking emulsion' concept improved the insecticidal efficacy of oil against citrus pests. An emulsified mixture is described as quick-breaking if the oil droplets coat the sprayed surface while the water phase runs off. Blood albumin spreader, first developed by Smith (1932), was used extensively until the 1960s, when it was replaced by other non-ionic emulsifiers (Davidson et al. 1991). In New York, it began to see widespread use beginning about 1941, because of its desirable dormant-oil-emulsifying properties, together with its cost, availability and ease of handling (Pearce & Chapman 1942). It was found to be preferable to other materials in use at the time, such as lignin pitch, Bancroft clay, Bordeaux mixture and skim milk powder, because it had greater oil-depositing properties. For instance, control of fruit tree leafroller eggs was obtained by using 4% oil with blood albumin, compared with 6% oil with lignin. It was typically applied at a rate of 15.6 mL/100 L (2 oz/100 US gal), and was usually sold as a 25% a.i. formulation with an inert filler such as diatomaceous earth.

During the 1950s, researchers began trying to codify what they had observed from previous years of work with emulsified oil sprays into guidelines for enhanced efficacy of these products. Chapman et al. (1952) pointed out that two factors determining the oil deposition rate on a plant surface are the kind and amount of emulsifying agent used. The emulsifying agent should maintain a uniform concentration of oil throughout the mixture, but this requires a stable emulsion. However, they argued that a stable emulsion usually lays down a low-oil deposit. To obtain moderate deposition, it is necessary to sacrifice some stability; therefore, agitation is required to maintain the emulsion. Pearce & Chapman (1952) advanced the theory that blood albumin was not a sufficiently surface-active emulsifier to provide good distribution of materials with large, highly non-polar molecules on the leaf surfaces. They felt that it

would probably be better to use a light petroleum solvent such as highly refined kerosene.

A more radical theory advanced by Smith (1954) concerned the influence of the emulsifier. He felt that, depending on the kind of emulsifier used (for a given concentration of oil), the deposit on the plant surface could vary by a factor of more than 3. The effect was the same for pre-mixed emulsions and emulsifiable oils. His argument was that the chief role of the emulsifier appeared to be in influencing deposit, which affects control. He proposed that, instead of recommending oil by percentage concentrate in the spray, it was better to indicate the effective deposit required (in mg per leaf area), based on experience, and then standardise the emulsion and oil to use for a given purpose. Fortunately, it was decided that this would be impractical and unlikely because of the large number of oils, emulsifiers and formulations available.

Currently, most oils in the USA contain a non-ionic surfactant dissolved in the oil at a concentration of 0.35% (w/w) for citrus and at 0.5% for deciduous use (Davidson et al. 1991). The mixture of spray oil plus water is agitated in the tank and cycled under pressure through the sprayer's pump, which thoroughly emulsifies the oil in the water.

Conclusion

It is clear that petroleum-derived spray oils have established themselves as permanent components of many pest management programs, and that they will continue to be developed and adapted to the increasingly specialised needs of modern agriculture. Technical improvements in the refining of petroleum have reduced the extent to which refiners are limited by the intrinsic quality of the crude, as it has become possible to produce an acceptable crop spray oil starting with crudes from an unprecedented range of types, qualities and blends. There is concern, however, that the practical upper limits of spray oil quality may have been reached, inasmuch as further improvements could make the products either too expensive or too impractical for widespread use. For instance, as UR is increased, solubility decreases, which makes the oil more difficult to emulsify; such a characteristic could compromise its pesticidal efficacy. Nevertheless, it appears certain that their availability, quality, pesticidal effectiveness, and safety characteristics for food, plants and the environment will ensure their continued use in agricultural systems for many years to come.

Acknowledgments

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