The Characteristics of Insecticidal Petroleum Emulsions

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THE discovery during the middle of the last century that mineral oils are highly toxic towards most of the insect pests the elimination of which is necessary if remunerative cultivation is to be carried on, has led to great progress being made in their application in this direction in recent years. Initially kerosene was experimented with, but it was found very soon that this oil, when allowed to remain on leaves, caused them to wither and was especially injurious to developing buds. In order to avoid, or minimize, this danger, the procedure of emulsifying the kerosene in water by means of soap was adopted from about 1875. The volatility of kerosene, however, was both an advantage and a disadvantage; on the one hand it did not permit the oil to remain in contact with the plants long enough to cause permanent injury, whilst on the other hand the toxic effects could not be as potent as in the case of a less rapidly evaporating substance.

Early in the present century it was discovered that a more powerful action was obtainable by the use of heavy oils, such as lubricating and fuel oils and by crude petroleum oils generally. Here again attempts were made to apply the oils directly in the undiluted state, but the results which followed were distinctly unsatisfactory even when a spray of the finest type was employed. The direct use of oils as a summer spray almost invariably resulted in severe damage. The danger was not quite so great when the application was made to trees in the dormant state, but even then bad scorching of the bark sometimes occurred.

It was then realized that the only effective way in which advantage could be taken of the valuable insecticidal properties of these oils was to use them in the form of stabilized emulsions, and the production of emulsions of uniform droplet size made under standardized conditions to take the place of the crude and variable types of temporary emulsions hitherto used, which were liable to cause injury, was developed.

Types of Emulsions

The type of emulsion required for insecticidal work is the oil-in-water type, in which minute globules of oil are dispersed in the aqueous medium in such a way that separation does not take place even on prolonged keeping. An emulsion lasting for a few moments can easily be made by simply agitating an oil violently with water, but if separation is to be inhibited an emulsifying agent must be added. This acts by entering the interface between the oil particles and the water and preventing their coalescence. Soaps are mainly employed, although very finely divided powders such as flour and many minerals (e.g. basic copper sulphate) and organic colloidal substances such as gelatine can effect the same result. The efficacy of powders in this direction is of importance, inasmuch as it enables materials such as the active agent in Bordeaux mixture to be employed as the suspending substance, thus providing a two-fold toxic activity in the product.

As a rule, those substances which are oil-soluble promote the formation of an oil-in-water type of emulsion, whereas water-soluble emulsifiers cause a water-in-oil type to be produced. This rule is, however, not general, and certain emulsifying agents are known which will produce emulsions of either type, depending on the conditions of manufacture. Stabilizers, which will be referred to again later, are sometimes added to render an emulsion less liable to break down. These may, if present to excess, cause the inversion of the emulsion to a water-in-oil type which is of no use for insecticidal purposes owing to the fact that it is not possible to dilute it with water. Inversion is also liable to occur through overheating, especially in the case of emulsions containing more than 75 per cent of oil. Once inversion has occurred it is usually impossible to cause reversion to the original type and it is necessary to start afresh.

Soaps of sodium and potassium and monovalent cations generally promote the formation of oil-in-water emulsions, whilst the divalent ions and those of higher valency, such as calcium, cause the dispersion to be of the water-in-oil type. For this reason, hard water will have the effect of breaking the emulsion, and there is, in fact, a so-called critical point at which the inversion takes place, when the two types of ions are in the critical ratio. This leads to the notion of "antagonistic emulsifiers," these being materials which facilitate the formation of emulsions of opposite types and should therefore not be used in the presence of one another. The reduction of inter-facial tension is, however, also an important factor in facilitating emulsification, yet it is possible in certain instances to actually reduce this figure by the combination of mutually antagonistic agents.

The production of emulsifiers for insecticidal purposes demands consideration of a number of different properties, including stability, the effects of dilution with different kinds of water, globule size, etc., before any general conclusions can be reached. Different parasites are also more vulnerable to one type of treatment than to another, and this also must be borne in mind in compounding a material for a specific purpose.

Soap Emulsifiers

The soap emulsifiers are based on a large range of saponifiable oils, but the potash soaps are best owing to the fact that they are generally fluid at room temperatures, which makes for easy manipulation. Of the many types of oils, mention may be made of fish oil, which has the advantage of low price besides being a good emulsifying agent; red oil and whale oil have also outstandingly good properties. Cottonseed oil, rape oil and linseed oil have all been employed for this purpose, although the oxidizing oils are best avoided, as they tend to form a varnish on the leaf. Other oils such as coconut oil, palm oil and peanut oil are available, but they are difficult to saponify without long boiling. Soaps which have been boiled for any length of time often show a decreased emulsifying power as far as mineral oils are concerned.

This may be due to the breaking up of long chain molecules or to oxidative processes. For this reason a good procedure is to make use of the so-called "nascent" soaps for the emulsification process. This consists in mixing the saponifiable oil directly with the mineral oil and adding the caustic potash to the mixture; thus the soap is formed directly in the presence of the oil which it is proposed to emulsify, so that emulsification can often be effected where the use of finished soap would not be successful.

In the case of the vegetable oils both the potash and soda soaps of oleic acid are better emulsifiers than those of either palmitic or stearic acids. In addition to the necessity for the presence of a vegetable oil to provide the soap for the emulsification process it has been shown that these glycerides have a definite toxic action of their own. An investigation by Tattersfield and Gimingham has shown that the toxicity of normal saturated monocarboxylic acids towards *Aphis rumicis* increases with increase in molecular weight, capric acid, $C_9H_{19}COOH$, and undecylic acid, $C_{10}H_{21}COOH$, being the most effective, the toxicity decreasing with acids higher in the series than these. The free fatty acids are most toxic, the gylcerides and sodium salts being less effective. These acids have also very good spreading powers and are stable in lubricating oils, so that their use is possible in order to make the action of the oil more certain. Nicotine has been added to lubricating oil emulsions for the same purpose, but the fatty acids have the advantage of cheapness.

The choice of the best type of soap depends on the oil to be emulsified, and upon the conditions of emulsification, such as temperature, agitation, etc. These conditions are very variable and have led to some extraordinary divergencies of opinion on the part of several workers in this field regarding the "emulsifying powers" of different substances. An attempt will be made in the succeeding paragraphs to coordinate the principles involved in the production of these emulsions and to clarify the requirements of an emulsion which is to have a high toxic effect upon the pests and yet not damage the plant to which it is applied. If the emulsion is of the oil-in-water type, i.e. the minute oil globules are suspended in an excess of water as a medium, it is clear that the emulsion can be diluted indefinitely by the addition of water. It has been shown by Pickering that if the water is greatly in excess the emulsion will separate into two phases, one of which he terms the "cream" or the real emulsion, the rest being the excess of the continuous phase. This "cream" generally contains from 65 to 82 per cent of oil by volume, which agrees with the hypothesis that if the oil globules are considered to be non-deformable spheres of the same size, and if they are assumed to be packed so that each is in contact with all its immediate neighbors, the percentage of the total volume occupied by the oil would be 74.05 per cent. It is therefore considered by Woodman that only emulsions containing this percentage of the disperse phase may be considered as being permanently stable. Thus any emulsion containing less than 74.05 per cent of oil would show a "creaming" tendency, with the result that on spraying, the oil would be deposited too heavily in certain areas. A method of overcoming this tendency to some extent is by the addition of a medium which may be termed a stabilizer, which would be soluble in the oil globules and lessen the difference in density between them and the external phase.

Cresylic acid is of value in this connection and by its use it is possible to stabilize kerosene emulsions in soap solution without creaming. Other such stabilizers which may be added to the soap to aid in bringing it into closer contact with the oil by acting to some extent as a mutual solvent are cresols, cyclohexanol, amyl alcohol (fusel oil), and butyl alcohol.

Other Emulsifying Agents

Soaps are not the only emulsifying agents employed, and other emulsifiers for particular types of products are to be found in the sulphonated oils and their soaps, whilst various solids such as finely divided carbon, kaolin, the basic carbonates of iron, nickel and copper, and so on, are all effective in varying degrees; gelatine also favors oil-in-water emulsification. The use of casein has extended in recent years, more especially in the form of calcium caseinate; such emulsions are valuable where soap emulsions are liable to break down owing to the use of hard water for their dilution. In using casein only oils of a specific gravity less than .818 are advisable; with these a fine stable emulsion can be obtained, but petroleums of a higher gravity than .874 cause an inversion of the emulsion type with the production of a water-in-oil emulsion which is not of any value for the present purpose. At gravities between these two figures the emulsions are either of a low stability or else they will not form at all. These conclusions are generally applicable provided the oils have been carefully fractionated so that fractions of higher specific gravity are not present to invalidate them.

Casein emulsions may be prepared without the use of heat by simply agitating the oil with an equal amount of water containing .2 to .3 per cent of finely ground casein in suspension.

The agitation process has itself been the subject of considerable study, the outcome of which shows that intermittent agitation is usually superior to continuous stirring. In certain specific instances the process of emulsification has been made to take place about a thousand times as fast by simply stirring the mixture for a few minutes and then allowing a rest period of one minute before recommencing to stir. The reasons for this phenomenon have been the subject of much interesting theoretical speculation, the most likely hypothesis being that the rest period enables the emulsifier to become orientated in the correct position with respect to the internal and the external phases, i.e. the hydrocarbon group being dissolved in the oil whilst the active group is dissolved in, or attached to, the water.

It is perhaps worthy of mention here that the use of finely divided solids as emulsifiers has been adversely criticized on the ground that it is liable to result in a decrease in insecticidal efficiency owing to adsorption of some of the oil by the suspending agent.

The rate of stirring is another factor influencing the perfection of an emulsion. There is an optimum speed above which the stirring efficiency is decreased. In a series of experiments on the emulsification of lubricating oils in water, Herschel found that on the average a speed of 1,500 revolutions per minute with a paddle type of stirrer gave a minimum separation of oil. He also found that no advantage was to be gained by continuing the stirring process longer than about five minutes, and in fact it appears that, in general, emulsification by agitation either takes place fairly quickly or not at all, so that there is little purpose in expending a great deal of power in attempting to achieve emulsification. Excessive agitation is to be avoided in any case, and it is, indeed, often possible to break an emulsion by agitation.

In mixing the two phases, the disperse phase should preferably be introduced through a spray nozzle below the continuous phase, and when agitation is to be carried out it should be conducted so as to avoid frothing and the incorporation of air. The reason for this is that when a froth is produced the emulsifier tends to concentrate at the gas-liquid interface, rendering the froth particularly stable, and at the same time is removed from the oil-water interface where its presence is required.

Some Practical Methods

Soap stabilized emulsions can be made in two ways, i.e. by boiling or by cold-stirring at lower temperatures. In the case of boiled emulsions the oil is usually mixed with half its volume of water containing soap in the proportion of about one pound of soap to one gallon of water and pumping the hot mixture repeatedly through a fine aperture. If the water is soft the quantity of soap may often be considerably reduced. The pumping process facilitates the necessary intimate contact between the soap and the oil and water phases. This may also be brought about by heating the soap and oil together until the former has become quite dispersed in the latter. The temperature is then raised considerably in order to reduce the viscosity sufficiently for the subsequent agitation to be most effective. At this stage boiling water is added whilst the soap dispersion is still hot, stirring continuously. As the temperature gradually falls a "swelling" process occurs and emulsification takes place. More water is then added until a suitable dilution is obtained, when the product will not gel at temperatures above freezing point.

Another procedure is to effect the saponification of a sulphonated oil in the presence of a mineral oil, thus producing a so-called "soluble oil" in which the emulsifier is already dissolved in the oil, emulsification only taking place when the product is actually mixed with excess water. A stable emulsifiable oil can be prepared from some such mixture as the following:

	Gallons
Lubricating oil (Viscosity 80-100 at 100° F.)	4½
Commercial oleic acid	2
Caustic soda (10° Bé.)	1¼
Sulphonated castor oil	10
Water	7½

The mineral oil is first mixed with the sulphonated oil, the whole agitated, and the caustic soda solution run into the mixture. The whole is then brought to the boil, allowed to stand overnight, and mixed with water to the required concentration. The presence of a small quantity of ammonia or alcohol has been found to aid in bringing about emulsification in case of difficulty. Rosin oil is a valuable substitute for oleic acid in the type of emulsion just described, but when it is employed the proportions of the other ingredients must be suitably adjusted.

The soluble oils give a fine emulsion on dilution, the globules being smaller than is the case with concentrated emulsions. They will tolerate dilution with moderately hard water, but it is difficult to cause them to disperse in water containing an appreciable amount of salt; in such waters it is often possible to form an emulsion by first emulsifying the soluble oil with a small amount of non-saline water and finishing off the dilution with the salt water. Soluble oils are usually clear and transparent, giving a milky emulsion on dilution. Sometimes when a small amount of alcohol is added to facilitate the solution of the emulsifier in the oil the resulting solution becomes cloudy; clarification can in such cases usually be effected by the incorporation of a small quantity of oleic acid. Excessive quantities of oleic acid are to be avoided, as they decrease the stability of the emulsion and cause it to break down more readily.

This last fact renders it possible for the manufacturer of soluble oils to make his product of a carefully regulated power. It must be borne in mind that the emulsion must break up when in contact with the insect in order to exercise its toxic effect, yet it must not break up so easily as to cause any considerable area of the plant to be covered with oil. By careful adjustment of the stability of the emulsion a suitable material can be obtained. For use as a winter wash, when the tree is not quite so susceptible to the destructive influence of the oil, a rather less stable emulsion can be employed and in this way a higher degree of toxicity towards larvae and ova is obtainable.

Miscible oils can be obtained with a much lower water content than the concentrated emulsion type, thus lowering the cost of transport, although this is perhaps counterbalanced by the higher cost of the necessary materials. They are also less liable to freeze at low temperatures. A basis for a miscible oil of low water content is as follows:

	Gallons
Lubricating oil	18
Rosin oil	2
Oleic acid	2

To this mixture add half a pound of caustic soda dissolved in one gallon of a mixture of equal quantities of industrial alcohol and water, heating until emulsification is complete.

The presence of rosin soap is of value apart from its emulsifying action, as it is a valuable insecticide even when used alone, particularly against scale insects. It acts by clogging the spiracles of the pests owing to the liberation of free rosin from the soap through the action of the carbon dioxide in the atmosphere.

Emulsification in the Cold

The cold-stirred emulsions are cheaper to produce than the other types, as they require less heating, or no heat at all. Their stability is, however, rather lower in some instances. A method has already been described in connection with casein, but when soaps are to be employed the usual procedure is to add small quantities of the oil at a time to the soap solution, stirring thoroughly after each addition. One pound of soap is required per gallon of oil. When the oil has all been incorporated, a thick, jelly-like mass results, and water is then stirred in gradually until about one-third of the total volume of the product is water.

In the preparation of cold-stirred emulsions a number of factors must be taken into account if success is to be assured. In the first place the soap solution must be of a suitable viscosity. If it is too thick thorough contact between the soap and the oil (which is also dependent upon the efficiency of the stirring) will not be able to take place, whilst if the solution is too thin the time of contact will be too short for an equilibrium to be established at the interface. Only potash soaps are able to satisfy these requirements, either alone or occasionally with a small amount of a soda soap. A slight excess of caustic potash in the saponification of most oils causes a rather more viscous soap to be formed, and is favorable towards emulsification, but a great excess will result in separation of the soap, with the consequent destruction of its emulsifying properties. Potash is also favorable from the point of view of egg destruction, as oil emulsions appear to have a greater ovicidal value in the presence of alkalies.

Too much water in the soap is also to be avoided as it leads to instability. A water content of 60 to 70 per cent is desirable. In order to render the soap sufficiently fluid for emulsifying purposes it is better to increase the fluidity by heating to 120° or 125° F. rather than to add excessive quantities of water. Effective stirring and moderate temperatures are the essential points in the preparation of emulsions of this type.

Dilution

In all emulsions based on soap, trouble is likely to occur when very hard water is used for dilution. In the first place the presence of calcium salts in the water will cause the precipitation of calcium soaps, which, being insoluble, will clog the spray nozzle. Also the deposition of the soap will cause the liberation of a certain amount of oil which will float on the surface of the water and may be sprayed on to the tree in the undiluted state, with regrettable results. The elimination of excessive agitation of the mixture has been shown to minimize this precipitation, which may also be lessened by the presence of free alkali. Various materials have been recommended for addition to oil-soap emulsions to render them less susceptible to the influence of hard water. These include glue, gelatine, starch, and other organic colloids. These are to be boiled with water and added to the emulsion just before dilution, in the proportion of one pound to three gallons of concentrated emulsion. If the addition is made at the time of manufacture a good preservative must be added to inhibit fermentation. These stabilizers are of special value in those cases where it is desired to use an oil emulsion in conjunction with lime-sulphur mixture, which is more effective than petroleum in the destruction of rust mites; the colloid will make the mixture of these materials fairly stable. The calcium soaps precipitated in the presence of these stabilizers are in a very finely divided state and no free oil is liberated.

Calcium caseinate is stable in most hard waters, but it is said that magnesium sulphate may cause some oil to be set free.

Lime-sulphur used in conjunction with an oil emulsion is particularly valuable against San José scale and similar pests, as the former has been shown to have the power of softening the waxy armor of the insect, thus speeding up the solvent action and penetrating properties of the petroleum. The softened wax also causes the insect to adhere to the leaf when the mixture dries off, whilst the polysulphides, owing to their high oxygen-absorbing capacity render the waxy membranes less permeable by this vital element, bringing about a slowing up of the insect's metabolism and its ultimate death.

Stability

Reference has already been made to the effect of the stability of the emulsion on its toxicity. The results of recent work have proved conclusively that the best results are obtained when the emulsion breaks fairly soon after it has been applied. In this way rapid contact with the insect is established; the oil has also a superior spreading power to that of the emulsion, provided, of course, that its viscosity is not too high. The size of the globules determines the stability of the emulsion; the larger they are the quicker the emulsion will break. Increase in the size of the oil globules may be brought about by decreasing the proportion of the emulsifier. Soap emulsifiers tend to form a strong, elastic interfacial membrane between the oil and the water, so that breakdown does not usually take place quickly; lime-casein or soda-casein is more likely to give quick breakdown, with an increased efficiency which makes it possible to use a weaker dilution to achieve equivalent results.

A quick-breaking spray containing larger oil droplets will also possess a lower surface energy and will therefore spread more easily. It has furthermore been shown that the droplets are probably negatively charged electrically, the surface of the leaves having a similar charge. Thus if the droplets are small there will be a definite repulsion between them and the leaf, with the result that a fair proportion of the oil will be lost in the form of drippings, inasmuch as a smaller globule has a greater charge in proportion to its mass than a larger one.

Causes of Toxicity

The action of petroleum sprays upon insects was at first thought to be due to volatility, the vapor preventing the access of the oxygen to the insect. This accounted for the use of the lighter fractions in the early days. The discovery that the heavier oils were more toxic than the paraffins, coupled with the knowledge that insects are able to exist for long periods in the absence of oxygen, led to more accurate conclusions being reached.

It has been shown that the toxic effects are due to the penetration of the trachea of the insect by the oil, both the emulsion and the oil itself being capable of doing this, although the oil does so rather better. Certain insects, such as the red scale insect, for example, can expel the lighter fractions but cannot so eliminate heavier oils, with the result that death by suffocation ensues. This shows that one of the most important factors to be considered is that of viscosity, as a low viscosity of, say, not more than 125 seconds Saybolt at 100° F. will facilitate rapid penetration of the trachea and will result in the formation of a non-volatile film on the body of the insect when the emulsion breaks. A similar influence is exercised on the eggs, whereby they are prevented from obtaining the oxygen necessary for them to hatch out, whilst another factor is the penetration of toxic chemicals into the egg itself.

The incorporation of various toxic materials into the emulsion to increase its potency has been practiced for a long time. Nicotine in the presence of a soap emulsified oil penetrates soft-bodied insects very readily. A concentration of about .05 per cent is usual; it is particularly useful where sawfly larvae, wooly aphis, or pea and bean thrips are to be destroyed. An emulsion which is stable in the presence of Bordeaux mixture or nicotine sulphate may be prepared from:

Potash fish oil soap (35%), lbs..	8
Fusel oil, lbs..................	2
Lubricating oil, gals...........	8
(Sp. gr. .88-.90)	
Water, gals.	4

The fusel oil is well stirred into the soap, and the lubricating oil added slowly with vigorous agitation. To the resulting thick mass the water is added until a creamy emulsion is produced.

The effect such sprays have on plants is an important consideration, but experiments have shown that properly made emulsions which contain up to 25 per cent. of oil can be used on peach trees in the dormant state. The use of highly refined oils has been established as being perfectly safe, the greatest danger resulting from the presence of olefine and other hydrocarbons, which are removable by treatment with sulphuric acid. A low volatility is to be sought, but the oil, on the other hand should not remain on the plant for excessively long periods, or delayed ripening of the fruit, yellowing of the leaves and a general stunting is liable to result. As to the likelihood of cumulative injury, this is remote if spraying of each tree is not carried out for two seasons in succession, a rest period of one season being allowed in between.