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INSECTICIDE

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3 Claims. (Cl. 167—43)

This invention relates to improved methods of compounding and producing insecticides employing as basal ingredients selected components of mineral oils and of fixed oils through segregating same from undesirable components to secure specific parasiticial material to meet requirements necessary to diversified insecticide practices, and more particularly it relates to methods of compounding together selected constituents of mineral oils and fixed oils in predetermined proportions and in company with smaller portions of other selected ingredients in a way to enhance the effectiveness of such oils as insecticide material and simultaneously to render not harmful or destructive to plant or animal tissue the unsaturated hydrocarbons inherent to mineral oils and found to be responsive to reactions when compounded with acids and also to overcome the similarly harmful properties of fixed oils employed as insecticides resulting from the presence in their compositions of free fatty acids and unsaturated glycerides found to be reactive to alkali. For the purpose of this petition fixed oils are understood to comprise vegetable, animal, or marine oils.

The material herein contemplated may be applied to the surface from which insects, germs, grubs, larvæ, or oviparous products are to be repelled or destroyed, using any convenient manner of application; but in general it is contemplated that the product may be applied in the form of a water soluble oil spray as is common in the use of oil and water emulsions. It is further contemplated that the material, as an object of this invention is to be used as a repellent or eradicator of germs, insects and such on trees, plants, animals, poultry, or the habitats of same.

The objects attained by this invention becomes more clear if viewed in the light of the difficulties encountered in the application, compounding, handling and transporting of the usual forms of paste type of oil in water emulsions, or of the more common forms of miscible oil, which operate as drawbacks to render the materials more costly and to restrict their use and applications as well as to restrict the number and character of oils that may be applied as oil sprays. For example, the usual emulsion type of oil spray material is compounded to contain on an average of fourteen per cent to twenty-five per cent of water contents. This fact necessitates an excess cost for shipping, handling, mixing and for containers, since the water is available for final mixing at the point of use. The heavy, non-free

flowing character of the emulsion demands the use of a special grease type of barrels rather than the usual oil barrels, while the capacity demanded by the extra water contents is a considerable item of expense. The excess water results in quick freezing during cold weather, causing separation of the oil and water emulsion; while exposure to the sun or other heat likewise destroys the value of the emulsion through separation. The miscible type of oil sprays, while not subject to all these drawbacks, also falls short in that they are commonly compounded with phenols of the coal tar derivative class. Such phenols are caustic to foliage and thereby restrict the use of miscible oils to dormant or winter season use. The product of this invention is not subject to these disadvantages.

The primary restriction of the emulsion type of oil spray is that the oil selected is subject to the exactions that it must possess an unsulphonated residue test of 85% or higher where used as a summer cover spray. (See Bureau of Mines Technical Paper 181.) This means that the phytocidal ingredients consisting of dissolved sulphur, naphthenic acids, sulfonic acid, unsaturated compounds, and other such products shall not be present in excess of 15%. It is usual to employ as a foliage oil spray a fraction of oil too light in viscosity to be available for use as a lubricating oil. The usual phytocidal ingredients of this light viscosity oil other than unsaturated compounds are commonly removed during the regular course of refinery processes. However, an unsulphonated residue as high as 85% is unusual and to obtain this high test a re-run at the refinery is necessary; greatly adding to the cost of the oil base material used as oil spray. For example, at this writing, light viscosity oils with an unsulphonated residue test of 78% to 82% are available in tank car shipments F. O. B. refinery at 3¢ to 4¢ per gallon. Other than the fact that the unsulphonated residue test on these oils falls below 85% as specified for deciduous fruit foliage spray they are suitable for use. On the other hand sixty viscosity oils with an unsulphonated residue test above 85% are only available at a cost of 15¢ per gallon and up in tank car lots F. O. B. refinery. It is seen therefore that if a method may be devised which minimizes the necessity for the high unsulphonated residue test that is compatible with the emulsion type oil sprays a great improvement and much economy may result.

In the following the petitioner sets forth in general terms the formula to be utilized in this in-

vention; thereafter it is developed wherein certain desirable new improvements are accomplished.

Formula for foliage oil spray solution

90% mineral oil of a viscosity @ 100 degrees Fahr. between 55 seconds and 85 seconds and of an unsulphonated residue test between 72% and 92%.

3% fixed oil, fluid at 35 degrees Fahr., of an iodine value between 110 and 150, and an acetyl value between .40 and .90, saponification number between 180 and 195.

2.5% oleoresin, preferably that of pinon pine (*Pinus edulis*), fractionating as 16% volatile oil distilling @ 314 to 383 degrees Fahr., 6% cadinene ($C_{15}H_{24}$) distilling above 383 degrees Fahr., and an amorphous non-vitreous rosin residue of specific gravity of 1.060 and saponification number of 164.1.

2% ethyl alcohol, preferably denatured Special Formula No. 1.

2% colloidal starch composition, formed of 5 parts potassium hydroxid to 29 parts starch, to approximately 340 parts water, making an aqueous solution of the empirical formula



.5% potassium hydroxid, forming with oleoresin potassium resinate and glycerol.

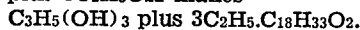
The foregoing combination of ingredients is subject to variations according to requirements of the specific insecticide spray practices encountered, and the resultant compounds are found widely different from the original materials incorporated. For example, the oleoresin in the foregoing when brought into contact with the potassium present is partially saponified and glycerine is set free. The mineral oil employed is found to consist of saturated compounds of hydrocarbons and unsaturated compounds of hydrocarbons according to the unsulphonated residue test of the mineral oil selected. It is the unsaturated compounds of hydrocarbons that are most destructive to plant tissue, and these may consist largely of mercaptans; formed by union of sulphur, native to crude mineral oil, with the oil molecules; one half of one percent of sulphur uniting with the oil to form fifteen or more percent of mercaptans. In turn oleoresin comprises largely abietic acid. This forms a compound with mercaptans as follows where R signifies the hydrocarbon radicle combining with hydrogen and sulphur in the mercaptan molecule:—

$C_{19}H_{29}(CO.OH)$ plus $H.SR$ makes



Alcohol will also react with any excess of abietic acid to form the ester, ethyl resinate; or it reacts with tri-glycerides after the following manner forming glycerine and alcoholic esters:—

$C_3H_5(C_{18}H_{33}O_2)_3$ plus $3C_2H_5OH$ makes



Both the alcoholic esters and the glycerine formed constitute useful insecticide material.

In general terms, therefore, the foregoing formula would show resultant compounds by analysis substantially as follows:—Less viscous, less volatile mineral oil existing as saturated compounds of hydro-carbon, 60% to 80%; mineral oil existing as unsaturated compounds of hydro-carbon combined with the organic fatty acids of oleoresins of coniferous trees selected as contain-

ing components of cadinene, 5% to 30%; organic fatty acids existing as mono-valent alkali soap, 2% to 3%; organic fatty acids existing as ethyl esters, 1¼% to 4%; glycerine 1¼% to 3%; turpene, .4% to 2%; cadinene, .15% to 5%; and soluble starch in aqueous solution with its molecular equivalent of alkali, 1½% to 3%.

Herein, the term fixed oil as used is to designate either animal, vegetable, or marine oil, from which the lighter and more volatile unsaponifiable fractions have been removed, leaving the glycerides.

It is to be shown later that certain preliminary treatments of the fixed oils incorporated have a pronounced effect upon the unsaturated compounds present in the mineral oils used. In compounding this formula fixed oils that are naturally liquid such as fish oils, cottonseed oils, or linseed oil are selected. These are first given a preliminary refinement by treatment with potassium hydroxid in an amount sufficient to accomplish about twenty per cent saponification. This settles out and makes possible the removal of the more heavy and unsaturated fatty acids. Also all traces of vegetable or animal residue are thereby removed that would tend to oxidize or settle upon the foliage and introduce a troublesome spray residue removal problem at the period of fruit washing. It is of great importance that linoleic acids be removed from oil spray materials, or neutralized, because when dispersed upon foliage, they absorb oxygen from the air and are oxidized to a varnish insoluble in either alkali or acid washes used in cleaning fruit. They are found in linseed oils and other drying oils, and also in olive and palm oils as well as semi-drying fish oils with a high iodine value. They are easily separated by the fractional saponification method because, being highly unsaturated, they are the first organic acids to respond to the potassium hydroxid introduced. Neither should oleic acids be left in the free state as a component of oil sprays because of the prevalent uses of calcium products used in spreaders and economic poisons. Calcium unites immediately without heat to form with oleic acid a lime soap insoluble in water or alkali washes, causing another troublesome spray residue removal problem. Oleic acids are also unsaturated and therefore quickly removed or neutralized.

The remaining glycerides are saponified by the cold process; an amount of KOH is used just insufficient to accomplish complete saponification, leaving the soap about one per cent acid in terms of the organic acids present. The soap thus formed is stirred into twenty per cent of the mineral oil required by the formula. The oleoresin is then dissolved in the remainder of the mineral oil and heated to 180° F. When complete solution is accomplished the portion of mineral oil carrying the soap is then added and the entire mass is kept agitated while at the same time being pumped back upon itself under a pressure of forty pounds or more. While this agitation and pumping is continued the spreader is added. Thereupon the heat is discontinued but the agitation remains in effect until the contents have cooled to 135 degrees. At this stage the alcohol is added in gradual portions until the mass clarifies and takes on a character indicating that all the ingredients have reacted and entered into complete solution.

The resultant product is found to be a completely transparent soluble oil free from turbidity. It

will be found to be completely soluble in all proportions in any water ordinarily used for irrigation. In this form the product will be found to be what is termed a tight emulsion forming oil spray.

After the alcohol is added and before the mass is cooled or before agitation has ceased, an additional amount of mineral oil may be slowly and gradually added to an amount equal to fifty per cent of the mineral oil already incorporated.

It thus remains highly soluble but has become of the class of quick breaking oil sprays equal in this property to the quick breaking emulsion type of oil sprays. The oil run-off from foliage is thereby reduced.

It is found that herring oil is ideal for producing the potassium soap. The oleoresin used may well be that obtained from pinon pine (*Pinus edulis*) since it carries a cadinene fraction, which is of itself an insecticide repellent. This particular oleoresin also possesses properties of readily absorbing other resinous insecticides such as rotenone and similar ketone bearing substances. Moreover, it has more pronounced attributes of rendering oil miscible with water than any of the other more usual resins. If this oleoresin is not available, or if the spray material is to be utilized only as a dormant oil spray, ordinary rosin or colophony may be substituted.

The alcohol used has several functions to be discussed later, but at this point it may be mentioned that it acts with the glycerine set free in the soap and along with the water contents of the spreader to establish a certain interfacial tension equilibria whereby the oil is rendered the internal phase such that the mass as a whole has a remarkably strong affinity for water. When diluted in the ratio of one part of soluble oil to one hundred parts of water or more a milk white solution is formed that undergoes no changes whatsoever upon months of standing. This is true however alkaline or hard the water used may be. In this respect the product is superior to the paste type emulsion oil spray materials; in addition it has better properties of holding in suspension certain economic poisons that may be incorporated in the final oil and water spray. This superior property of the product produced from this invention is also manifest when it is observed that there is no separation or creaming in the spray tanks from standing without agitation. The latter failing of less stable types of emulsions has accounted for the increased oil dosages resulting in burning of foliage.

The water soluble neutral spreader is formed by dissolving ten parts of flour to ninety parts of water and boiling until the flour particles are completely ruptured and hydrolyzed. A more complete and intimate solution may be attained by incorporating five per cent by weight of potassium hydroxid per weight of flour. Starch, casein, agar agar, or other like neutral spreaders may be substituted for flour. In addition to imparting spreading properties, this spreader material acts along with the unsaponified fixed oil to give the spray material the proper element of adhesiveness.

In the foregoing formula it is to be observed that all the ingredients except the small percentage of water included in the soap and spreader are active insecticide materials, including the alcohol; thus the inert materials present are reduced from 15% to 25% common to paste type emulsions to the low percentage of some three to four per cent. Also a soluble oil is attained without recourse to undesirable creosote or coal tar

phenols. Thus great economies in handling and shipping are accomplished and a soluble oil is at hand suitable for foliage as well as dormant oil spray applications.

This new oil spray material has been used and given working applications as a summer foliage spray and found both effective and free from harmful caustic properties.

In addition to olefines, the phytocidal ingredients in mineral oil harmful as insecticides may consist of naphthenic acids and phenols. The alcohol compounded in this formula serves to convert any free naphthenic acids present to esters, while the glycerol set free in the formation of the potassium soap combines to form glycerides, the latter being not harmful as insecticide material. In like manner phenols if present are neutralized and rendered neutral to plant or animal tissue to which the spray material may be applied. The chemical actions thereby involved are set forth at length on page 88, of *The Scientific Principles of Petroleum Technology*; Chapman & Hall, Ltd.

From the foregoing it is seen that the alcohol used in the formula possesses several important functions. It operates primarily to maintain the phase relationship between the various ingredients and maintain interfacial tension equilibria, thereby imparting to the soluble oil its high character of miscibility in all proportions with water. It is titrated into the solution after the other ingredients have been added and serves to establish a balance between the base or alkaline components and the glycerides or organic acids. It also serves to effect a complete solution of one material within the other that results in a clear and translucent product. Its additional functions as set forth are to neutralize portions of the phytocidal ingredients.

The positive manner in which ethyl alcohol reacts with the unsaturated compounds and other phytocidal ingredients present in mineral oils is illustrated by a working example. As a case in point, utilizing the foregoing general formula, a water soluble oil spray material was produced by the petitioner wherein the resultant product possessed exactly balanced interfacial tension equilibria of phases. The portions of ingredients employed were vegetable oil, saponified with KOH, to the amount of 5.23%; oleoresin, 3.33%; ethyl alcohol, 1.76%; neutral spreader, 1.68% making for these materials a total of 12% of the completed composite product. Mineral oil to the amount of 88% and having a viscosity of 60@100 degrees Fahr. and an unsulphonated residue test of 96% was incorporated after a manner to establish phase balance. For purposes of comparison, a second water soluble oil spray material was compounded like the first with the portions of ingredients remaining the same and fixed, with the mineral oil used also being the same in all particulars excepting that the unsulphonated residue test was decreased to 92%. A balance of phase relations producing a water soluble oil spray material was not attained by incorporating ethyl alcohol to the amount 1.76% as used in the first test, but interfacial tension equilibria was accomplished and a soluble oil material resulted when the ethyl alcohol portion was increased to 2.045%; all other factors remaining constant excepting the proportions of phytocidal ingredients in the mineral oil used. In similar manner, a yet much lower unsulphonated residue test mineral oil may require portions of alcohol as high as 2.6% to 3%, to produce phase balance. It becomes evident, therefore, that the incorporation of alcohol into

an oil spray material has a more far reaching effect in neutralizing harmful phytocidal ingredients in mineral oils than merely converting naphthenic acids into esters. Thus alcohol as an oil spray material ingredient is found to serve a useful purpose in extending the availability of the lower unsulphonated residue test mineral oils for insecticidal uses.

Besides the chemical reactions that play a part in off-setting the effects of a relatively low unsulphonated residue test in the mineral oils incorporated as spray material, there is a decided physical manifestation that serves to render not harmful the phytocidal ingredients present. This is based upon the effects of incorporating into a mineral oil a small percentage of fixed oils, animal or vegetable, or the glycerides or the free fatty acids thereof. It has to do with the greater affinity of the oxygen containing fixed oils as compared with mineral oils in adhering to other surfaces with which brought into contact, and the tendency, when the two forms of oils are mixed, for the fixed oil to take precedence in forming a molecular layer immediately adjacent to the surface, upon which the mineral oil molecular layers are superimposed. The complications of interfacial tension equilibria are involved; and the effects are so pronounced that when applied to the flotation processes of ore separation in refining minerals cases are on record where thousands of gallons of flotation material employing a pine oil base suffered disruption through the destruction of equilibria caused by the accidental addition of a few drops per minute of mineral oils into the mixtures. Less technical illustrations may serve to make clear the case in point.

For many years it has been recognized that petroleum products such as kerosene and other mineral oil fractions with low unsulphonated residue tests may be applied to animals or poultry as insecticides without cauterization where there is an admixture of fixed oil material such as lard or cream. Human beings for generations have used as poultice remedies for colds on the chest kerosene and other caustic materials diluted with lard, cream, or other neutralizing fats. That this medicinal and animal insecticide and germicide principle may equally be applicable to insecticides involving mineral oils for horticultural uses is believed to be a fact not heretofore recognized nor applied.

To test the neutralizing effects of the admixture of fixed animal or vegetable oils upon mineral oils of low unsulphonated residue tests, or of high phytocidal ingredients, a mineral oil with a viscosity of 100 @ 100 Fahr. and an unsulphonated residue test of only 58% was incorporated into this formula. The product, after processing as described, was used repeatedly over a long period of time as a lotion upon human epidermis. No caustic effects were evident. As a further test the material was applied to surface portions of an epidermis previously inflamed and raw due to heat chafing. Irritation was diminished rather than increased. The test was continued by applying to the hides of dogs. Fleas and mange were eradicated but the animal showed no signs of discomfort. The uncompounded mineral oil so applied resulted in the dogs showing unmistakable signs of discomfort that were only relieved by the subsequent applications of fixed oils. In like manner, lower viscosity oils with an unsulphonated residue test of 78% were incorporated into the formula and ap-

plied to summer foliage in the usual dosages without ill effects.

It is recognized as a principle of lubrication that the adhesiveness of mineral oils to metallic surfaces is greatly increased by being compounded with oxygen bearing fixed oils. It is even found that the affinity of oils for surfaces is greater if organic fatty acids are added to mineral oils rather than the glycerides. Again it has been determined that unsaturated fatty acids increase this affinity more than do the saturated. The technical literature has carried articles describing X-ray micro-photostats showing that where a mineral oil is compounded with a fixed oil and applied to a metal surface equilibria is established by a layer of the oxygen bearing molecules adhering directly to the metal; the remainder of the oil products being superimposed thereupon. It becomes probable, therefore, that this intervening layer of oxygen bearing molecules serves as a protective coating against the caustic properties of mineral oils where compounded with fixed oils and applied to vegetable or animal tissue. This becomes more evident when it is remembered that fish oils with low iodine values may be applied as spray materials with the same impunity that falls to high unsulphonated residue tests mineral oils. From this point of view it is held that the highly unsaturated abietic acid carried in the oleoresins of pinon pine for other oleoresins used in this formula along with the glycerides present in the other fixed oils used, serve as an enveloping medium interposing between the caustic properties present in the mineral oil and the plant or animal tissue subjected to the spray materials. The interfacial tension factors involved are set forth in detail in the aforementioned Scientific Principles of Petroleum Technology, page 436. The application of these principles though old in the realms of medicine, lubrication, and flotation processes of mining, are believed to be novel as applied to insecticide oil spray technique. Particularly the process is novel by which the necessity is obviated for refining mineral oils to a very high degree at great expense through the incorporation of fixed oils into the mineral oils.

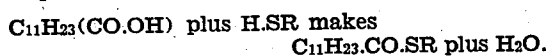
In foregoing initial and resultant formulas, oleoresins bearing cadinene are indicated as ingredients. Cadinene, in addition to being an insect poison, possesses a pungent odor that also serves to act as an insect repellent. Oil spray practices, however, at times require merely a so-called contact insecticide; in which case other forms of glycerides or fatty acids besides the oleoresins bearing cadinene may be substituted providing they conform to the requirements of the resultant product.

The fundamentals underlying this invention are best understood by viewing the characteristics of the components in mineral oils harmful to plant tissues with the like components of fixed oils; after which it is seen that the two when combined are rendered mutually negative in action. Saturated compounds of hydrocarbon in mineral oils are not harmful to plant tissue in regulated applications. Therefore generally accepted mineral oil orchard sprays comprise oils from which the unsaturated hydrocarbons have to a large extent been removed, though at a greatly increased cost for refining. The molecular structure of mineral oil unsaturates shows that their too active chemical characteristic is due to hydrogen being present in the molecule in insufficient amount to saturate all of the four

bonds that fixes the valency of the carbon atoms. These unattached bonds may absorb a foreign substance such as sulphur, producing mercaptans. This fact is accepted as a fundamental in the art of applying mineral oil insecticides. However, as an outgrowth of developing this invention, the petitioner has discovered that in like manner the components in fixed oils harmful to plant tissue also consist of unsaturated compounds, which comprise free organic fatty acids and tri-glycerides wherein hydrogen exists in the molecule in insufficient amounts to fully saturate all the carbon and oxygen atoms present. Therefore, where fixed oil is used as insecticide material, either by itself or in combination with mineral oils, to be used safely, it must comprise saturated tri-glycerides. The unsaturates must either be removed from the oil or they must be rendered negative in action by being compounded with some other substance upon which they may exhaust their chemical activity. The unsaturates in mineral oil are reactive to acids, whereas the unsaturates of fixed oil are reactive to alkali; hence the desirability of combining the two forms of unsaturates for insecticide practice is obvious.

A test for unsaturates in fixed oil may be made with alcohol. Free fatty acids are dissolved out by forming alcoholic esters. Unsaturated tri-glycerides form alcoholic esters more slowly than fatty acids but in advance of saturated tri-glycerides; whereas the latter only esterify after a prolonged time reaction or under the influence of heat. Saturated tri-glycerides may be segregated by merely incorporating into the fixed oils a quantity of caustic sufficient to saponify the fatty acids and unsaturated tri-glycerides, but short of the amount required to act upon the saturates. So segregated, the saturated fixed oil becomes a useful and specific insecticide material used either singly or in combination with mineral oils. In the first of the foregoing formulas the fixed oils are designated by iodine number and by acetyl value, which means merely that the saturated tri-glycerides are selected.

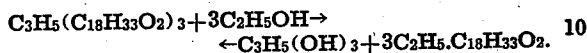
Irrespective of what process may be utilized in producing the oil spray product disclosed in this invention, the chemical reaction that stands out distinct as of prime importance has to do with the neutralization of phytocidal impurities present in refined mineral oils and harmful to plant tissue in foliage. Of these mercaptans, or naturally occurring sulphonic compounds found native to mineral oils, are held to be the most actively caustic. Mercaptans are naturalized through esterification by reaction with their molecular equivalent of fixed oils. For example, lauric acid, composing some 48% of the various fractions constituting cocoanut oil, is esterified with the formation of water by mercaptans according to the following formula, where R signifies the hydrocarbon radicle combining with hydrogen and sulphur in the mercaptan molecule:—



As references substantiating in part the physical and chemical manifestations involved, citation is made to the Scientific Principles of Petroleum Technology, pp. 323-326; Bureau of Mines Technical Paper 262; and Lubrication and Lubricants, Archbutt, p. 39, pp. 56 and 57.

Primary alcohols perform a necessary function in this invention of far reaching importance in consideration of the fact that the generic claims rest upon improvements in insecticide

materials accomplished by mixing with refined mineral oils certain oxygen bearing fixed oils of selected characteristics along with alcohol to produce esterification. For example, the addition of ethyl alcohol to olein present in cocoanut oil produces a reversible time reaction forming glycerol plus the ester, ethyl oleate, as is shown by the following equation:—



The other glycerides in animal or vegetable oils react also with alcohol to form esters and glycerol, or esters and water where the alcohol chances to encounter free fatty acids. The reaction in forming esters differs from saponification in that it is reversible. This is important because in spray practice the maximum amount of free oil is desirable with the minimum of soaps. The esters perform all the functions of a soap in rendering the mineral oils in which they are contained water soluble or miscible with water. However, they quickly revert when in the form of a diluted oil in water emulsion spray in contact with plant foliage. Thus fixed oils are set free to act as insecticide material along with the mineral oils.

As has been cited, the caustic properties of mineral oil fractions have been neutralized medicinally by compounding with fixed oils, and this has also been done with poultry and animal insecticides; but not in a manner to secure a chemical plus a physical neutralization. Nor has a product been developed manifesting such convenient forms of application. For example, merely mineral oil and grease compounded is too concentrated for extensive use as an insecticide upon poultry, dogs, or stock. Such a product applied as an insecticide in poultry habitats would leave an excess of oil to be carried by the hens to the nests upon their feet, thereby spoiling eggs for hatching. As opposed, the product of this invention may be mixed with water in any proportion without affecting the neutralizing properties of the fixed oil and mineral oil combination, and be applied for such purposes in any desired degree of concentration.

Similarly the patent literature has been reviewed and it is disclosed that many of the ingredients used herein have previously been employed as insecticide materials in combination with mineral oils, but not in a manner or with objectives to conflict with this invention. In general such patents deal at length upon the necessity of removing the phytocidal ingredients of the mineral oil to a point below 15% where used as foliage spray materials. None discovered by the petitioner disclose, the use of alcohols, fixed oils, and special processing as a means of rendering available for general use mineral oils not possessing this low degree of phytocidal ingredients. Patent No. 1,707,469 of April 2, 1929, discloses very ably that such unsaturated organic acids as oleic, linoleic, abietic, and the like acids when compounded with mineral oils have a decided influence upon interfacial tension equilibria, or "polar" effects, in stimulating mineral oil and water emulsions and in affecting the manner of dispersion upon foliage. The disclosure, however, limits the fixed oils in application and reveals only a quick breaking emulsion miscible with water only under the influence of agitation; and subject to separation or creaming when the agitation is suspended. In fact that patent deals with a mineral oil rendered capable of maintain-

ing an oil in water emulsion while under the influence of agitation, such property being imparted to the mineral oil through the admixture of an organic fatty acid. No representation is made
 5 that a miscible or soluble mineral oil base product is produced. As opposed, this invention treats of a water soluble mineral oil product having such an affinity for water as to become miscible without any agitation and to remain in solution, with
 10 the quick breaking properties under control. The stable character of the emulsion insures against separation in spray apparatus with the consequent unusual dosages of oil applied. Moreover, the organic acids present are rendered neutral
 15 and not left free to form linoleic acid varnish through oxidization or to combine with calcium products that may be used, whereby, insoluble spray residues are left behind to form spray residue removal problems. As a consequence this
 20 invention is held to have different objectives with the accomplishments of a different category of results, and not to be in conflict.

What is claimed and desired to secure by Letters Patent, is:—

25 1. An oil composition made effective as an insecticide adapted for spraying in aqueous dispersions upon plants and trees in foliage by being made from ingredients adjusted in such
 30 amounts of one component with another that the resultant compound shall be lethal to insect life but not caustic nor destructive to plant tissue being composed substantially of less viscous, less
 35 volatile, mineral oil existing as saturated compounds of hydrocarbon, 60% to 84%; mineral oil existing as unsaturated hydrocarbons combined with the organic fatty acids of fixed oils,
 6% to 30%; organic fatty acids existing as mono-valent alkali soap, 2% to 3%; organic fatty acids
 40 existing as ethyl esters, 1½% to 4%; glycerine 1¼% to 3%; soluble starch in aqueous solution with its molecular equivalent of mono-valent alkali, 1½% to 3%.

2. An oil composition made effective as an

ovicide, larvicide, fungicide, lethal contact insecticide, and aromatic insect repellent, adapted for spraying upon plants and trees in foliage, by being made from ingredients adjusted in such
 5 amounts of one component with another that the resultant compound shall be lethal to insect life but not caustic nor destructive to plant tissue being composed substantially of less volatile, less
 10 viscous, mineral oil, existing as saturated compounds of hydrocarbon, 60% to 80%; mineral oil existing as unsaturated compounds of hydrocarbons combined with the non-vitreous organic
 15 fatty acid oleoresins of coniferous trees selected as containing components of cadinene, 5% to 30%; organic fatty acids existing as mono-valent alkali soap, 2% to 3%; organic fatty acids existing as ethyl esters, 1¼% to 4%; glycerine 1¼%
 20 to 3%; turpene, .4% to 2%; cadinene, .15% to 5%; and soluble starch in aqueous solution with its molecular equivalent of alkali, 1½% to 3%.

3. An oil composition made effective as an insecticide for dispersions upon plants and trees in foliage, lethal to insect life but not caustic nor destructive to plant tissue, characterized for
 25 not depositing insoluble oil residues upon fruits and for not leaving upon plants a permanent oil film interfering with plant respiration, comprising substantially the more fluid, less viscous, less
 30 volatile, non-drying fixed oils existing as saturated triglycerides, 20% to 80%; less viscous, less volatile mineral oil existing as saturated compounds of hydrocarbon, 15% to 60%; less viscous, less volatile, mineral oil existing as unsaturated
 35 compounds of hydrocarbon combined with organic fatty acids, 2% to 18%; glycerine, 1% to 2½%; organic fatty acids existing as ethyl esters, 1% to 3%; organic fatty acids existing as mono-valent alkali soap, ½% to 2½%; and soluble
 40 starch with its molecular equivalent of alkali in aqueous solution, 1½% to 3%.

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