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## INSECTICIDE

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This invention relates to insecticides and has for its particular object the provision of an oil readily dispersible in water to form an emulsion therewith, in which the emulsifier comprises a benzene compound having insecticidal qualities not contained in methane derivatives.

The preferred emulsifier to be mixed with a crude oil, or a distillate thereof which has been more or less highly refined by well known treatment with sulfuric acid or a selective solvent (e. g., liquid sulfur dioxide) or a combination of these to remove more or less of the unsaturated (phytocidal) hydrocarbons therefrom, comprises addition products of hydroxylic derivatives of benzene and its homologues, containing an hydroxyl group directly attached to the benzene nucleus, e. g., phenol, cresol, xylenol, with unsaturated aliphatic acids like oleic or ricinoleic acid.

Because the chemical structure of such addition products has not been definitely ascertained, they are so far not characterized by definite names and for brevity and convenience they will be designated herein broadly as benzene hydroxylic fatty acids, of which specific types include phenol-oleic acid, cresol-ricinoleic acid, xylenol-oleic acid, etc.

In the preparation of such compounds as an emulsifier for oils, the benzene derivative is caused to react with the unsaturated fatty acid by mixing them in the proportion of their molecular weights, at a temperature above their melting points, as for instance 94 parts by weight of phenol with 282 parts by weight of oleic acid to form the addition product called phenol-oleic acid, and 108 parts by weight of cresol with 298 parts of ricinoleic acid to form cresol-ricinoleic acid. It should be understood, however, that other ratios of phenol or its homologues to unsaturated fatty acids are included and that the invention is not limited to these proportions, though equi-molecular proportions are preferred.

Whereas the reaction between the fatty acid and the phenol homologue takes place when both constituents are in a fluid state, the minimum temperature required for the reaction is the melting point of the homologue of phenol desired to be used, if the melting point of the fatty acid is below that of the homologue of phenol. On the other hand, if the melting point of the fatty acid desired for use is higher than that of the homologue of phenol, then obviously it is necessary to use a temperature higher than the melting point of the fatty acid. For instance, in order to form the addition product phenol-oleic acid, the minimum temperature required will be 105° F., as the phenol melts at 105° F.; for the formation of phenol-chaulmoogric acid the minimum temperature is 155° F., which corresponds to the melting point of chaulmoogric acid.

The following table gives the melting points of several materials suitable for the preparation of addition products in accordance with the invention.

Homologues of phenol:

| | M. P. ° F. |
|---|---|
| Phenol | 105 |
| Ortho-cresol | 86 |
| Meta-cresol | 39 |
| Para-cresol | 95 |
| Xylenol (1,2) (3) | 167 |
| Xylenol (1,2) (4) | 149 |
| Xylenol (1,3) (2) | 120 |
| Xylenol (1,3) (4) | 79 |
| Xylenol (1,3) (5) | 147–154 |
| Xylenol (1,4) (3) | 165 |
| Thymol | 111 |
| Carvacrol | 32 |
| Fatty acids: | |
| Oleic acid | 57 |
| Iso-oleic acid | 112 |
| Elaidic acid | 124 |
| Ricinoleic acid | 63 |
| Linolic acid | 0 |
| Linoleic acid (below) | 0 |
| Linolenic acid (below) | 60 |
| Clupanodonic acid (below) | 60 |
| Telfairic acid | 43 |
| Erucic acid | 92 |
| Isolinoleic acid (below) | 60 |
| Chaulmoogric acid | 155 |

The commercially obtainable mixtures of xylenols, which form liquids at ordinary temperatures, can be used without further purification for the preparation of oil soluble addition products similar in efficiency to phenol-oleic acid, for instance. Likewise, unsaturated fatty acids containing impurities may be used. Such impure acids have melting points which vary and which may be considerably below the melting point of the pure acids.

The maximum temperature which may suitably be employed is one at which there is no appreciable loss of the constituents due to volatilization. Furthermore, as the temperature is increased there is a noticeable tendency to form esters instead of the desired addition products. Temperatures up to 350° F. have been satisfactorily employed in the manufacture of

addition products in accordance with the invention.

Addition products prepared as described above may readily be distinguished from ordinary mixtures and from esters. For example, whereas phenol is soluble in either water or glycerol and should be extracted from a mixture of phenol and oleic acid thereby, water or glycerol will not extract phenol from the addition product phenol-oleic acid. Furthermore, the specific gravity, refractive index, and specific refractive power of the addition product will be found to differ from similar tests applied to the corresponding mixture or ester. The following table shows, as an example, these tests applied to the addition product, ester, and mixture of parametacresol and oleic acid:

| | Oleic acid | Para-meta-cresol | My association or addition product | Cresyl-oleate | Calculated values for a theoretical mixture |
|---|---|---|---|---|---|
| Spec. grav. at 20° C. | 0.8984 | 1.0354 | 0.9315 | 0.9093 | 0.9363 |
| Refr. index at 20° C. | 1.4622 | 1.5398 | 1.4818 | 1.5047 | 1.4836 |
| Spec. refr. power | 0.5133 | 0.4237 | 0.5173 | 0.5547 | 0.4885 |

The specific refractive power is calculated as follows:

$$\frac{\text{Refractive index at 20° C.}-1}{\text{Specific gravity at 20° C.}}$$

Such phenol-oleic acid, or other benzene hydroxylic fatty acid, may be mixed with crude petroleum, or a distillate thereof more or less refined up to the point of containing no phytocidal hydrocarbons, for example in the proportion of from about 0.1% to 10% by volume, preferably from 0.5 to 5.0% by volume, of the hydrocarbon oil to form an insecticidal spray oil which may be used as is alone when dispersed or emulsified in water for spraying on trees, foliage, fruit etc. in some cases, but in other cases is desirable to be used in combination with a spreader or flux, which has the function of spreading the oil in a film of desirable and uniform thickness over the surface to be sprayed and causing it to adhere to the same for a desired length of time.

The emulsion formed by the dispersion of the emulsifiable oil in water in the proportion of from ½% to 10%, the desirable rate being determined by the season in which the spraying is done, the type of water used in making the spray-mixture, the type of insect to be destroyed and the plants to be protected, is of the quick-breaking type, or non-stable type, in that such emulsion almost instantly resolves itself into its components of oil and water when it is sprayed on plants, letting the water run off the leaves and leaving the insecticidal oil on the plant to form an insecticidal film.

As the described addition products are miscible with hydrocarbon oil in all proportions the invention is not to be limited to the proportions given above but contemplates their use in any proportion. When mixed with suitable hydrocarbon oil the resultant emulsifiable oil is harmless to plant life if used in proper dispersion with water; all of which is important in the preparation and application of any insecticide. These addition products, without dilution with hydrocarbon or other oil, are valuable for use as insecticides; and, due to their emulsifying properties, can be dispersed in water, with or without the assistance of spreaders, in proper proportion to render them harmless to plant life.

In order to control the thickness of the film as well as the degree of adhesion to the plant surface, considering that the mineralization of the water used in the preparation of the spray mixture will influence dispersion and film-properties, the inclusion of spreaders, or a flux, has been found desirable to counteract adverse reactions due to heavy mineralization and to produce an oil-film utilizing the full insecticidal effect of the oil, which film will contain the correct amount of oil and poison per square unit of surface covered, without causing injury to the plants.

The spreaders desired are:

(1) 100% soda ash or sodium carbonate ($Na_2CO_3$), to be used when an especially fine dispersion of the emulsifiable oil is desired and when the water used for dispersion is not very soft. In the average the rate of one pound soda ash for 300 gallons water has been found efficient.

| | Per cent |
|---|---|
| (2) Soda ash | 16.5 |
| Brock clay (a magnesium silicate) | 16.5 |
| Sodium metasilicate | 16.5 |
| Trisodium phosphate | 16.5 |
| Powdered skim milk | 34.0 |
| | 100.0 |

This spreader is desirable when the water used for dispersion is rated hard. The amount of such spreader depends on the degree of hardness of the water and also on the degree of dispersion desired and may vary from ½ pound per 300 gallons up to six pounds per 300 gallons or even more.

When preparing a spray mixture, say of 100 gallons volume, the following procedure will be found the most efficient:

(A) Using no spreader: Run into the spray tank 25% or less of the water, add the desirable amount of emulsifiable oil, which may or may not contain an oil soluble insecticide poison, and agitate the mixture until the desired degree of dispersion has been obtained, then add the balance (75 gals.) of the water. The spray-mixture is then ready for use.

(B) When a spreader is used: Run into the spray tank 25% (or less) of the water, dissolve the desirable amount of spreader, add the desirable amount (say 2 gals.) of the emulsifiable oil, which may or may not contain an oil soluble insecticide poison, agitate this mixture until the desired degree of dispersion has been obtained, and finally add the balance (75 gals.) of water. The spray-mixture is then ready for use.

In place of the poisons and spreaders above described, a single substance may be added to act as a combined spreader and poison. Such a substance can be lead arsenate, which in the average is used at the rate of two pounds per 100 gallons of water.

From the above description it will be clear that an emulsifiable insecticide, non-injurious to plant life when properly dispersed in water, but sufficiently toxic to all classes of insects may be obtained by forming an addition product of phenol or its homologues with unsaturated fatty acids. Such addition product may be added to a crude oil or preferably to a more or less highly refined distillate thereof, to obtain a compound easily dispersible in water with and without a

spreader forming an emulsion reverting to the oil and water components thereof substantially as quickly as it comes in contact with the point of application so that an oil-film of desirable properties will coat the same. Incorporated therewith may be a poison of such character as not to be water soluble but to be soluble in the oil whereby an even distribution of the poison in the oil film may be had.

This application is a continuation-in-part of my copending application Serial No. 707,853, filed January 22, 1934.

I claim as my invention:

1. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid while at a temperature above the melting point of both, and below a temperature at which substantial volatilization or esterification occurs, to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

2. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid while at a temperature above the melting point of both and below about 350° F. to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

3. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid while at a temperature between about 105° F. and 350° F. to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

4. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid in the proportion of their molecular weights while at a temperature above the melting point of both, and below a temperature at which substantial volatilization or esterification occurs, to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

5. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid in the proportion of their molecular weights while at a temperature above the melting point of both and below about 350° F. to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

6. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring alone with an unsaturated fatty acid in the proportion of their molecular weights while at a temperature between about 105° F. and 350° F. to form an addition product unaccompanied by the formation of reaction products differing from the components of said mixture.

7. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a phenol alone with an unsaturated fatty acid while at a temperature above the melting point of both, and below a temperature at which substantial volatilization or esterification occurs, to form a phenol-fatty acid addition product alone.

8. The process of preparing an emulsifier for hydrocarbon oils, which comprises: mixing a phenol alone with an unsaturated fatty acid while at a temperature between about 105° F. and 350° F. to form a phenol-fatty acid addition product alone.

9. An emulsifier for hydrocarbon oils comprising an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated fatty acid.

10. An emulsifier for hydrocarbon oils comprising: phenololeic acid.

11. An emulsifier for hydrocarbon oils comprising: cresolricinoleic acid.

12. An emulsifiable insecticide comprising an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated fatty acid.

13. An emulsifiable oil comprising: a hydrocarbon oil containing from about 0.1% to 1.0% of its volume of an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated fatty acid.

14. An emulsifiable oil comprising: a hydrocarbon oil containing from about 0.5% to 5.0% of its volume of an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated acid.

15. An emulsifiable oil comprising: a non-phytocidal hydrocarbon oil containing from about 0.1% to 10% of its volume of an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated fatty acid.

16. An emulsifiable oil comprising: a non-phytocidal hydrocarbon oil containing from about 0.5% to 5.0% of its volume of an addition product of a mono-hydroxylic benzene derivative having its hydroxyl directly attached to the benzene ring with an unsaturated acid.

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