Patented Feb. 12, 1935 1,990,490

UNITED STATES PATENT OFFICE

1,990,490

METHOD OF PRODUCING INSECTICIDE AND THE LIKE

Joseph W. Horne and Carl P. Hopkins,
Boulder, Colo.

No Drawing. Application June 29, 1931,
Serial No. 547,788

8 Claims. (Cl. 167—28)

Our invention relates to insecticides, germicides, fungicides, ovicides, and the like. The principal object of the invention is to take advantage of the toxic value of shale oil for such purposes.

Another important object of the invention is to provide such a product that is an oily liquid that will be readily miscible with hot or cold water. In practice, the material is usually mixed with water in the orchard, vineyard, or other place where it is to be used. It is impractical to have to mix the toxic material with water under heat.

A further object is to provide a material for the purpose stated that will contain a relatively large amount of the toxic shale oil (preferably more than eighty-five per cent) and a relatively small amount of material to render the oil miscible with water (less than fifteen per cent).

Heretofore experiments have been made to make an emulsion of the oil and water by the use of a mechanical mixture with soap. The difficulty has been that a relatively large amount (approximately fifty per cent) of such reagent had to be used to make such an emulsion. The result was a soapy mass in a pasty condition. Of course, it is much more preferable to use as little reagent as possible, for otherwise it dilutes the toxic shale oil too much.

However, the shale oil must undergo some treatment in order to render it miscible with water and especially with cold water. Untreated shale oil will rise to the top of water in a very short time, as in the case of any oil, but after being treated in accordance with our invention becomes miscible with water.

A still further object of the invention consists in the hydrolysis of certain constituents of the shale oil so as to form products which will combine with the remainder of the oil rendering the shale oil product miscible with water.

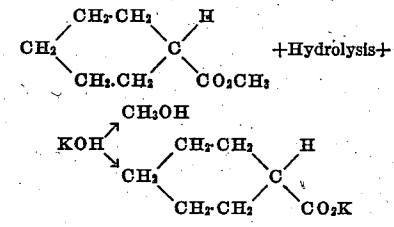
A still further object of the invention consists in taking advantage of the acid reacting constituents naturally present in shale oil, such as naphthenes, phenols and cresols and the hydrolysis of these compounds in the presence of an alkali with heat, rendering the acid reacting constituents of shale oil miscible with water.

Another object of the invention consists in taking advantage of the alkaline constituents naturally present in shale oil, such as naphthaline, secondary amines such as diethylamine, tertiary amine such as triethylamine, sutidine, collidine and higher compounds in the series, and the pyrolysis of these compounds in the presence of heat with a fatty acid, such as oleic acid, renders the oily alkaline constituents of shale oil miscible with water.

Other objects reside in details of the invention, in the materials used to treat the shale oil and in the proportions thereof, which will appear in the course of the following detailed description.

Our process consists principally in treating a shale oil product, such as pressure distillate of shale oil, from which the shale oil gasoline has been removed, and has a Baumé gravity of, for example, thirty-four degrees to forty-two degrees, with a small percentage (two per cent to five per-cent is preferable) of unsaturated fatty acid such as oleic acid. To the foregoing is added a small amount (one per cent to one and one-half per cent) of an alkali, such as potassium hydrate in solution. It is important not to mix the reagents together before mixing same with oil, for a different reaction results.

The combining is done under heat and the ingredients are continuously agitated and heated for approximately an hour. Hydrolysis of a portion of the shale oil takes place by means of a series of chemical reactions, such as the following:



Reactions similar to this occur between the natural naphthenic acids and related compounds present in the shale oil products in the presence of an active alkali, the presence of which render the shale oil product partially miscible. The soporific and miscible qualities are improved and completed by the reactions between the unsaturated fatty acid and the active alkali, which are separately added. Salts so formed in the above process are soluble in the phenolic acids and cresolic acids naturally present in the shale oil used and aid in forming a homogenous liquid of the finished product.

It is readily apparent from the material when the reactions have taken place, because the properties of the oil are changed; viz., the viscosity of the oil has been increased by the formation of new and/or other compounds, and the oil is now miscible with water.

Moreover, the reaction which takes place between a portion of the oleic acid and the excess of potassium hydrate forms a compound which

provides a valuable spreader in the finished shale oil product.

Instead of oleic acid, other unsaturated fatty acids may also be used, or naphthenic oil or acid, phenolic oil or acid, or cresolic oil or acid. Animal or vegetable oil may also be used, as well as sludges resulting from refining petroleum oils.

Instead of some of the fatty acid, sulphonated products resulting from water used to wash the concentrated sulphuric acid sludge recovered from refining shale oil products may be used. When this partial substitution is made, it is preferred to use about ten per cent of the sulphonated products, in which case, one per cent of the oleic acid is dispensed with. All of these compounds neutralize the nitrogenous compounds of the shale oil distillate.

In place of the potassium hydrate, other alkalis may be used, such as sodium or ammonium hydrate. Instead of one of said alkalis, an alkali wash resulting from refining shale oil products may be used. Such washes contain salts of naphthenic acid, phenolic acid and cresolic acid. In lieu of or in addition to such washes, condenser water resulting from retorting oil shale may be used.

Pressure distillate of shale oil, treated by one of the foregoing processes, has desirable properties as an insecticide, germicide, ovicide, and fungicide, but will not burn foliage of plants when sufficiently diluted, and is thoroughly miscible with water. As stated, an emulsion approaching a perfect emulsion is obtained on dilution with water.

As further proof that a chemical change has taken place in the shale oil when treated by the foregoing process, a mixture of untreated shale oil and water does not change the color of the oil, even though violently agitated. In a mixture of water and pressure distillate of shale oil, treated in accordance with the foregoing process, the oil turns a very light tan or cream color—quite unlike the dark brown color of the original, untreated shale oil.

Any user can mix the present product and water anywhere by just pouring the two together and stirring. With a pasty mass, which was obtained in the prior art, the water must be heated and the agitation must continue until the paste is thoroughly dissolved. It is usually quite impractical for the ordinary user to heat the water, so the advantages of the present product are thought apparent.

An important feature of the invention is the hydrolysis of the natural constituents of shale oil and the addition of certain reagents to produce changes in the oil which renders the oil miscible with water.

It is to be understood that changes may be made in the invention, as by the use of equivalents for the above ingredients, and that changes may be made in proportions thereof, without departing from the spirit and scope of the invention. The term "alkali-containing material" as used in the claims includes potassium and sodium compounds and ammonium compounds.

What we claim and desire to secure by Letters Patent is:

1. The process of rendering a pressure distillate of shale oil miscible with water, comprising first chemically combining pressure distillate of shale oil containing nitrogeneous compounds with oleic acid, and then chemically combining the resulting composition with sufficient alkali in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

2. The process of rendering a distillate of shale oil miscible with water, comprising first chemically neutralizing the nitrogenous bases of the shale oil distillate, and then adding sufficient base to the so-treated shale oil in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

3. The process of rendering a shale oil distillate miscible with water, comprising chemically combining said shale oil distillate with an unsaturated fatty acid, and then treating the resulting reaction product with sufficient base in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

4. The process of rendering a shale oil distillate miscible with water, comprising chemically combining said shale oil with oleic acid, allowing the mixture to react, and then adding sufficient alkali-containing material to the reaction product in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

5. The process of rendering a shale oil distillate miscible with water, comprising chemically combining said shale oil with an unsaturated fatty acid, allowing the mixture to react, and then adding sufficient alkali-containing material to the reaction product in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

6. The process of rendering a shale oil distillate miscible with water, comprising chemically combining said shale oil distillate with oleic acid in an amount varying between 2% and 5%, allowing the mixture to react, and then adding about 1% of an alkali-containing material to the reaction product in the presence of heat, whereby the final composition is rendered miscible with hot or cold water.

7. The process of rendering a shale oil distillate miscible with water, comprising chemically combining said shale oil distillate with oleic acid in an amount varying between 2% and 5%, allowing the mixture to react, and then adding about 1% of potassium hydrate to the reaction product in the presence of heat, whereby the final composition is rendered miscible with hot or cold water.

8. The process of rendering a shale oil distillate miscible with water, comprising chemically combining the shale oil distillate with a mixture of a fatty acid and sulphonated wash water derived from the treatment of sulphuric acid sludge recovered from refining shale oil, allowing the latter mixture to react with the shale oil, and then adding sufficient alkali-containing product to the reaction product in the presence of heat to form a soap, whereby the final composition is rendered miscible with hot or cold water.

JOSEPH W. HORNE.
CARL P. HOPKINS.