

L197,289



PATENT SPECIFICATION

DRAWINGS ATTACHED

L197,289

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Date of Application (No. 56671/67) and filing Complete Specification: 13 Dec., 1967.

Application made in United States of America (No. 604,790) on 27 Dec., 1966.

Application made in United States of America (No. 653,659) on 17 July, 1967.

Complete Specification Published: 1 July, 1970.

Index at acceptance:—A5 E(1C4A3, 1C4A4, 1C12)

International Classification:—A 01 n 9/04

COMPLETE SPECIFICATION

Promoted Mosquito Control Oil

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to the killing of aquatic stages of insects by application of an oily material to the surface of the aquatic breeding grounds of the insect.

The prior art has utilized hydrocarbon oils, such as diesel fuel, as a surface-applied insecticide for killing aquatic stages of insect life. However, it has been necessary to use about 20 gallons per acre as a treat rate. In an attempt to avoid the high cost of application with such a high application rate of the diesel fuel, chemical insecticides have been used instead of diesel fuel. However, this is also expensive and has not been particularly effective due to the rapid development of resistant strains in the mosquito population. The addition of surfactants also has been tried, but the effect of the surfactant has merely been that the oil has spread more evenly across the pond surface, thereby increasing the chance that the mosquito larvae and pupae would come in contact with the oil. The effectiveness of the oil as a toxic material per se has not been affected.

The present invention relates to a promoted oil having toxicity towards the aquatic stages of insect life, particularly the larvae and pupae of mosquitoes. More particularly, the present invention relates to a novel mixture of materials whereby an oil, having a toxicity towards mosquito larvae and pupae, is enhanced many times in its toxicity and effectiveness, allowing the use of much smaller treat rates when applying the oil to the surface of breeding ponds. According to the invention a mosquito control oil comprises a hydrocar-

bon oil containing at least 60% by volume saturated hydrocarbons and having a toxicity toward immature mosquitoes and ethoxylated 2,4-dinonyl phenol, which contains an average of from 6 to 14 ethoxy units in the ethoxylated substituent and which is present in a concentration of at least 0.2 wt.% of the mixture. The invention further provides a method of using this promoted mixture in the control of mosquito proliferation.

Mosquitoes are well known as carriers of such pathogens as the encephalitis virus and malaria bacteria. It is essential in preventing diseases caused by such pathogens to control the proliferation of the mosquito carriers of the pathogen. This can best be accomplished by breaking the mosquito life cycle rather than by attacking the adult mosquito itself.

The mosquito in its life cycle passes through three stages before obtaining maturity: egg, larva, and pupa. The most effective way of controlling mosquito proliferation is by breaking the life cycle; i.e., by attacking the proliferating mosquitoes before they reach maturity. Since the early stages of mosquito development are aquatic, the means chosen to break the life cycle must be adapted to kill the immature mosquito while it is in the water.

Heretofore the use of oils for covering the surface of mosquito breeding ponds has not been too effective unless used in high concentrations. For example, No. 2 diesel oil is applied in amounts ranging from 2 to 40 gallons per acre of surface. This is uneconomical. The present invention provides promoted oil which, by use of a very small amount of a relatively cheap material, enhances many times the toxicity of the oil itself, and the mixture can be used effectively in amounts as low as one gallon per acre of water surface.

The present invention, although encompassing the admixture of the promoter with diesel oil, is most valuable in allowing the use of more expensive and more effective oils for mosquito control, rather than the diesel fuel.

[Price 5s. Od. (25p)]

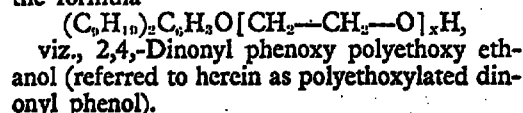
Further, since the amount of oil that is to be applied can be reduced to a very small level, the use of the cheaper diesel fuel can be enhanced in its effectiveness.

- 5 The present invention involves the use of ethoxylated 2,4-dinonyl phenol as a promoter for oils which already have a toxicity toward the aquatic stages of mosquito life. The ethoxylated 2,4-dinonyl phenol is not itself toxic toward mosquito life and does not render toxic those oils which are not in themselves toxic (for example, heavy paraffinic oils boiling above about 750°F.). The precise role of the promoter is not known, but by inspection of the larvae, it has been concluded that the promoter is effective because of changes which occur within the organism itself, and not merely in enhancing the spreadability of the oil on the water surface (i.e., acting as a surfactant).
- 10 A number of other surfactants have been checked, and no other surfactant has been found to give the same effect as the ethoxylated dinonyl phenol. Some of these other surfactants are ethoxylated nonyl phenols (9 species) and ethoxylated octyl phenols (5 species) with various numbers of ethoxy units in the substituent; ethoxylated amines (2 species); ethoxylated fatty acids (2 species); and 9 other ethoxylated materials.

- 15 The present invention can best be understood by a discussion of each of the aspects in sequence. Thus, hereinbelow will be discussed the specifics of the ethoxylated dinonyl phenol, including the method of preparation and a comparison with other surfactants, the amount of promoter which should be included, the hydrocarbon oils which can be used in connection with the promoter, and the methods of applying the promoted oil for the control of proliferating mosquitoes.

- 20 *Promoter.* The promoter of the present invention is an ethoxylated 2,4-dinonyl phenol. This compound is a surfactant, but its activity in the present mixture appears to involve toxic effects of the mixture on the mosquito larvae and pupae themselves, rather than merely enhancing the spreadability of the hydrocarbon oil.

- 25 The promoter of the present invention has the formula



In the above formula, x is the number of ethoxy units in the ethoxylated substituent. From 6 to 14 units (average) will be present in the ethoxylated substituent, so that x can be from 6 to 14.

The number of ethoxy units in the ethoxylated substituent is determined by Nuclear Magnetic Resonance (NMR) analysis wherein the amounts of the alkyl, aromatic, ethoxy and hydroxy hydrogens are measured. One third of the aromatic hydrogen measurement should be equal to 1/38th of the alkyl hydrogen measurement. This provides an internal calibration factor (F) for determining the ethoxy chain length. First, the ethoxy hydrogen measurement is divided by the factor F, thereby obtaining the number of ethoxy hydrogens. The number of ethoxy hydrogens divided by 4 gives the average number of ethoxy units in the molecule.

An ethoxylated 2,4-dinonyl phenol is prepared by the liquid phase ethoxylation of 2,4-dinonyl phenol. In this process, a liquid-phase charge of preferably 85% + pure dinonyl phenol and up to 0.2% NaOH by weight (based on the amount of dinonyl phenol) is placed in a pressure reactor, and is raised to a temperature of about 260 to 300°F. Gaseous ethylene oxide is bubbled into the reaction zone, wherein an exothermic reaction takes place between the ethylene oxide and the dinonyl phenol. The rate of addition is controlled to maintain a temperature of about 320 to 340°F. From 6 to 14 mols of ethylene oxide per mol of dinonyl phenol are introduced and reacted. The average number of ethoxy units in the ethoxylated substituent can be fairly closely controlled by the ratio of ethylene oxide to dinonyl phenol introduced into the reaction zone.

The reaction is preferably carried out at a temperature within the range of 320 to 340°F., and a pressure from atmospheric to 30 psig. The ratio of ethylene oxide to phenol is preferably 8 to 1:1 mols of ethylene oxide per mol of dinonyl phenol. The process is preferably carried out in a semibatch process, with the ethylene oxide being continuously introduced at a controlled rate into a batch reactor. Conditions are preferably controlled so that there is no ethylene oxide in the exhaust gas (i.e., all of the ethylene oxide is reacted). Exemplary products may have the following physical characteristics:

TABLE I

Ethoxylated Product: Average number of Ethoxy Units	Specific Gravity at 77°F.	Viscosity, at 77°F., Centistokes
11	1.0164	384
8	.9703	382

The ethoxylated dinonyl phenol is very effective in promoting the toxic effects of mosquito control oils. This same effect has not been noted with other surfactants. In Table II below, EODP(8) is compared with exemplary other surface active agents. Note that the use of EODP(8) alone, without an oil, did not produce any appreciable mortality in the test larvae.

TABLE II

Description of Material	Interfacial Tension Dynes/cm.	% Mortality 24 Hrs. Exposure Larvae		
		1.25*	2.5*	5.0*
500—600°F. Paraffinic Oil	5.0	—	53	65
500—600°F. Paraffinic Oil with 0.5 wt. % ethoxylated (5) octyl phenol	2.2	—	36	80
500—600°F. Paraffinic Oil with 0.375 wt. % EODP (8)**	About 1	100	100	—
500—600°F. Paraffinic Oil with 0.5 wt. % ethoxylated oleic acid having 10 ethoxy units	2.5	36	69	—
EODP (8)**	—	—	1	0

* Gallons per acre.

** EODP (8) is ethoxylated 2,4-dinonyl phenol having 8 ethoxy units (average).

Note that the toxic activity of the paraffinic oil was substantially enhanced by employing the promoter of the present invention; whereas the use of ethoxylated (5) octyl phenol (Triton X45, "Triton" is a Registered Trade Mark, commonly used in 0.25 wt.% combination with diesel fuel for mosquito control) showed no perceptible increase in activity at the low treat rate, nor did the use of ethoxylated (10) oleic acid, although the number of ethoxy units is within the range employed in the present invention.

The purity of the 2,4-dinonyl phenol feed-stock into the ethoxylation reaction zone should be at least 85%, resulting in a product purity of at least 85%. The main impurity will normally be nonyl phenol, which can itself be ethoxylated to produce a surface active agent which appears to interfere with the activity of the promoter of the present invention. As will be discussed hereinafter, solubilizers such as aromatic hydrocarbons (and especially dinonyl phenol) as well as surface active agents tend to reduce the effectiveness of the promoter, requiring the use of higher concentration of promoter in the oil or a higher oil treat rate, or both. With up to about 10 wt.% impurities in the product, the impurities act primarily as diluents. (The concentration of EODP is always calculated on an impurity-free basis.) Above 15 wt.%, however, deleterious effects are observable and this 15% limit preferably should not be exceeded.

To illustrate the deleterious effect of other surface active agents (particularly, the ethoxylated nonyl phenol), mortality studies were

made with a 500—600°F. paraffinic oil containing 1 wt. % EODP (8.7), and companion runs to which were added one or two additional 0.25 wt.% increments of EONP (8).

TABLE III

Description of Material	24 Hr. Larvae Mortality	
	0.5 gal/A	1.0 gal/A
500—600°F. Paraffinic Oil with 1 wt. % EODP (8)*	87	99
500—600°F. Paraffinic Oil with 1 wt. % EODP (8.7) and 0.25 wt. % EONP (8)**	13	854
500—600°F. Paraffinic Oil with 1 wt. % EODP (8.7) and 0.50 wt. % EONP (8)**	—	41

* EODP (8.7) is ethoxylated 2,4-dinonyl phenol containing an average of 8.7 ethoxy units per molecule.

** EONP (8) is ethoxylated nonyl phenol containing an average of 8 ethoxy units per molecule.

Note: gal/A = gallons per Acre.

Note that the addition of ethoxylated nonyl phenol reduced the effectiveness of the promoter from 99% to 84% to 41%. This is not a dilution effect since the amount of EODP (8.7) is not reduced. Thus, high purity dinonyl phenol is to be preferred.

The promoter of the present invention can be utilized in varying concentrations. As will be seen from Table IV below, the use of at least 0.1875 wt.% is required before any effect is seen.

TABLE IV

Relation of Toxicity of an Oil* with Ethoxylated Dinonyl Phenol at Various Concentration Levels

Concentration of EODP, Wt. %	Interfacial Tension Dynes/cm.	Percent Mortality 24—Hr. Exposure Gal./A			
		Larvae		Pupae	
		1.25	2.5	1.25	2.5
None	50	—	55	4	56
0.0750	About 1	21	65	64	87
0.1875	" 1	45	67	87	99
0.3750	" 1	100	100	92	97
0.7500	" 1	100	100	100	96
1.8750	" 1	100	100	100	95
3.7500	" 1	100	100	100	99

* 500—600°F. Paraffinic Oil.

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As the treat rate decreases, the required concentration at which the effectiveness increases sharply has been found to be higher than that required at higher treat rates. For example, at 1.0 gallon per acre treat rate, the oil of Table IV should contain 0.75 wt.% EODP if a 24-hour mortality rate higher than 90% is desired. Preferably, about 0.375 wt.% is employed in the mixture, since at this point the spread rate of one gallon per acre shows essentially a 100% mortality in both larvae limit, although the use of higher concentrations of 1.0% would represent an upper economic limit, although the use of higher concentrations (e.g., 3.75 wt.%) is technically feasible although prohibitively costly. The presence of aromatic hydrocarbons, solubilizers such as nonyl phenol, and other surfactants will require the use of greater than normal amounts of EODP.

Ethoxylated 2,4-dinonyl phenol is very effective in reducing interfacial tension. As seen from the accompanying drawing, 0.03 wt.% reduces the interfacial tension of 500—600°F paraffinic oil to about 2 dynes/cm. From 0 to 0.03 wt.% concentration

provides the most striking reduction in interfacial tension, and the spreadability of the hydrocarbon oil would be most substantially benefitted in this range. As has been seen in Table IV, however, use of 0.1875 wt.% ethoxylated (8) 2,4-dinonyl phenol (preferably about 0.375) is required before a substantial effect is seen on the larvae. This concentration is substantially above the level of 0.03 wt.% which is seen to substantially modify interfacial tension and illustrates that this invention is not merely related to spreadability of the hydrocarbon on the water surface. However, in view of the deleterious effects of other surfactants, solubilizers, and aromatic hydrocarbons, it is believed that the presence and activity of the promoter at the oil/water interface is important.

The amount of the promoted oil mixture which is used can also be a function of the number of ethoxy groups in the ethoxylated substituent. This can be seen in Table V below which compares the effectiveness at 0.5 wt.% concentrations of 2,4-dinonyl phenols having different average numbers of ethoxy units in the ethoxylated substituent.

TABLE V
Percent Mortality, 24—Hr. exposure
Gal./Acre

Average Number of Ethoxy Units on 2,4-Dinonyl Phenol	Larvae					Pupae		
	1.0	1.25	1.5	2.5	5.0	1.25	2.5	5.0
0	—	—	—	23	67	67	99	100
5.6	—	47	—	73	—	93	93	—
8.0	—	60	—	99	—	—	100	93
11.0	—	95	—	97	—	100	91	—
14.0	16	—	59	—	—	—	—	—

Note: Promoter is used in 0.5 wt. % concentration in a 500—600°F. paraffinic acid.

From Table V it is seen that at 5.6 units (average) per molecule, a certain amount of effectiveness is provided. However, at an average of 8 and 11 units per molecule, a much greater effect on the larvae is seen, and therefore the range of 8 to 11 units (possibly higher) is preferred. Note that even at 5.6 units per molecule, the toxicity to pupae is enhanced so that essentially the same effectiveness is obtained at 1.25 gallons per acre as is accomplished by an oil promoted with 2,4-dinonyl phenol and applied at twice that rate (2.5 gal./acre). Also note that at 14 units per molecule, the larvae toxicity is beginning to decrease rapidly.

Suitable Oils. The promoter of the present invention may be used with a number of hydrocarbon oils which themselves have toxicity for the aquatic stages of mosquito life. In general, these oils will boil within the range of 500 to 800°F., and may include paraffinic oils, alkylate oils, diesel fuel, and C_{12} to C_{16} paraffins, preferably having a midpoint below 650°F. The preferred boiling range is from 500 to 725°F., and the preferred oil will be in the higher regions in this range, e.g., 550—650°F. A suitable, economically available oil, however, may be a paraffinic oil boiling from 500 to 600°F. A midpoint of 650°F. or less is preferred (Table VII).

Examples of suitable oils are shown below, with an example of each type being given along with the inspection data. An aromatic oil is shown for comparison, to illustrate the

deleterious effect of aromatics. Other aromatic oils which have been evaluated show similar results. See Table VIII, for example.

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TABLE VI

Suitable Oils	Amount of Ethoxylated (8) dinonyl phenol added, wt. %	Percent Mortality 24—Hr. Exposure					
		Larvae			Pupae		
		1.25*	2.5*	5.0*	1.25*	2.5*	5.0*
Paraffinic Oil (1)	None	—	53	65	—	56	64
Paraffinic Oil	0.375	100	100	—	92	93	98
Alkylate Oil (3)	None	—	36	68	77	99	—
Alkylate Oil	0.375	100	100	—	100	100	—
Diescl Fuel (5)	None	11	19	60	32	83	97
Diesel Fuel	0.375	97	100	—	92	99	100
n-C ₁₆ Paraffin (7)	None	—	—	71	—	100	93
n-C ₁₆ Paraffin	0.375	92	100	—	100	100	—
Aromatic Oil (9)	None	—	—	67	—	—	33
Aromatic Oil	0.375	—	28	59	—	21	—

* Gallons per acre.

TABLE VI (Continued)

Inspection	Oil:	Inspection Data				
		1	3	5	7	9
Mid-boiling pt., °F.		572	542	515	548	585
95—5% boiling range, °F.		65	120	150	—	170
Distillation Data, ASTM D—86						
IBP, °F.		508	433	401	—	544
5		535	499	444	—	560
50		572	542	515	548	585
95		599	620	604	—	730
FBP		609	620	625	—	(93.5%)
Aromatics, Vol. %		12	3.0**	24	0.0	90
API Gravity		31.5	41.2	36.5	—	16.6
Viscosity, SSU at 100°F.		50	—	—	—	—

** Weight percent.

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Note that the promoter of the present invention is effective on a wide range of oil types and is particularly effective in enhancing the toxicity of paraffinic oils. The higher boiling

oils are not desirable since some of them do not possess the requisite toxicity. Thus, the midpoint should be less than 650°F. as shown below in Table VII.

TABLE VII

Oil	Unsulphonated Residue, %	Midpoint °F.	SSU 100°F.	<i>Culex fatigans</i> , Larvae Percent Mortality			
				1.0	Gal./Acre		2.5
					1.25	1.5	
A ¹	91	572	42	93	94	93	100
B ²		576		99			
C ³		580		97			
D ⁴	90+	542		—	100	—	
E ⁵	90+	594	94	100	—	—	—
F ⁵	90+	623	164	91	—	—	—
G ⁵	90+	623+	1024	85	—	—	—
H ⁶	95	643	49.5	92	—	—	100
I ⁶	96	647	50.5	76	—	—	100
J ⁶	100	681	59.4	15	—	23	59
K ⁶	95	684	76.3	4	—	25	61
L ⁶	96	719	74.0	—	21	—	41

All oils contained 1 wt. % EODP (8) except D, which contained 0.5 wt. %.

- ¹ Same as oil (1) in Table VI.
- ² Oil (1) with low 20% cut removed.
- ³ Oil (1) with low 40% cut removed.
- ⁴ Same as oil (3) in Table VI.
- ⁵ E, F and G are higher-boiling cuts of an oil similar to oil (3).
- ⁶ H, I, J, K and L are 50—70 viscosity lube stocks.

10 In Table VII note that at a treat rate of one gal. acre, a drop-off in effectiveness occurs at about 650°F. midpoint; at 681°F., even a treat rate of 2.5 gal./acre shows a pronounced

drop-off in effectiveness. Thus, a midpoint less than 650°F. is preferred.

The deleterious effect of aromatic hydrocarbons has been mentioned. This is shown in Table VIII below.

TABLE VIII

24 Hr. Mortality, *C. fatigans* Larvae,
Oil containing 1 Wt. % EODP (8)

Hexadecane Vol %	HAN* Vol %	Aromatic Content Vol %	Gal./Acre			
			0.75	1.0	1.25	1.5
100	0	0	87	95	97	100
90	10	9	45	96	95	97
80	20	18	23	91	89	89
70	30	27	8	85	71	83
60	40	36	—	41	73	76
50	50	45	—	49	69	64
40	60	54			71	
30	70	63			57	
20	80	72			35	
10	90	81			12	
0	100	90			5	

* HAN is a heavy aromatic naphtha boiling from 360 to 530° F. with a 10.1 API gravity and a 90% aromatic content. Hexadecane boils at 548°F.

Note from Table VIII that an increasing aromatic content decreased the effectiveness of the promoted oil. It is believed that this is due to the solubilizing effect of the aromatic hydrocarbons, which disturbs in some way not known the activity of the EODP at the oil-water interface. From Table VIII it appears that the oil should contain at least 60% by volume saturated hydrocarbon at higher treat rates, and at least 80% by volume desirably at least 90% volume, for treat rates of about 1.0 gal./acre, if 90% + mortality is desired.

The mixture of oil and promoter can be applied to the surface of breeding ponds in a number of different ways. It can obviously be poured as a liquid mixture directly onto the surface of the ponds or can be sprayed on the surface of the ponds by devices carried

by hand, mounted on trucks, or carried by aerial applicators such as airplanes and helicopters. The present invention provides a method of killing immature mosquitoes comprising applying to the surface of a mosquito breeding pond the mosquito control oil of this invention at a rate of at least 0.5 gallon per acre of exposed pond surface. Preferably the range is from 0.5 to 2.5 gallons per acre. Suitably 1 to 3 gallons per acre may be employed. The upper limit of the application rate is based upon economics and would be probably about 10 gallons per acre; although in some circumstances, it may be economic to apply even greater quantities.

As is seen below in the table, the volatility of the oil influences the effectiveness of the mixture.

TABLE IX

Residual Toxicity to *C. fatigans* Larvae

Material	IBP	% Mortality, 5 Gal./Acre Dosage							
		0	1	2	3	4	5	6	7 *
A. Paraffinic Oil with 0.5 Wt. % EODP (8)	500°F.	100	100	100	83	68	33	28	0
B. Diesel Fuel with 0.5 Wt. % EODP (8)	400°F.	100	100	8	—				
C. Diesel Fuel	400°F.	29	1	—	—				

* The numerals 0 to 7 designate the age of the test surface before the addition of the test animals.

Table IX shows that, as the volatile components or the oil are lost with time, the effectiveness is decreased. Thus, the use of higher boiling oil fractions (that are toxic in themselves) are preferred for more effective control. New eggs hatch in 2 to 3 days, thus the lasting effectiveness of the oil is beneficial.

The data tabulated in preceding tables II to VII was obtained by the following experimental procedure. Beakers (400 ml capacity and 7.4 cm internal diameter) containing 250 ml of distilled water were used for all tests. The test animals were laboratory specimens of *C. fatigans* selected at random from pools or larvae or pupae representing combined rearing pans. Twenty-five fourth instar larvae or pupae were used per beaker. Untreated and diesel oil controls were included in each test.

To test toxicity, the larvae (or pupae) were placed in each beaker, following which 0.005 ml, 0.01 ml or 0.02 ml of oil was dropped on the water surface with a pipette. These quantities represent a rate of 1.25 gal./acre, 2.5 gal./acre and 5.0 gal./acre, respectively. Twenty-four hours later the number of living and dead specimens was recorded and the percent mortality determined. This test was conducted in triplicate, with 25 specimens being used per replicate.

To establish the residual effectiveness Table IX) of the promoted oils, the following tests were made. The oils were pipetted onto the surface of water in beakers at the rate of 5 gallons per acre and *C. fatigans* larvae were introduced into the separate beakers at various times up to 7 days after the oil was deposited on the water surface, and the 24-hour toxicity was observed.

WHAT WE CLAIM IS:—

1. A mosquito control oil comprising
 - (a) a hydrocarbon oil containing at least 60% by volume saturated hydrocarbons and

having a toxicity toward immature mosquitoes, and

(b) ethoxylated 2,4-dinonyl phenol which contains an average of from 6 to 14 ethoxy units in the ethoxylated substituent, and which is present in a concentration of at least 0.2 per cent by weight.

2. A mosquito control oil in accordance with claim 1, wherein the hydrocarbon oil contains at least 80% by volume paraffinic hydrocarbons.

3. A mosquito control oil in accordance with any one of claims 1 or 2, wherein the hydrocarbon oil contains at least 90% by volume paraffinic hydrocarbons.

4. A mosquito control oil in accordance with any one of claims 1—3, wherein the hydrocarbon oil boils substantially within the range 500°F. to 800°F.

5. A mosquito control oil in accordance with claim 4, wherein the hydrocarbon oil boils substantially within the range 550°F. to 650°F.

6. A mosquito control oil in accordance with any one of claims 1—4, wherein the hydrocarbon oil boils substantially within the range 500°F. to 600°F.

7. A mosquito control oil in accordance with any one of the preceding claims 1 to 4, wherein the hydrocarbon oil is a paraffinic oil having a boiling range from 500°F to 600°F, a viscosity of about 50 S.S.U. at 100°F, and an aromatic content of about 12 volume percent, and an A.P.I. gravity of 31.5.

8. A mosquito control oil in accordance with any one of claims 1—4, wherein the hydrocarbon oil has a midpoint no greater than 650°F.

9. A mosquito control oil in accordance with any one of claims 1—8, wherein the ethoxylated 2,4-dinonyl phenol is present in a concentration substantially within the range from 0.2 to 3.75 weight percent.

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B. Diesel Fuel with 0.5 Wt. % EODP (8)	400°F.	100	100	8	—	—	—	—	—
C. Diesel Fuel	400°F.	29	1	—	—	—	—	—	—

* The numerals 0 to 7 designate the age of the test surface before the addition of the test animals.

Table IX shows that, as the volatile components or the oil are lost with time, the effectiveness is decreased. Thus, the use of higher boiling oil fractions (that are toxic in themselves) are preferred for more effective control. New eggs hatch in 2 to 3 days, thus the lasting effectiveness of the oil is beneficial.

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To test toxicity, the larvae (or pupae) were placed in each beaker, following which 0.005 ml, 0.01 ml or 0.02 ml of oil was dropped on the water surface with a pipette. These quantities represent a rate of 1.25 gal./acre, 2.5 gal./acre and 5.0 gal./acre, respectively. Twenty-four hours later the number of living and dead specimens was recorded and the percent mortality determined. This test was conducted in triplicate, with 25 specimens being used per replicate.

To establish the residual effectiveness Table IX) of the promoted oils, the following tests were made. The oils were pipetted onto the surface of water in beakers at the rate of 5 gallons per acre and *C. fatigans* larvae were introduced into the separate beakers at various times up to 7 days after the oil was deposited on the water surface, and the 24-hour toxicity was observed.

WHAT WE CLAIM IS:—

1. A mosquito control oil comprising
 - (a) a hydrocarbon oil containing at least 60% by volume saturated hydrocarbons and

having a toxicity toward immature mosquitoes, and

(b) ethoxylated 2,4-dinonyl phenol which contains an average of from 6 to 14 ethoxy units in the ethoxylated substituent, and which is present in a concentration of at least 0.2 per cent by weight.

2. A mosquito control oil in accordance with claim 1, wherein the hydrocarbon oil contains at least 80% by volume paraffinic hydrocarbons.

3. A mosquito control oil in accordance with any one of claims 1 or 2, wherein the hydrocarbon oil contains at least 90% by volume paraffinic hydrocarbons.

4. A mosquito control oil in accordance with any one of claims 1—3, wherein the hydrocarbon oil boils substantially within the range 500°F. to 800°F.

5. A mosquito control oil in accordance with claim 4, wherein the hydrocarbon oil boils substantially within the range 550°F. to 650°F.

6. A mosquito control oil in accordance with any one of claims 1—4, wherein the hydrocarbon oil boils substantially within the range 500°F. to 600°F.

7. A mosquito control oil in accordance with any one of the preceding claims 1 to 4, wherein the hydrocarbon oil is a paraffinic oil having a boiling range from 500°F to 600°F, a viscosity of about 50 S.S.U. at 100°F, and an aromatic content of about 12 volume percent, and an A.P.I. gravity of 31.5.

8. A mosquito control oil in accordance with any one of claims 1—4, wherein the hydrocarbon oil has a midpoint no greater than 650°F.

9. A mosquito control oil in accordance with any one of claims 1—8, wherein the ethoxylated 2,4-dinonyl phenol is present in a concentration substantially within the range from 0.2 to 3.75 weight percent.

10. A mosquito control oil in accordance



with claim 9, wherein the ethoxylated 2,4-dinonyl phenol is present in a concentration from 0.2 weight percent to 1.0 weight percent.

5 11. A mosquito control oil in accordance with claim 10, wherein the ethoxylated 2,4-dinonyl phenol is present in a concentration of about 0.75 weight percent.

10 12. A mosquito control oil in accordance with any one of claims 1—11, wherein the ethoxylated 2,4-dinonyl phenol contains from 8 to 11 ethoxy units.

13. A mosquito control oil in accordance with claim 12, wherein the ethoxylated 2,4-dinonyl phenol contains about 8 ethoxy units.

15 14. A mosquito control oil in accordance with any one of claims 1—13 wherein the ethoxylated 2,4-dinonyl phenol has a purity of at least 85 weight percent.

20 15. A mosquito control oil as claimed in any preceding claim, containing only the hydrocarbon oil and the ethoxylated 2,4-dinonyl phenol.

16. A mosquito control oil consisting of:

25 (a) a hydrocarbon oil boiling substantially within the range 500°F to 800°F and having a mid-point no greater than 650°F, containing at least 60% by volume of saturated hydrocarbons and having toxicity toward immature mosquitoes, and

(b) from 0.2 to 3.75 weight percent concentration of polyethoxylated 2,4-dinonyl phenol, which contains an average of from 6 to 14 ethoxy units in the ethoxylated substituent.

30 17. A mosquito control oil as claimed in any preceding claim, substantially as described herein.

35 18. A method of killing immature mosquitoes which comprises applying to the surface of a mosquito breeding pond at a rate of at least 0.5 gallon per acre of exposed pond surface a mosquito control oil as claimed in any preceding claim.

40 19. A method in accordance with claim 18, wherein the application rate is from 0.5 gallon to 2.5 gallons per acre.

45 20. A method in accordance with claim 18 or 19, wherein the ethoxylated 2,4-dinonyl phenol contains about 8 ethoxy units and is present in a concentration of about 0.75 weight percent.

50 21. A method as claimed in any one of claims 18 to 20, substantially as described herein.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.



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