

UNITED STATES PATENT OFFICE

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INSECT REPELLENTS

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8 Claims. (Cl. 167—22)

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Many and varied have been the expedients to which people have resorted from time to time in attempting to protect themselves from biting and blood sucking insect pests, and substances which repel the insects and discourage biting by these pests constitute one of the important protections for health and comfort. The effectiveness of oil of citronella, widely known as a repellent, was reported as early as 1901, and prior to and since that time many other essential oils, mixtures of various kinds of oils, greases and ointments and powders have been tried with various degrees of success.

A substance to be generally acceptable as a repellent should possess durability or effectiveness over a relatively long period of time against one or more of such biting or blood sucking pests as mosquitoes, flies, fleas, chiggers and the like. To this end it should be relatively stable chemically, and not readily dissipated by evaporation or vaporization, although it is believed that at least some degree of volatility is essential. For dermal application, a repellent should be non-irritating and easy to apply with the hands or a swab. For use under wet-skin conditions, that is, skin which may be moist or wet as by perspiration, the repellent preferably should be relatively insoluble in water.

Repellents which may affect clothing by staining, bleaching or weakening of the fiber, or which leave an objectionable "oily" appearance or feel on the skin are limited in their usefulness. Preferably, the repellent should be free of odor, especially such odors as may be regarded as unpleasant or disagreeable, and difficult to mask. Preferably, also, the repellent substance should have little or no solvent action on various finishes, paints, varnishes, lacquers and the like.

I have found that the desirable qualities or characteristics enumerated above, as well as excellent repellent activity, are combined to an exceptionally high degree in relatively non-volatile organic compounds, containing carbon, hydrogen and oxygen, in which two oxygen atoms are present in alcoholic hydroxyl groups attached to different carbon atoms, and the carbon and oxygen are present in a ratio of more than two carbon atoms for each oxygen atom. The compounds with which this invention is more particularly concerned contain not less than seven carbon atoms to the molecule with not more than four carbon atoms separating each hydroxyl group from the nearest oxygen atom, with the number of carbon atoms in the chain directly connecting the two alcoholic hydroxyl groups being at least

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two less than the total number of carbon atoms in the molecule and not exceeding seven. In general, these compounds, chemically classified as diols, have been found to have boiling points between 85° C. and 160° C. at an absolute pressure of about 3 to 7 millimeters of mercury, and particularly good results have been obtained with diols distilling between 95° to 150° C. at 5 mm. pressure, equivalent approximately to a range of 80° C. to 135° C. at 2.0 mm. pressure. Especially useful diols are those which are free of carbonyl oxygen atoms, i. e. having no oxygen atom attached by more than one bond to the same carbon atom.

The repellent diols are for the most part liquids, at ordinary temperatures, which have but a limited miscibility with water and which may be placed directly in contact with the skin without substantial irritant effect. Where the sensitivity of the skin to irritants is a predominant factor the lower molecular weight members may, in general, be more suitable. The appearance or feel when first applied in an effective amount is not unduly "oily" and within a short time becomes practically unnoticeable. The odor, if any, is mild and may be readily masked. The solvent action on materials or articles with which the diols are likely to come in contact during ordinary use is slight, and fabrics, paints, varnishes, lacquers, plastics and the like are not appreciably attacked by them, if at all.

These repellent diols afford relatively lasting protection against one or more of such biting and blood sucking pests as: fresh water mosquitoes, *Aedes hirsuteron*, *Aedes stimulans*, *Aedes aegypti*, *Anopheles quadrimaculatus*, *Aedes triseriatus*, *Culex pipens*, *Aedes trivittatus*, and *Aedes vexans*; salt marsh mosquitoes, *Aedes sollicitans*, *Aedes cantator*, and *Aedes taeniorhynchus*; black flies, *Simulium* spp.; sand flies, *Culicoides* spp.; stable flies, *Stomoxys calcitrans*; deer flies, *Chrysops* spp.; cat fleas, *Ctenocephalides felis*; dog fleas, *Ctenocephalides canis*; stick tight fleas, *Echidnophaga gallinacea*; and chiggers or red bugs, *Trombicula* spp.

The protection against mosquitoes which is afforded by the repellents of the present invention is superior to that given by oil of citronella, as measured according to the method for comparing repellent effectiveness which is described in the Journal of Economic Entomology, volume 33, pp. 563 and 566, July 20, 1940. The substance to be tested is applied to an arm from wrist to elbow or a leg from ankle to knee and the area thus treated exposed to attack. In determining the

protection afforded by the substance, the time in minutes to the first bite on the treated area may be designated as the repellent protection time for that substance. During the time of the test the insect activity is determined by observation of the biting frequency (bites per minute) on corresponding untreated areas as a control. As might be expected, the repellent protection time for a given substance is not the same for different biting frequencies but decreases with an increase in biting rate on untreated areas. Comparative tests on a number of repellents have shown that for a given pair of repellents the ratio of their repellent protection times at the same biting frequency may be taken to be approximately constant over the entire range of biting frequency on corresponding untreated areas. This ratio may be designated the average repellency rating of a repellent with respect to a given standard, and the ratings given herein are on the basis of oil of citronella=100.

In general, the diols of the present invention are from about one to upwards of seven times as effective as oil of citronella against a particular insect for biting frequencies over a range from about 0.4 to 40 bites per minute, average, on corresponding untreated areas.

Within the above defined class of substances with which this invention is broadly concerned, saturated 1,2-diols and 1,3-diols composed of carbon, hydrogen and only two oxygen atoms to the molecule are preferred. These 1,2- and 1,3-diols may be regarded as substitution products of ethylene glycol and trimethylene glycol (1,3-propylene glycol) in which one or more of the hydrogen atoms attached to the carbon atoms are replaced by a corresponding number of hydrocarbon radicals, as represented by the following formula: $A(OH)_2$, in which A is a saturated hydrocarbon radical having from seven to sixteen carbon atoms, including an open chain of from two to three aliphatic carbon atoms, and in which the hydroxyl groups are alcoholic and attached to different carbon atoms in said chain.

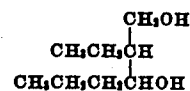
It has been found by test that, in addition to being superior repellents for ordinary use, the effectiveness of these preferred diols is good even under severe conditions of service. For instance, they are effective repellents on the moist or wet skin met with under such conditions as high humidity and profuse perspiration resulting from physical activity, although it may be necessary to repeat the treatment more frequently than upon a dry skin for equivalent results. Furthermore it is difficult to remove these diols from the treated area, to an extent sufficient to eliminate completely their repellent effect, by rubbing or brushing with clothing or such other material or substances as are likely to come in contact with the skin, for instance grass, weeds, leaves, bushes, trees and other vegetation, dirt, sand and the like.

Specific 1,2- and 1,3-diols which are useful as insect repellents include:

2-ethylhexanediol-1,3
3,5-dimethylhexanediol-2,3
6-methylheptanediol-2,4
3-methyloctanediol-2,3
2-ethyl-2-methyloctanol-1 (2-ethyl-2-butylpropanediol-1,3)
2-butyloctanediol-1,3
2,2,4-trimethylpentanediol-1,3
2-amylnonanediol-1,3
2-(1-hydroxyethyl)cyclohexanol

The invention may be further illustrated by the following examples:

EXAMPLE 1



2-ethylhexanediol-1,3

(2-ethyl-3-propylpropanediol-1,3)

2-ethylhexanediol-1,3 was applied to a forearm, from wrist to elbow, in an amount providing 0.01 milliliter of substance per square inch of skin surface, the other forearm being untreated. Every one half hour to one hour over the test period, the treated surface and the untreated surface were exposed for about one to two minutes in a test cage (30 x 30 x 30 inches) containing from 500 to 1000 mosquitoes, of which about one half were females. The first bite on the treated surface determined the end of the test period. The temperature was maintained at 75° to 78° F. and the relative humidity about 50 to 60 per cent. An average of seven tests on the undiluted material over a range of biting frequencies from 10 to 40 bites per minute, average, on the untreated area, gave an effective repellency rating of at least 500 against *Aedes aegypti*.

A series of field tests which gave a rating of about 580 against salt marsh mosquitoes, mainly *Aedes sollicitans*, were carried out in the vicinity of Barnegat, N. J. In these field tests the 2-ethylhexanediol-1,3 was applied to the arm from wrist to elbow and to the leg from ankle to knee in amounts providing 0.01 milliliter per square inch. The treated areas were exposed continuously and the untreated area was exposed every half hour for a period of two minutes, as a control. The average number of bites per minute on the untreated area ranged from 4 to 27. A temperature between 74° to 92° F. and a relative humidity of about 50 to 70 percent prevailed throughout the tests. Tests on deer flies, *Chrysops* spp. and stable flies or dog flies, *Stomoxys calcitrans* showed that they were repelled for about one half to three fourths of the time that the treated surfaces were protected against the mosquitoes.

Additional field tests against upland swamp mosquitoes, mainly *Aedes trivittatus* and some *Aedes vexans*, in the vicinity of Chatham, N. J., gave an average value of about 790 for the effective repellency rating. The temperature was about 80° to 84° F. with a relative humidity about 50 to 60 percent and the average number of bites on the untreated area ranged from about 15 to 28 per minute. Otherwise the tests were carried out in the same manner as the field tests against the salt marsh mosquitoes.

On various dilutions up to about 70 percent of the diluent, by volume, with various compatible carrier substances, the effective repellency rating of the compositions were found on the whole to be slightly higher than corresponded to the dilution of the repellent substance present. This was the case with such diluents as ethanol, isopropanol, monopropylene glycol, castor oil, vanishing cream and the like.

2-ethylhexanediol-1,3 was found to evaporate only slowly when spread thinly over relatively large areas. For instance, slightly less than 0.01 gm. spread over about 13 square inches of a ground glass plate evaporated only about 12 per-

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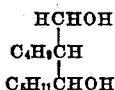
cent in 24 hours at a room temperature of about 74° F., and about 50 to 60 percent in 24 hours on heating the plate to a temperature of about 94° to 96° F., the room conditions otherwise remaining the same.

Extended field tests with a group of subjects under wet skin conditions were also carried out in a grove in Florida where *Aedes taeniorhynchus* were abundant. During the course of the tests the subjects engaged in moderate physical activity with care being taken to prevent the treated surfaces from coming into rubbing contact with clothing, vegetation and the like. The temperature and humidity were sufficiently high to cause the subjects to perspire freely, with consequent wetting of the treated skin area. The average repellency rating against *Aedes taeniorhynchus* in these tests was about 520.

A more severe type of test was also carried out under substantially the same conditions. In these tests attempts were made to rub off or brush off the repellent about 30 minutes after it had been applied. The test subjects walked through grasses and weeds about shoulder high and tried to rub the repellent from treated arm and leg areas. Handfuls of vegetation were used as brushes and the treated areas were rubbed vigorously. In some instances the subjects were on the ground in contact with the dirt and in others the treated areas were rubbed thoroughly on the clothing of the subject or with a paper towel. It was found that under ruboff conditions the repellent must be applied more frequently than under normal conditions, for equivalent protection. On the average the time until the first bite was received was reduced to about two hours under ruboff conditions, amounting to a reduction of about four hours.

2-ethylhexanediol-1,3 as used is a slightly oily liquid distilling at 244.2° C. at 760 mm.; at 163° C. at 50 mm.; at 129° C. at 10 mm. and 102° C. at 3 mm. of mercury absolute pressure. Its vapor pressure at 20° C. was less than 0.01 mm. of mercury and it had a gravity of 0.9422 (20°/20° C.). Its absolute viscosity was 271 centipoises and solubility in water was 0.6 percent by weight, both at 20° C. At the same temperature water was soluble in it to 10.8 percent by weight. 2-ethylhexanediol-1,3 was found to be physiologically safe under the conditions of use for which it is intended.

EXAMPLE 2

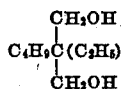


2-butylactanediol-1,3

(2-butyl-3-pentylpropanediol-1,3)

2-butylactanediol-1,3 which is a liquid boiling at 115° C. at 1.0 to 1.5 mm. pressure (about 143° C. at 5 mm.) was found to have a repellency rating of about 480 against captive *Aedes aegypti*.

EXAMPLE 3



2-ethyl-2-methylolhexanol-1

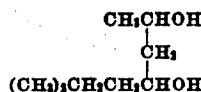
(2-ethyl-2-butylpropanediol-1,3)

2-ethyl-2-methylolhexanol-1 distilling at 130° C. at 7 mm. pressure (about 123° C. at 5 mm.) was found to have an effective repellency rating above 590 against captive *Aedes aegypti*.

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Similar tests on propanediol-1,3 distilling at 214° C. at 760 mm. gave a value for the repellency rating of about 9 against captive *Aedes aegypti*, by way of comparison.

EXAMPLE 4

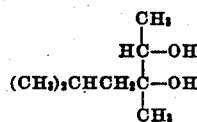


6-methylheptanediol-2,4

(1-methyl-3-isobutylpropanediol-1,3)

The repellency rating of 6-methylheptanediol-2,4 which was a rather viscous liquid distilling at 93°-94° C. at 3 mm. pressure (about 105° C. at 5 mm.) was found to be 593 against captive *Aedes aegypti*. This rating is to be compared with an effective repellency rating of 90 which was obtained on testing 2 methylpentanediol-2,4 (1,3,3 trimethylpropanediol-1,3) against captive *Aedes aegypti*.

EXAMPLE 5

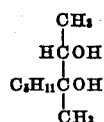


3,5-dimethylhexanediol-2,3

(2-isobutylbutanediol-2,3)

3,5-dimethylhexanediol-2,3 distilling at 110°-111° C. at 21 mm. pressure (about 84° C. at 5 mm.) was found to have an effective repellency rating of about 120 against captive *Aedes aegypti*. It boils substantially below the 2-ethylhexanediol-1,3 of Example 1.

EXAMPLE 6



3-methyloctanediol-2,3

(2-pentylbutanediol-2,3)

3-methyloctanediol-2,3 distilling at 94° C. at 3 mm. pressure (107° C. at about 5 mm.) was found to have a rating of about 470 against captive *Aedes aegypti*. This substance is somewhat higher boiling than the 3,5 dimethylhexanediol-2,3 of the preceding example and had a slight, not unpleasant odor. It was observed also that the mosquitoes did not light on the treated areas up to the time of the first bite.

For purposes of comparison, similar repellency tests against captive *Aedes aegypti* were made with butane diol-2,3 distilling at 184° C. at 760 mm. and 2-methylbutanediol-2,3 distilling at 83° C. at 20 mm. pressure (68° C. at 5 mm.). The ratings were found to be about 25 and 30, respectively.

EXAMPLE 7



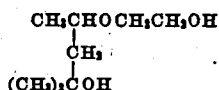
Tripropylene glycol

Tests on tripropylene glycol distilling at 111° C. at 3 mm. pressure (about 126° C. at 5 mm.) gave a rating of about 250 against captive *Aedes aegypti*.

Tests on triethylene glycol distilling at 288° C. at 760 mm. (144° C. at 5 mm.) gave a rating of 49 against captive *Aedes aegypti* under similar conditions, for purpose of comparison.

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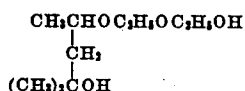
EXAMPLE 8



2-methylpentanediol-2,4 monoethylene glycol ether

The monoethylene glycol ether of 2-methylpentanediol-2,4 distilling at 90° C. at 2.5 mm. (102° C. at 5 mm.) was found to have a rating of about 370 against captive *Aedes aegypti*.

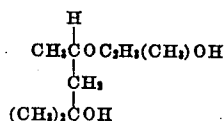
EXAMPLE 9



2-methylpentanediol-2,4 diethylene glycol ether

The diethylene glycol ether of 2-methylpentanediol-2,4 distilling at 110° C. at 2.5 mm. pressure (123° C. at 5 mm.) was found to have a rating of about 360 against captive *Aedes aegypti*.

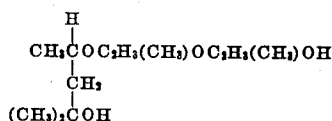
EXAMPLE 10



2-methylpentanediol-2,4 monopropylene glycol ether

The repellency rating of the monopropylene glycol ether of 2-methylpentanediol-2,4 distilling at 108° C.-114° C. at 9 mm. pressure (about 99° C. at 5 mm.) was found to be about 480 against captive *Aedes aegypti*.

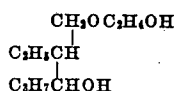
EXAMPLE 11



2-methylpentanediol-2,4 dipropylene glycol ether

The dipropylene glycol ether of 2-methylpentanediol-2,4 distilling at 122°-128° C. at 8 mm. pressure (about 119° C. at 5 mm.) was found to have a repellency rating of about 550 against captive *Aedes aegypti*.

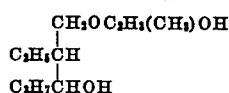
EXAMPLE 12



2-ethylhexanediol-1,3 monoethylene glycol ether

The monoethylene glycol ether of 2-ethylhexanediol-1,3 distilling at 110° C. at 2 mm. pressure (about 134° C. at 5 mm.) was found to have a repellency rating of about 250 against captive *Aedes aegypti*.

EXAMPLE 13



2-ethylhexanediol-1,3 monopropylene glycol ether

The monopropylene glycol ether of 2-ethylhexanediol-1,3 distilling at 112° C. at 2 mm. pressure (about 131° C. at 5 mm.) was found to have a repellency rating of about 370 against captive *Aedes aegypti*.

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Various modifications of the invention will be apparent within the scope of the appended claims.

I claim:

1. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof an organic diol distilling between 95° C. to 150° C. at an absolute pressure of about 5 millimeters of mercury, carbon and oxygen being present in a ratio of more than two carbon atoms for each oxygen atom; said diol containing not less than seven carbon atoms to the molecule with the hydroxyl groups of said diol attached to different carbon atoms in an open chain and not more than four carbon atoms separating each hydroxyl group from the nearest oxygen atom; the total number of carbon atoms in the chain directly connecting the two alcoholic hydroxyl groups being at least two less than the total number of carbon atoms in the molecule and not exceeding seven.
2. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof a saturated aliphatic diol in which carbon and oxygen are present in a ratio of more than two carbon atoms for each oxygen atom; said diol containing from seven to sixteen carbon atoms to the molecule with the hydroxyl groups of said diol attached to different carbon atoms in an open chain and not more than four carbon atoms separating each hydroxyl group from the nearest oxygen atom; the total number of carbon atoms in the chain which directly connects the alcoholic hydroxyl groups being at least two less than the total number of carbon atoms in the molecule and not exceeding seven.
3. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof a saturated aliphatic diol distilling between 95° C. and 150° C. at an absolute pressure of about 5 millimeters of mercury, carbon and oxygen being present in a ratio of more than two carbon atoms for each oxygen atom; said diol containing from seven to sixteen carbon atoms to the molecule with the hydroxyl groups of said diol attached to different carbon atoms in an open chain and not more than four carbon atoms separating each hydroxyl from the nearest oxygen atom; the total number of carbon atoms in the chain which directly connects the alcoholic hydroxyl groups being at least two less than the total number of carbon atoms in the molecule and not exceeding seven.
4. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof a diol of the general formula $\text{A}(\text{OH})_2$ in which A is a saturated aliphatic hydrocarbon radical having from seven to sixteen carbon atoms, including an open chain of from two to three carbon atoms, and in which the hydroxyl groups are alcoholic and attached to different carbon atoms in said chain.
5. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof an open chain alkane diol containing from seven to sixteen carbon atoms to the molecule and distilling between 95° C. and 150° C. at an absolute pressure of about 5 millimeters of mercury, in which the alcoholic hydroxyl groups are in the 1,3 position relative to each other.
6. A method of repelling insects which includes

applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof an octane diol in which the alcoholic hydroxyl groups are in the 1,3 position relative to each other.

7. A method of repelling insects which includes applying to a zone to be treated an insect repellent comprising as an essential repellent ingredient thereof 2-ethylhexanediol-1,3.

8. A method of repelling insects which includes

applying to a zone to be treated an insect repellent composition comprising as an essential repellent ingredient thereof an open chain alkane diol containing from seven to sixteen carbon atoms to the molecule and distilling between 95° C. and 150° C. at an absolute pressure of about 5 millimeters of mercury in which the alcoholic hydroxyl groups are attached to adjacent carbon atoms.

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