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(51) **International Patent Classification (Int. CL 7):** A01N 47/02; A01N 43/56

(54) **Title:** Use of Phenylpyrazole Derivatives for Surface Treatment to Control Cockroaches or Ants

(57) **Abstract:** Use of 1-phenyl pyrazole derivatives for surface treatment to control cockroaches or ants.

NEW METHOD OF COMBATING INSECTS

5 This invention relates to a new method of combating insects such as cockroaches or ants at a locus connected to public health, that is to say at a locus frequented by humans, either private or public.

Many insecticidally active compounds are known, such as the insecticidal pyrazoles described in International Patent Publications No. WO 87/03781, WO 93/06089 and WO 94/21606, as well as in European Patent Publications
10 0295117, 0403300, 0385809, and 0679650, German Patent Publication 19511269 and United States Patents 5,232,940 and 5,236,938. The use of such compounds to kill cockroaches or ants has already been contemplated, but such use was essentially in connection with baits or ingested materials or food that the insect is supposed to eat, or also in connection with direct contact application to the said
15 insects.

The use of baits can be problematic because there is a need to place the baits at a proper locus where the cockroaches are supposed to come. Furthermore the baits can become a safety hazard to children, an undesirable situation.

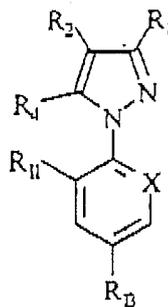
20 An object of the instant invention is to provide a method of control of cockroaches or ants avoiding the use of baits or ingestible material.

An object of the instant invention is to provide a method of control of cockroaches or ants avoiding the direct application of the active material to the insect itself, as with baits for example.

25 The object of the instant invention is to provide a simplified and efficient method of control of cockroaches or ants.

The present invention is thus directed to a method of control of cockroaches or ants, preferably cockroaches, or of a population of cockroaches whereby an effective amount of an active ingredient which is a 1-phenylpyrazole derivative is applied to a surface on which the insect makes contact or moves or is
30 moving or is expected to move.

The 1-phenylpyrazole derivatives which can be used in the invention are generally compounds of formula (I) :



(I)

wherein :

R₁ may be CN or methyl ;

5 R₂ may be S(O)_nR₃ ;

R₃ may be alkyl or haloalkyl ;

R₄ represents a hydrogen or halogen atom ; or a NR₅R₆, S(O)_mR₇, or C(O)O-R₇, alkyl, haloalkyl or OR₈ radical ; or a -N=C(R₉)(R₁₀) radical ;

10 R₅ and R₆, independently, may be a hydrogen atom or a radical alkyl, haloalkyl, C(O)alkyl or S(O)_rCF₃; or R₅ and R₆ may form together a divalent alkylene radical which may be interrupted by one or more divalent heteroatoms such as oxygen or sulfur ;

R₇ may be an alkyl or haloalkyl radical ;

R₈ may be an alkyl or haloalkyl radical, or a hydrogen atom ;

15 R₉ may be a hydrogen atom or an alkyl radical ;

R₁₀ may be a phenyl or heteroaryl group, optionally substituted by one or more halogen atoms or group such as OH, -O-alkyl, -S-alkyl, cyano, or alkyl;

R₁₁ and R₁₂ , independently, represent a hydrogen or halogen atom

20 R₁₃ represent a halogen atom or a haloalkyl, haloalkoxy, S(O)_qCF₃ or SF₅ group ;

m,n,q,r may be independently be an integer equal to 0, 1 or 2 ;

X represent a trivalent nitrogen atom or a C-R₁₂ radical, the three remaining free bonds of the carbon atom being part of the aromatic ring ;

25 provided that, when R₁ is methyl, then R₃ is haloalkyl, R₄ is NH₂, R₁₁ is Cl, R₁₃ is CF₃, and X is N.

The alkyl or acyl groups of the formula (I) are preferably lower alkyl or acyl, that is to say radicals having one to four carbon atoms.

5 A preferred class of compounds of formula (I) comprises the compounds of formula (I) wherein R_1 may be CN, and/or R_3 may be haloalkyl, and/or R_4 may be NH_2 , and/or R_{11} and R_{12} are independently a halogen atom, and R_{13} may be haloalkyl.

Still further preferred active ingredients which may be used in the invention are those of formula (I) wherein R_{11} and R_{12} are chlorine ; R_3 and R_{13} are trifluoromethyl ; R_5 is amino.

10 Such most preferred insecticides are 5-amino-3-cyano-1-(2,6 dichloro-4-trifluoromethyl)phenyl-4-trifluoromethylsulfinylpyrazole (hereafter referred to as compound A), 5-amino-3-cyano-1-(2,6 dichloro-4-trifluoromethyl)phenyl-4-trifluoromethylthiopyrazole pyrazole (hereafter referred to as compound B), 5-amino-3-cyano-1-(2,6 dichloro-4-trifluoromethyl)phenyl-4-trifluoromethylsulfonylpyrazole (hereafter referred to as compound C).

15 It should be understood that in the instant invention, the active ingredient is rather in the form of a thin layer or imbedded in a thin layer, and that this layer is covering totally or partially the surface where the insect is making contact or is moving or walking or going to walk or expected to be walking or supposed to be walking. Due to this thin layer the insect is not able to seize or bite or eat directly a
20 discrete volume of composition comprising the ingredient of formula (I). This is connected with the unobviousness of the invention.

25 -According to a further aspect of the invention, it provides a method of control of a population of cockroaches or ants able to walk or travel in public or private housing or building or household or home, whereby a non seizable, but insecticidally effective, amount of active ingredient is lying on a surface located in the area to be treated.

30 According to a further aspect of the invention, it provides a method of control of a population of cockroaches or ants able to walk or travel in public or private housing or building or household or home, whereby a thin layer is covering the surface where the cockroaches or ants are supposed to walk.

According to a further aspect of the invention, it provides a method of control of a population of cockroaches or ants that are able to walk or travel in public or private housing or building or household or home, whereby the said

cockroaches or ants are caused to walk on a thin layer covering a surface in or near the area where the said insects are to be killed.

According to a preferred and most efficient embodiment, the invention is applied specifically to cockroaches.

5 The method of the invention is especially advantageous because it is very easy to apply the active ingredient, preferably by mean of spraying a liquid formulation to the appropriate surface.

10 The surface which is treated according to the invention may be smooth or rough or rugged. Smooth surfaces are more effective. Various kinds of surface may be used such as glass, ceramics, concrete ; plastics surface such as vinyl plastics, melamine, linoleum ; metallic or wooden surface such as furniture ; textiles such as clothes.

15 The deposited layer of active ingredient according to the invention may be wet just after application, or may be dried or dry sometime after. The creation of this layer may be made by all known methods of covering, for example as a spray coat, paint, dip, wash, soak, lacquer, foam, dust, powder, aqueous suspension, paste, cream, wetttable powder, aerosol, emulsifiable concentrate, concentrated suspension, flowable suspension, aqueous suspension, oil suspension, oil solution, pressure pack, or other standard formulation well known by those skilled in the art.

20 Compositions comprising an active ingredient of formula (I), especially liquid compositions, have already been described in the here above cited prior art.

25 Treatment of cockroaches in public health in public housing or building for the control of so-called American cockroaches (Periplaneta americana), but also of other cockroaches like German cockroaches (Blatella germanica), is a preferred feature of the instant invention.

The invention accordingly provides a method for controlling cockroaches or ants which comprises applying to a surface with which the cockroaches or ants make contact or are to make contact a compound of formula I. The compound is preferably applied as a thin layer.

30 The preparation of compounds of formula (I) may be performed according to any process described in the here above cited patent applications, or other process according to the knowledge of a person skilled in the art of chemical synthesis.

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5 The effective compositions which may be used in the invention may be offered or presented in different amounts. Usually, it is advantageous to offer the active compositions comprising the compound of formula (I) in an amount between 0.0001 g to 20 g per 100 square meters, preferably between 0.01 g and 10 g/100 m².

10 The compositions which are useful in the invention (and which are to be spread on surfaces to control cockroaches or ants) comprise generally 0.0001 up to 15 % w/w of active ingredient, preferably from 0.1 to 6 w/w. They may be in the form of a liquid before application, especially in the form of an emulsifiable concentrate, aqueous emulsion, concentrated suspension or flowable suspension. But after drying of the liquid in the form of a thin layer.

15 The insecticidal compositions may also contain all kind of compatible surface active agent and/or carrier. Adjuvants may also be used, such as sticking agents, dyestuffs, film forming agent or the like. The carrier itself may be solid or liquid.

20 The compounds of formula (I) may be used in sequence or admixture, particularly admixtures with another pesticide e.g. an insecticide, acaricide or fungicide.

The compositions may be prepared by admixing the ingredients.

25 The invention is illustrated by the following examples which should not be considered as limiting or restricting the invention.

30 EXAMPLE 1

Compounds A and B were dissolved in an acetone/water mixture and deposited on glass and left overnight to dry. The following results were observed :

COMPOUND	DOSE LEVEL mg/100 m ²	Mortality % 90 min. after introduction of the cockroaches	Mortality % 18 h. after introduction of the cockroaches
B	125	100	100
B	31	100	100

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B	10	0	91
A	125	100	100
A	31	100	100
A	10	5	100

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Example 2

Compound A was formulated as a 12.5 grams per liter liquid formulation in three compositions: (i) an emulsifiable concentrate (EC-wetting agent and an organic solvent); (ii) an aqueous emulsion (EW- wetting agent plus water plus an organic solvent); and (iii) a concentrated suspension (SC- dispersing agent and water). Each formulation was dissolved in water and deposited on samples of painted cement and plastic flooring (as described in Méthode C.E.B. n° 159 Chapitre I I / §1, "Méthode d'essai d'efficacité pratique de spécialités insecticides destinées à la destruction des blattes dans les locaux Novembre 1992," paragraph 2.6.) to provide deposits of 125 mg/100 m², 500 mg/100 m², and 1250 mg/100 m². *Blattella germanica* (German cockroaches) between 2 and 15 days old were placed on the surfaces for four hours and then removed, put in an untreated jar and observed after 96 hours from the beginning of the exposure. Each treatment was replicated 3 times. The following results were observed. Mortalities are reported as percentages of dead insects among living ones.

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	10.2	100
EC / 500 mg/100 m ²	100	100
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	93.3	100
EW / 500 mg/100 m ²	88	95.7
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	93.3	100

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SC / 500 mg/100 m ²	67.7	100
SC / 1250 mg/100 m ²	100	100

Example 3

5 The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 24 hours. The infestation and observations of Example 2 were repeated. The following results were observed:

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	14	100
EC / 500 mg/100 m ²	100	100
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	49	100
EW / 500 mg/100 m ²	74	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	43	100
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

Example 4

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The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 14 days. The infestation and observations of Example 2 were repeated. The following results were observed:

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Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	13.6	100
EC / 500 mg/100 m ²	100	100
EC / 1250 mg/100 m ²	100	100

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EW / 125 mg/100 m ²	37.7	100
EW / 500 mg/100 m ²	77.7	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	44.3	100
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

Example 5

5 The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 30 days. The infestation and observations of Example 2 were repeated. The following results were observed:

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	6.7	72.3
EC / 500 mg/100 m ²	100	100
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	53.3	100
EW / 500 mg/100 m ²	82.3	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	51	100
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

Example 6

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The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 90 days. The infestation and observations of Example 2 were repeated. The following results were observed:

15

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	8.9	24.3
EC / 500 mg/100 m ²	95.7	100
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	69	100
EW / 500 mg/100 m ²	95.7	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	84.3	100
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

Example 7

- 5 The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 120 days. The infestation and observations of Example 2 were repeated. The following results were observed:

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	4.3	8.8
EC / 500 mg/100 m ²	95.7	97.7
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	69	100
EW / 500 mg/100 m ²	88.7	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	86.7	100
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

Example 8

The samples of plastic flooring and cement of Example 2 were held at 25°C in the dark for 180 days. The infestation and observations of Example 2 were repeated. The following results were observed:

Formulation / Dose	Mortality % on Plastic	Mortality % on Cement
EC / 125 mg/100 m ²	0	0
EC / 500 mg/100 m ²	100	100
EC / 1250 mg/100 m ²	100	100
EW / 125 mg/100 m ²	60	100
EW / 500 mg/100 m ²	93.3	100
EW / 1250 mg/100 m ²	100	100
SC / 125 mg/100 m ²	24.4	75.5
SC / 500 mg/100 m ²	100	100
SC / 1250 mg/100 m ²	100	100

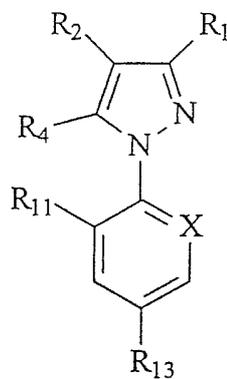
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Example 9

10 Porous concrete is impregnated with a 20 ppm solution acetone/water solution of Compound B and cockroaches (*Blattella germanica*) were permitted to walk on the surface. One day after treatment, the insects were observed. 50% of the insects had died.

CLAIMS

1. Method of control of cockroaches or ants or of a population of cockroaches or ants wherein an effective amount of an active ingredient which is a 1-phenylpyrazole is applied to a surface on which the insect is moving or expected to move, the active ingredient being in the form of a thin layer or embedded in a thin layer, which layer the insect is not able to seize or bite or eat directly and wherein the 1-phenylpyrazole derivatives are compounds of formula (I):



(I)

20 wherein;

R_1 may be CN;

R_2 may be $S(O)_nR_3$;

R_3 may be alkyl or haloalkyl;

R_4 represents a hydrogen or halogen atom; or a NR_5R_6 , $S(O)_mR_7$, or $C(O)O-$
 25 R_7 , alkyl, haloalkyl or OR_8 radical; or a $-N=C(R_9)(R_{10})$ radical;

R_5 and R_6 , independently, may be a hydrogen atom or a radical alkyl, haloalkyl, $C(O)$ alkyl or $S(O)_rCF_3$; or R_5 and R_6 may form together a divalent alkylene radical which may be interrupted by one or more divalent heteroatoms such as oxygen or sulfur;

30 R_7 may be an alkyl or haloalkyl radical;

R_8 may be an alkyl or haloalkyl radical, or a hydrogen atom;

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R₉ may be a hydrogen atom or an alkyl radical;

R₁₀ may be a phenyl or heteroaryl group, optionally substituted by one or more halogen atoms or group such as OH, O-alkyl, -S-alkyl, cyano, or alkyl;

R₁₁ and R₁₂, independently, represent a hydrogen or halogen atom ;

5 R₁₃ represent a halogen atom or a haloalkyl, haloalkoxy, S(O)_qCF₃ or SF₅ group;

m, n, q, r may be independently an integer equal to 0, 1 or 2;

X represent a trivalent nitrogen atom or a C-R₁₂ radical, the three remaining free bonds of the carbon atom being part of the aromatic ring;

10

2. Method of control according to claim 1 wherein R₃ may be haloalkyl, and/or R₄ may be NH₂, and /or R₁₁ and R₁₂ are independently a halogen atom, and R₁₃ may be haloalkyl.

15

3. Method of control according to claim 1 or 2 wherein R₁₁ and R₁₂ are chlorine; R₃ and R₁₃ are trifluoromethyl; R₅ is amino.

20

4. Method of control according to any one of the foregoing claims which is a method of control of a population of cockroaches or ants able to walk or travel in public or private housing or buildings or household or home.

25

5. Method of control according to any one of the foregoing claims which is a method of control of a population of cockroaches or ants able to walk or travel in public or private housing or buildings or household or home, wherein the said cockroaches or ants are caused to walk on a thin layer covering a surface in or near the area where the said insects are to be killed.

30

6. Method according to any one of the foregoing claims when applied to cockroaches.

7. Method according to any one of the foregoing claims wherein the insecticidal

compositions comprising the compound of formula (I) in an appropriate form are applied in an amount from 0.0001 g to 20 g per 100 square metres.

8. Method according to any one of the foregoing claims wherein the insecticidal compositions comprising the compound of formula (I) in an appropriate form are applied in an amount from 0.01 g to 10 g per 100 square metres.

9. Method according to any one of the foregoing claims wherein the insecticidal compositions comprise from 0.0001 to 15% w/w of active ingredient.

10. Method according to any one of the foregoing claims wherein the insecticidal compositions comprise from 0.1 to 6% w/w of active ingredient.

11. A composition for the control of cockroaches or ants which comprises from 0.0001 to 15% w/w of active ingredient as defined in any one of claims 1 to 3 in the form of a thin layer as defined in claim 1.

12. A composition according to claim 1 which comprises from 0.1 to 6% w/w of active ingredient.

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