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**Process and composition for the antiparasitic treatment of
the surroundings of animals by treating their litter with 1-
arylpyrazole insecticides**

(57) Abstract:

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** End of report **

PROCESS AND COMPOSITION FOR THE ANTIPARASITIC
TREATMENT OF THE SURROUNDINGS OF ANIMALS

The present invention relates to a process for the antiparasitic
5 treatment of the surroundings of animals, in particular of animal litter and of rearing
buildings, in particular for the purpose of protecting them against parasites from the
darkling beetle family.

In the present text, animal litter is taken in the broad sense, that is to
say that this term comprises beds made of plant or other material on which the
10 animals lie or gather, including open-air sites or places, in particular those of the
"feed lot" type in North America.

The invention also encompasses the treatment of liquid manure, in
particular in the vicinity of animal rearing sites. The invention applies to the litter
and liquid manure of all types of animals but is very particularly applied in the avian
15 field (in particular chickens, turkeys, guinea fowls, ducks, geese and laying hens).
The invention also applies to ready-to-use litter or to litter components treated by the
process according to the invention.

The intensive rearing of animals intended for consumption results in a
large number of animals being confined in a restricted space. This applies both to
20 small animals, such as poultry and rabbits and others, and to large animals, such as
cattle, pigs and the like.

Broilers are, for example, reared for 8 weeks on average. Between
two groups, that is to say between two rearing cycles, the breeder generally cleans
the site, with the site being left empty for several days for health reasons.

25 However, the frequency at which breeders clean the rearing area and
more particularly the litter is always limited by rearing requirements. Animal rearing
sites are therefore centres for the development of parasites in the general sense,
including insects. This naturally has a direct impact on the sanitary condition of the
sites and on the health of the animals and indirectly on rearing productivity.

30 Poultry litter is basically composed of materials of plant origin, such
as, for example, sawdust or wood chippings, with which dejecta or excrement from
the animals will be mixed in time. As the litter is not changed at each rearing cycle,
the thickness of the soiled litter frequently reaches several tens of centimetres. In
particular, beetles from the Tenebrionidae family, also known as darkling beetles,
35 develop therein. The treatment of poultry litter is a problem which is particularly
difficult to solve in that any product used to treat this litter has a tendency to be

absorbed by the litter, either by the excrement which is found therein or by the plant matter which is found therein. Moreover, the continuous arrival of fresh excrement tends to isolate the insecticidal materials from the site to be treated.

Darkling beetles comprise various species. One of the main species is
 5 *Alphitobius diaperinus*; this species is particularly well controlled by the present invention. Another darkling beetle species is *Tenebrio molitor*. Another species of parasite which infests poultry litter is *Dermestes maculatus*.

The presence of these parasites, especially darkling beetles, has two impacts with serious economic consequences.

10 The first impact is on the growth of the poultry. In poultry rearing, the speed of the rearing cycle is an economically determining factor and the least disturbance to food intake has consequences for the growth of the animals. Now, these beetles are ingested by poultry, and particularly by chicks, and they can then cause slow-down in growth.

15 The second impact is on the very structure of the rearing buildings. In fact, at the adult stage, in particular between two rearing cycles, the adult beetles can ascend into the structures of the buildings and lay their eggs there. The larvae, before redescending into the litter, have a tendency to devour the heat-insulation materials, such as polystyrene. Now, poultry is very sensitive to the temperature, so that the
 20 consequences of such a deterioration can be catastrophic with respect to the progression of the rearing. The rearing buildings must therefore frequently be repaired or replaced.

Laying hens and rabbits are both raised on gratings and their dejecta or excrement are continuously discharged and generally stored in the vicinity of the
 25 rearing buildings. The liquid manure which thus accumulates itself also exhibits the disadvantages cited above with respect to the sanitary condition of the sites and the health of the animals.

Another problem frequently encountered is the presence of flies, in particular the house fly, the larvae of which develop within the soiled litter and the
 30 liquid manure. These flies are a nuisance both to animals and to man, in and in the vicinity of the animal rearing site. In addition, these flies can be the vector for infectious agents and can be responsible for epidemic pathologies.

Darkling beetles are insects/parasites which are particularly difficult to remove. This difficulty is illustrated by the fact that there is only a single product
 35 which has been successful commercially: this is the product known under the name of carbaryl [1-naphthyl methylcarbamate]. This is all the more surprising since this

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product is an old product, being at least forty years old, and although a number of insecticides have been developed since, none has been in a position to supplant carbaryl with respect to poultry. Unfortunately, carbaryl is a product which, in a number of respects, has a limited performance, both as regards effectiveness and as regards the duration of this effectiveness. An explanation for this currently existing lack of worthwhile products probably results from the difficulty of treating animal litter, as has been explained above.

A first object of the invention is to provide a process and compositions which can completely or partially solve the problems indicated above; and/or to provide means for combating darkling beetles or insects from the Tenebrionidae family, especially *Alphitobius diaperinus*; and/or

to provide means for combating parasitic insects commonly found in animal litter and known under the name of *Dermestes maculatus* or under the name of insects from the Tenebrionidae family, such as *Alphitobius diaperinus* and *Tenebrio molitor*; and/or

to provide a process for the antiparasitic treatment of floors, litter or liquid manure which is particularly effective against darkling beetles and flies, while being easy and practical to use in commercial rearing, especially poultry rearing; and/or

to provide a process for the antiparasitic treatment of sites where poultry lives or should live, the said sites being infested or capable of being infested by darkling beetles; and/or

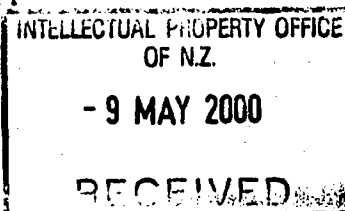
to provide a process which only requires treatments at widely spaced intervals and even, in particular in the case of the rearing of broilers, which only requires a single treatment per rearing cycle, before installing the young animals; and/or

to provide a process suitable for the preparation of litter components or of ready-to-use litter which have been treated against these parasites, in particular for the whole of their period of use; and/or to provide the public with a useful choice.

These objects are met in whole or in part by the present invention.

A subject of the present invention is therefore a process for the antiparasitic treatment of sites infested or capable of being infested by darkling beetles, in which an effective amount of a composition comprising at least one compound corresponding to the formula (I) defined below is applied to the said site.

AMENDED SHEET



According to another aspect, a subject of the present invention is a process for the antiparasitic treatment of sites infested or capable of being infested by darkling beetles, in which an effective amount of a composition comprising at least one compound corresponding to the formula (I) is applied to the said site. the
 5 said sites comprising floors, litter, liquid manure or the like.

According to another aspect, a subject of the present invention is a process for the antiparasitic treatment of rearing places or buildings, in particular for commercial rearing, in particular of poultry, and more especially of sites infested or capable of being infested by darkling beetles, the said process comprising the
 10 application to the said site of an effective amount of a composition comprising at least one compound corresponding to the formula (I).

According to another aspect, the invention relates to a means for combating darkling beetles or insects from the Tenebrionidae family, especially *Alphitobius diaperinus*, the said process comprising the application to the sites
 15 infested or capable of being infested by the said darkling beetles of an effective amount of a composition comprising at least one compound corresponding to the formula (I).

Another object of the invention is to provide means for combating the insects known under the name of *Dermestes maculatus*, the said process comprising
 20 the application to the sites (floors, litter, liquid manure, places or buildings) of an effective amount of a composition comprising at least one compound corresponding to the formula (I).

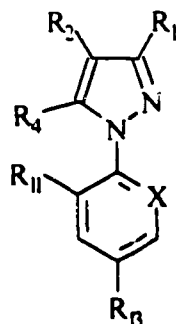
The present invention further relates to a process for the antiparasitic treatment of the surroundings of animals, in particular of sites infested or capable of
 25 being infested by a parasite from the group composed of a darkling beetle and/or *Alphitobius diaperinus* and/or *Dermestes maculatus* and/or *Tenebrio molitor*, the said treatment comprising the application to the said surroundings or to the said site of an effective amount of a composition comprising at least one compound corresponding to the formula (I). According to one aspect of this invention, these
 30 infested sites or sites capable of being infested are floors, litter or liquid manure or the like. According to another aspect, these sites are commercial rearing places or buildings.

The present invention therefore further relates to a process for the antiparasitic treatment of sites infested or capable of being infested by an insect from
 35 the group composed of darkling beetles and/or *Alphitobius diaperinus* and/or *Dermestes maculatus* and/or *Tenebrio molitor*, in which an effective amount of a

composition comprising at least one compound corresponding to the formula (I) is applied to the said site, the said process being carried out at a frequency of less than once per month.

The present invention therefore further relates to a process for the antiparasitic treatment of sites infested or capable of being infested by an insect from the group composed of darkling beetles and/or *Alphitobius diaperinus* and/or *Dermestes maculatus* and/or *Tenebrio molitor*, in which an effective amount of a composition comprising at least one compound corresponding to the formula (I) is applied to the said site, the said process being carried out at a frequency not exceeding once per rearing cycle.

The products of formula (I) used in the invention are products, the formula of which is:



(I)

in which:

R₁ is a halogen atom or a CN or methyl group;

R₂ is S(O)_nR₃ or 4,5-dicyanoimidazol-2-yl or haloalkyl;

R₃ is alkyl or haloalkyl;

R₄ represents a hydrogen or halogen atom; or an NR₅R₆, S(O)_mR₇, C(O)R₇ or

C(O)O-R₇, alkyl, haloalkyl or OR₈ radical or an -N=C(R₉)(R₁₀) radical;

R₅ and R₆ independently represent a hydrogen atom or an alkyl, haloalkyl,

C(O)alkyl, alkoxycarbonyl, S(O)_rCF₃ radical; or R₅ and R₆ can together form a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen or sulphur;

R₇ represents an alkyl or haloalkyl radical;

R₈ represents an alkyl or haloalkyl radical or a hydrogen atom;

R₉ represents an alkyl radical or a hydrogen atom;

R₁₀ represents a phenyl or heteroaryl group optionally substituted by one or a number of halogen atoms or groups such as OH, -O-alkyl, -S-alkyl, cyano or alkyl;

R_{11} and R_{12} represent, independently of one another, a hydrogen or halogen atom and optionally CN or NO_2 but H or halogen are preferred;

R_{13} represents a halogen atom or a haloalkyl, haloalkoxy, $\text{S}(\text{O})_q\text{CF}_3$ or SF_3 group;

m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

5 X represents a trivalent nitrogen atom or a C-R_{12} radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl,

R_4 is NH_2 , R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl,

R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is $=\text{C-Cl}$.

10 The alkyl radicals of the definition of the formula (I) generally comprise from 1 to 6 carbon atoms. The ring formed by the divalent alkylene radical representing R_5 and R_6 and by the nitrogen atom to which R_4 and R_6 are attached is generally a 5-, 6- or 7- membered ring.

A preferred class of compounds of the formula (I) comprises the
15 compounds such that R_1 is CN and/or R_3 is haloalkyl and/or R_4 is NH_2 and/or X is C-R_{12} and/or R_{11} and R_{12} are, independently of one another, a halogen atom and/or R_{13} is haloalkyl.

A compound of formula (I) which is very particularly preferred in the invention is 1-[2,6- Cl_2 -4- CF_3 phenyl]-3-CN-4-[SO-CF_3]-5- NH_2 pyrazole, hereinafter
20 known as compound A.

Compounds of formula (I) can be prepared according to one or other of the processes described in Patent Applications WO 87/3781, 93/6089 or 94/21606 or European Patent Applications 295,117, 403,300, 385,809 or 679,650 or German Patent Application 19511269 or in US Patents 5,232,940 and 5,236,938 or any other
25 process coming within the competence of the person skilled in the art who is an expert in chemical synthesis. For the chemical preparation of the products of the invention, the person skilled in the art is regarded as having available, inter alia, all the contents of "Chemical Abstracts" and of the documents which are cited therein. Compositions comprising the compounds of formula (I) can also be prepared
30 according to the teaching of this same prior art or of a similar prior art.

According to another aspect of the present invention, the latter relates to pesticidal compositions intended to be used in the processes defined above. These pesticidal compositions comprise at least one active compound of formula (I) mixed with solid or liquid vehicles and/or surface-active agents, these various constituents
35 being acceptable in agriculture and/or in aviculture and/or in the veterinary field

and/or, preferably, in the field of animal rearing. In particular, the inert and conventional vehicles and the conventional surface-active agents can be used.

The compositions used in the invention can either be compositions, generally diluted, which are ready to be applied to the site infested or capable of
5 being infested by the parasite or can be concentrated compositions (better suited to commercialization or storage), which have to be diluted before application. The dilute composition can be prepared either by diluting with water from a commercial concentrated composition containing the active material (the concentrated mixture being called "ready mix") or by means of the mixture prepared at the time of use
10 (called "tank mix") of compositions separately comprising the various constituents or vehicles.

The compositions used in the invention can also contain any kind of other ingredients such as, for example, protective colloids, adhesives, thickening agents, thixotropic agents, penetrating agents, stabilizing agents, sequestering agents
15 and the like. More generally, these compositions can be combined with all the solid or liquid additives corresponding to the conventional formulating techniques.

Generally, the compositions according to the invention usually contain from 0.00001 to 95 % of active material(s) of formula (I), preferably 0.5 to 90 % for the concentrated compositions.

20 Except when otherwise indicated, the percentages given in the present account are percentages by weight.

In the present account, the term "vehicle" denotes a natural or synthetic, organic or inorganic material with which the active material(s) is combined to facilitate its application to the parts of the plant. This vehicle is thus
25 generally inert and it must be acceptable in agriculture and/or in aviculture and/or in the veterinary field and/or, preferably, in the field of animal rearing. The vehicle can be solid (clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers and the like) or liquid (water, alcohols, especially butanol, and the like).

The surface-active agent can be an emulsifying, dispersing or wetting
30 agent of ionic or nonionic type or a mixture of such surface-active agents. There may be mentioned, for example, salts of polyacrylic acids, salts of lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, substituted phenols (especially alkylphenols or arylphenols), salts of esters of sulphosuccinic acids,
35 taurine derivatives (especially alkyltaurates), phosphoric esters of polyoxyethylenated phenols or alcohols, esters of fatty acids and of polyols, and the

derivatives of the above compounds containing sulphate, sulphonate and phosphate functional groups. The presence of at least one surface-active agent is generally indispensable when the active material(s) and/or the inert vehicle is/are not soluble in water and when the carrier agent for application is water.

5 The surface-active agent content of the compositions according to the invention is advantageously between 2 % and 40 %.

The compositions according to the invention can be in fairly diverse, solid or liquid forms.

10 There may be mentioned, as forms of solid compositions, powders for dusting, wettable powders (or powder to be sprayed with water) and granules, in particular water-dispersible granules.

15 Wettable powders (or powder to be sprayed) generally contain 1 to 90 % of active material(s), as well as, in addition to the solid vehicle, from 1 to 30 % of a wetting agent, from 2 to 20 % of a dispersing agent and, when this is necessary, from 0.1 to 10 % of one or more stabilizing agents and/or other additives, such as penetrating agents, adhesives, or anticlumping agents, dyes, and the like.

20 To obtain powders to be sprayed or wettable powders, the active materials are intimately mixed, in suitable mixers, with the additional substances and the mixture is milled with mills or other suitable grinders. Powders to be sprayed are thereby obtained with advantageous wettability and suspensibility; they can be suspended in water at any desired concentration and these suspensions can be used very advantageously, in particular for application, for example, to litter.

Various compositions of wettable powders (or powders to be sprayed) are given here as examples:

25

WP Example 1:

- active material(s)	50 %
- ethoxylated fatty alcohol (wetting agent)	2.5 %
- ethoxylated phenylethylphenol (dispersing agent)	5 %
- chalk (inert vehicle)	42.5 %

30

WP Example 2:

- active material(s)	10 %
- C13 branched-type synthetic oxo alcohol, ethoxylated with 8 to 10 molecules of ethylene oxide (wetting agent)	0.75 %

35

- neutral calcium lignosulphonate
(dispersing agent) 12 %
- calcium carbonate (inert filler) q.s. for 100 %

WP Example 3:

5 This wettable powder contains the same ingredients as in the above example, in the proportions below:

- active material(s) 75 %
- wetting agent 1.50 %
- dispersing agent 8 %
- 10 - calcium carbonate (inert filler) q.s. for 100 %

WP Example 4:

- active material(s) 90 %
- ethoxylated fatty alcohol (wetting agent) 4 %
- ethoxylated phenylethylphenol (dispersing
15 agent) 6 %

WP Example 5:

- active material(s) 50 %
- mixture of anionic and nonionic surface-
active agents (wetting agent) 2.5 %
- 20 - sodium lignosulphonate (dispersing agent) 5 %
- kaolin clay (inert vehicle) 42.5 %

Aqueous dispersions and emulsions, for example the compositions obtained by diluting a wettable powder according to the invention with water, come within the general scope of the present invention. Emulsions can be of the water-in-oil or oil-in-water type and they can have a thick consistency, like that of a
25 "mayonnaise".

The compositions according to the invention can be formulated in the form of granules, in particular of water-dispersible granules.

30 The granules can be obtained by extrusion, by compacting, by impregnation of a granulated vehicle or by granulation from a powder (the active material content in these granules being between 0.5 and 85 % for the latter cases).

The water-dispersible granules, with a bulk density generally of between approximately 0.2 and 0.8 (preferably 0.3 to 0.6), have a particle size generally of between approximately 0.1 and 3 mm and preferably between 0.3 and
35 1.5 mm.

The active material content of these granules is generally between approximately 1 % and 90 %, and preferably between 25 % and 85 %.

The remainder of the granule is essentially composed of a solid filler and, optionally, of surface-active adjuvants which confer water-dispersibility properties on the granule. These granules can be essentially of two distinct types according to whether the filler used is soluble or insoluble in water. The filler can be inorganic or organic. Excellent results were obtained with urea. Kaolin or bentonite can also be used. The granules advantageously comprise surface-active agents (in a proportion of 2 to 20 % by weight of the granule), of which more than half consists of, for example, at least one dispersing agent, essentially anionic, such as an alkali metal or alkaline-earth metal polynaphthalenesulphonate or an alkali metal or alkaline-earth metal lignosulphonate, the remainder consisting of nonionic or anionic wetting agents such as an alkali metal or alkaline-earth metal alkylnaphthalenesulphonate.

Moreover, although this is not indispensable, it is possible to add other adjuvants such as antifoaming agents.

The granule according to the invention can be prepared by mixing the necessary ingredients and then granulating according to several techniques known per se (granulator, fluid bed, atomizer, extrusion, and the like). The preparation generally finishes with a crushing followed by a sieving to the particle size chosen within the limits mentioned above. It is also possible to use granules obtained as above and then impregnated with a composition containing the active material(s).

It is preferably obtained by extrusion, by carrying out the preparation as indicated in the examples below.

DG Example 1: Dispersible granules

90 % by weight of active material(s) and 10 % of urea in the form of pearls are mixed in a mixer. The mixture is then milled in a pin mill. A powder is obtained which is moistened with approximately 8 % by weight of water. The moist powder is extruded in a perforated-roller extruder. A granule is obtained which is dried, and then crushed and sieved, so as to retain respectively only the granules having a size of between 0.15 and 2 mm.

DG Example 2: Dispersible granules

The following constituents are mixed in a mixer:

35	- active material(s)	75 %
	- wetting agent (sodium alkylnaphthalene-	

- sulphonate) 2 %
 - dispersing agent (sodium polynaphthalene-sulphonate) 8 %
 - water-insoluble inert filler (kaolin) 15 %

5 This mixture is granulated on a fluid bed in the presence of water and then dried, crushed and sieved so as to obtain granules having a size of between 0.15 and 0.80 mm.

DG Example 3: Dispersible granules

10 The following constituents are mixed in a mixer:

- active material(s) 80 %
- wetting agent (dioctyl sodium sulposuccinate) 2 %
- dispersing agent (sodium polycarboxylate) 5 %
- antifoaming agent (silicone oil) 0.3 %
- 15 - alkaline lignosulphonate 2.7 %

This mixture is granulated on a fluid bed in the presence of water and then dried, crushed and sieved so as to obtain granules having a size of between 0.15 and 0.80 mm.

20 These granules can be used alone or in solution or dispersion in water so as to obtain the required dose. They can also be used to prepare combinations with other active materials, the latter being in the form of wettable powders, or of aqueous suspensions or granules.

25 There may be mentioned, as forms of liquid compositions or those intended to constitute liquid compositions at the time of application, solutions, in particular water-soluble concentrates, emulsions, emulsifiable concentrates or suspension concentrates, which can be suspoemulsions (suspensions of a solid in a liquid emulsion).

30 The suspension concentrates, applicable by spraying, are prepared so as to obtain a stable fluid product which does not settle out and they generally contain from 5 to 75 % of active material(s), from 0.5 to 25 % of surface-active agents, from 0.1 to 10 % of thixotropic agents and from 0 to 10 % of suitable additives, such as antifoaming agents, corrosion inhibitors, stabilizing agents, penetrating agents and adhesives and, as vehicle, water and/or an organic liquid in which the active material(s) is/are insoluble or nearly insoluble: certain organic solid
35 materials or inorganic salts can be dissolved in the vehicle to aid in preventing sedimentation or as antigels for water.

These suspension concentrates used in the invention preferentially comprise 10 to 35 % of active material of formula (I), 20 to 40 % of water, 20 to 40 % of vegetable oil and 2 to 20 % of surface-active, wetting or dispersing agents, in particular salts and esters of ethoxylated polystyrylphenols and ethoxylated alkylphenols.

A suspension concentrate composition is given here as an example:

SC Example 1:

	- active material(s)	500 g
	- polyethoxylated tristyrylphenyl	
10	phosphate	50 g
	- polyethoxylated alkylphenol	50 g
	- sodium polycarboxylate	20 g
	- ethylene glycol	50 g
	- organopolysiloxane oil (antifoaming	
15	agent)	1 g
	- polysaccharide	1.5 g
	- water	316.5 g

SC Example 2:

20	- active material(s)	200 g
	- polyethoxylated tristyrylphenyl	
	phosphate	100 g
	- polyethoxylated alkylphenol	79 g
	- sodium polycarboxylate	20 g
25	- organopolysiloxane oil (antifoaming	
	agent)	1 g
	- water	300 g
	- sunflower or soya oil	300 g

30 The invention also relates to the method of application of the compositions described above. For the process for the treatment of floors, litter and liquid manure, it is preferable to use granules, in particular water-dispersible granules. For non-horizontal sites, in particular the parts of buildings other than the floors, it is preferable to spray dilute liquid formulations, which can be obtained

35 from solid or liquid concentrated compositions, preferably by dilution with water.

As regards the application of solid formulations, in particular of granules, to floors, litter or liquid manure, it is possible to use several tens of grams of the composition for treating an animal rearing site with an area of 2000 m^2 , in particular between 0.5 and 5 g per 100 m^2 , depending on the concentration of compound (I) in the granules.

It is preferable to dissolve or disperse the granules in a suitable volume of water in order to treat the places, which can advantageously be done by spraying.

In accordance with this embodiment, it is also possible, after having spread the granules over the floor, to moisten the latter.

In the present application, when speaking of dissolving the granules in water, this must, of course, be understood as the dissolution of the excipient which forms the granules, the compound (I) then becoming dispersed in this water.

According to a second preferred embodiment of the invention, use is made of a suspension obtained by diluting a suspension concentrate or an emulsified concentrate of compound (I) in a given volume of water. The amount of compound of formula (I) applied is generally between 0.05 and 100 mg per m^2 , in particular preferably between 0.5 and 50 mg/m^2 and more preferentially still between 10 and 15 mg/m^2 .

Generally, the volume of composition applied per m^2 can be between 0.1 and 1 litre.

Generally, the application of the compositions according to the invention is preferably carried out in the absence of animals.

The invention is applied not only in the treatment of litter and liquid manure associated with small animals in intensive rearing but also in the rearing of large animals, in particular cattle, and in all cases of grouping together animals, in particular animals for rearing. Mention may be made, for example, of the "feed lot" of North America, which is an open-air grouping together of a large number of cattle (for example 1000 to 20,000) over a period of 1 to several months before slaughter.

Another subject of the invention is a process for combating darkling beetles according to the characteristics described above relating to the process for the treatment of the various sites (floors, litter, liquid manure, places or buildings).

A further subject of the invention is a ready-to-use litter or a litter with litter components which are capable of being obtained by the process according to the invention. In other words, the invention also relates to such products

comprising at least one compound according to the invention, in particular at a dose of 0.01 to 50 mg/kg of ready-to-use litter, preferably of 0.1 to 10 mg/kg.

According to another aspect of the present invention, the latter relates to pesticidal compositions, especially insecticidal compositions, comprising an
5 active compound of formula (I) [preferably the compound (A)] as a mixture with carbaryl, this mixture optionally additionally comprising the various other formulation components as described above for the compositions comprising only the compound of formula (I) as active material.

The compositions comprising two active materials, one of formula (I)
10 and the other being carbaryl, are particularly advantageous due to their broad spectrum with respect to all kinds of pests or parasites, in addition to darkling beetles, in particular spiders, ants, flies, ticks and white grubs (cockchafer grubs), as well as due to their speed of action (shock effect) and their persistence. These compositions with two active materials are particularly effective and inexpensive in
15 their application.

These compositions provide an unexpected synergistic effect which potentiates the activity ranges of both a compound of formula (I) and carbaryl. The compositions achieve a high degree of pest control where the individual active materials are substantially inactive at low concentrations. This feature permits on
20 the one hand a broadening of the activity spectrum against pests and on the other hand an enhancement of safety of application.

These compositions containing two active materials (of formula (I) + carbaryl), when they are concentrated compositions, generally comprise a) 0.000001 % to 10 % of active material of formula (I) preferably 0.00001 % to 10 %, more
25 preferably 0.0001 to 0.001 %, and b) 0.0005 to 95% of carbaryl, preferably 0.5 to 90 %, more preferably 1 to 50 %. The solid formulations generally comprise from 0.5 to 60 % of carbaryl. The liquid formulations generally comprise from 5 to 90 % of carbaryl, preferably 40 to 80 %. For applications in private houses and gardens, the carbaryl content is generally between 1 and 20 %, preferably from 2 to 8 %; for
30 applications by professionals, the content is generally between 10 and 50 %.

The compound of formula (I)/carbaryl ratio by weight is generally between 0.005 and 0.5, preferably between 0.01 and 0.1.

These two-constituent compositions are also particularly useful in treating lawns, gardens, private houses and various buildings.

The description of the invention will now be described in more detail, in its application, using embodiments intended to illustrate the invention in a non-limiting way and to show how it can be implemented

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EXAMPLE 1

A poultry house was treated with water-dispersible granules containing 80 % of compound (A) at the rate of 150 g/ha = 1.5 g/100 m². The treatment took place on the clean litter before the poultry was installed therein. The clean litter was essentially composed of straw.

10

On the day after the treatment, a group of chicks aged 1 to 2 days was installed in the rearing house at the rate of approximately 7 animals per m².

15

The change in the population of darkling beetles (*Alphitobius diaperinus*) in the litter was regularly monitored using 9 homogeneously distributed traps. Measurements were carried out each week from the second week after the treatment until rearing was halted.

20

The total population of darkling beetles in the 9 traps of the treated poultry house varied between 11 and 96 until the 9th week after treatment whereas, in a similar but untreated poultry house, the population of darkling beetles (larvae and adults) oscillated between 1000 and 3000 at each counting point.

25

A mean control (or degree of destruction of the darkling beetles) of 95 to 97 % was thus obtained according to the invention, with a control of 86 % during the 10th week (end of a rearing cycle).

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EXAMPLE 2

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A 5 millilitre liquid mixture comprises the compound (A) and carbaryl, as well as water and acetone. This mixture is poured onto 40 g of wheat flour. The water/acetone ratio by volume is equal to 9/1. The amount of active material is such that there is a concentration of 0.4 ppm = 0.00004 % for the compound (A) and 100 ppm = 0.0001 % for the carbaryl.

40

10 adult *Tenebrio molitor* insects are placed in a flask containing the treated flour. The insects are observed to have a mortality of 100 %.

EXAMPLE 3

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An application was carried out at the surface of poultry dung and of cow dung treated beforehand with fly larvae. At a dose of 25 ppm of compound (A),

Receptacles containing a floor, poultry litter and poultry dung were treated with compound (A). These substrates were infested with larvae of the house fly and of the darkling beetle (*Alphitobius diaperinus*).

Treatments were carried out with doses of 1, 10 and 100 ppm administered on a single occasion using compositions of emulsion type or of granule type. 100 % inhibition of the development of the larval stages (fly or darkling beetle) was observed for doses of 10 and 100 ppm. 99 to 100 % inhibition of the development of the larval stages (fly or darkling beetle) was observed for the dose of 1 ppm.

10

EXAMPLE 5

Ten (10) gram pieces of potato were placed into individual jars. Carbaryl and compound (A) and combinations thereof, as shown below in Tables I and II, were substantially dissolved in a mixture of water: acetone-surfactant solution: DMF in a ratio of 90:9:1. The acetone-surfactant solution comprised acetone, Triton® 152, and Triton® 172 mixed in volumetric ratio of about 785:1:3. Two (2) ml aliquots of solution were added to 10 gm potato pieces and the treated potato pieces were dried overnight to provide concentrations of active materials in parts per million according to Table I and II. Adult *Tenebrio molitor* and a strip of paper towel 1 cm by 3 cm were added to each jar. Mortality was rated at 1 day after treatment.

20

A synergistic effect is obtained whenever the activity of the combination of the compound of formula (I) with carbaryl is greater than the sum of the activities of the individually applied compounds.

25

For example, the expected pesticidal activity We of a given combination of two pesticides can be calculated as follows (q.v. Colby, S.R., "Calculating synergistic and antagonistic response of herbicide combinations". Weeds 15 1967 pp. 20-22): $We = X + [Y \cdot (100 - x)] / 100$ wherein X is the percentage mortality, compared with untreated controls, after treatment with compound (A) at a rate p in parts per million; and Y is the percentage mortality, compared with untreated controls, after treatment by carbaryl at rate q in parts per million; and We is thus the expected mortality after treatment with compound (A) and carbaryl at a rate of application of $p + q$ ppm. If the actually observed value is greater than the expected value We then there is synergism

35

Table I

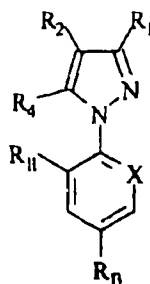
Individual Materials			
Rate Compound(A) (ppm)	% Mortality	Rate Carbaryl (ppm)	% Mortality
2	100	400	93
0.5	87	100	80
0.125	7	25	27
0.03	0	6.25	0

Table II

Combinations		
Rates of Compound (A), Carbaryl (ppm)	Expected % Mortality	Actual % Mortality
0.125, 25	32	87
0.125, 6.25	7	80
0.03, 25	27	53
0.03, 6.25	0	13

CLAIMS

1. Process for the antiparasitic treatment of sites infested or capable of being infested by darkling beetles, in which an effective amount of a composition comprising at least one compound corresponding to the formula (I)



(I)

in which:

R₁ is a halogen atom or a CN or methyl group;

R₂ is S(O)_nR₃ or 4,5-dicyanoimidazol-2-yl or haloalkyl;

10 R₃ is alkyl or haloalkyl;

R₄ represents a hydrogen or halogen atom; or an NR₅R₆, S(O)_mR₇, C(O)R₇ or

C(O)O-R₇, alkyl, haloalkyl or OR₈ radical or an -N=C(R₉)(R₁₀) radical;

R₅ and R₆ independently represent a hydrogen atom or an alkyl, haloalkyl,

C(O)alkyl, alkoxycarbonyl, S(O)_rCF₃ radical; or R₅ and R₆ can together form

15 a divalent alkylene radical which can be interrupted by one or two divalent heteroatoms, such as oxygen or sulphur;

R₇ represents an alkyl or haloalkyl radical;

R₈ represents an alkyl or haloalkyl radical or a hydrogen atom;

R₉ represents an alkyl radical or a hydrogen atom;

20 R₁₀ represents a phenyl or heteroaryl group optionally substituted by one or a number of halogen atoms or groups such as OH, -O-alkyl, -S-alkyl, cyano or alkyl;

R₁₁ and R₁₂ represent, independently of one another, a hydrogen or halogen atom and optionally CN or NO₂ but H or halogen are preferred;

25 R₁₃ represents a halogen atom or a haloalkyl, haloalkoxy, S(O)_qCF₃ or SF₅ group; m, n, q and r represent, independently of one another, an integer equal to 0, 1 or 2;

X represents a trivalent nitrogen atom or a C-R₁₂ radical, the other three valencies of the carbon atom forming part of the aromatic ring;

with the proviso that, when R_1 is methyl, then either R_3 is haloalkyl, R_4 is NH_2 , R_{11} is Cl, R_{13} is CF_3 and X is N; or else R_2 is 4,5-dicyanoimidazol-2-yl, R_4 is Cl, R_{11} is Cl, R_{13} is CF_3 and X is $=\text{C}-\text{Cl}$, is applied to the said site.

2. Process according to Claim 1, in the formula (I) of which R_1 is CN and/or R_3 is haloalkyl and/or R_4 is NH_2 and/or X is CR_{12} and/or R_{11} and R_{12} are, independently of one another, a halogen atom and/or R_{13} is haloalkyl.

3. Process according to either of the preceding claims, in which the compound of formula (I) is 1-[2,6- Cl_2 -4- CF_3 phenyl]-3-CN-4-[SO- CF_3]-5- NH_2 pyrazole, hereinafter known as compound A.

4. Process for the antiparasitic treatment of the surroundings of animals, in which an effective amount of a compound of formula (I) as defined in one of Claims 1 to 3 is applied.

5. Process according to one of the preceding claims, in which the treated sites are the floor or a litter or a liquid manure or a place or a building or a building for commercial rearing.

6. Process according to one of the preceding claims, in which the treated sites are the floor or a litter or a liquid manure or a place or a building or a building for commercial rearing intended to receive poultry.

7. Process according to one of the preceding claims, in which the treated sites are infested or capable of being infested by *Alphitobius diaperinus*.

8. Process according to one of the preceding claims, in which the treated sites are infested or capable of being infested by *Dermestes maculatus*, *Tenebrio molitor* or a darkling beetle from the Tenebrionidae family.

9. Process according to one of the preceding claims, in which the treatment is carried out at a frequency of less than once per month.

10. Process according to one of the preceding claims, in which the treatment is carried out at a frequency not exceeding once per rearing cycle.

11. Process according to one of the preceding claims, in which the treatment is carried out with a composition containing from 0.00001 to 95 % of active material(s) of formula (I), preferably 0.5 to 90 %.

12. Process according to one of the preceding claims, in which the treatment is carried out with a composition having a surface-active agent content of between 2 % and 40 %.

13. Process according to one of the preceding claims, in which the treatment is carried out from a composition in the dispersible granule or suspension or emulsifiable concentrate form.

14. Process according to one of the preceding claims, in which the treatment is carried out from a composition in the form of a dispersible granule with a density of between 0.2 and 0.8, preferably between 0.3 and 0.6, and with a size of between 0.1 and 3 mm, preferably between 0.3 and 1.5 mm.

5 15. Process according to one of the preceding claims, in which the treatment is carried out by application of the active material of formula (I) at the rate of 0.05 to 100 mg per m², preferably between 0.5 and 50 mg/m² and more preferentially still between 10 and 15 mg/m².

10 16. Process according to one of the preceding claims, in which the treatment is carried out in the absence of animals.

17. Process according to one of the preceding claims, in which a floor or litter or liquid manure is treated at the rate of 0.01 to 50 mg of active material of formula (I) per kg of ready-to-use litter, preferably of 0.1 to 10 mg/kg.

15 18. Animal litter comprising an effective amount of antiparasitic active material of formula (I) as defined in one of Claims 1 to 3.

19. Poultry litter comprising an effective amount of antiparasitic active material of formula (I) as defined in one of Claims 1 to 3.

20. Floor, litter or liquid manure comprising an effective amount of antiparasitic active material of formula (I) as defined in one of Claims 1 to 3.

20 21. Floor, litter or liquid manure according to one of Claims 18 to 20, comprising between 0.05 and 100 mg per m², preferably between 0.5 and 50 mg/m² and more preferentially still between 10 and 15 mg/m² of antiparasitic active material of formula (I).

25 22. Litter according to one of Claims 18 to 20, comprising between 0.01 and 50 mg of active material of formula (I) per kg of ready-to-use litter, preferably from 0.1 to 10 mg/kg.

END