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(21) International Application Number: PCT/GB91/00779 (22) International Filing Date: 17 May 1991 (17.05.91) (30) Priority data: 9011187.3 18 May 1990 (18.05.90) GB (71) Applicant (for all designated States except US): CHILTERN FARM CHEMICALS LIMITED [GB/GB]; 11 High Street, Thornborough, Buckingham MK18 2DF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : MISSELBROOK, John [GB/GB]; 12 The Grove, Sholing, Southampton SO2 9LX (GB). DAVIES, Margareta [GB/GB]; Wheelers Bo- thy, Saddleheath Road, Alderholt, Fordingbridge SP6 3EG (GB).		(74) Agent: GALLAFENT & CO.; 8 Staple Inn, London WC1V 7QH (GB). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, PL, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i> <i>With amended claims and statement.</i>
(54) Title: METALDEHYDE-CONTAINING PESTICIDES (57) Abstract <p>The pesticidal effectiveness of metaldehyde, which is difficult to dissolve or disperse, can be improved by mixing it with one or more surface active agents and milling to a fine particle size, preferably less than 30 microns, and subsequent application, optionally with the addition of a suitable film-forming polymer, such as a styrene acrylic latex, to a carrier material such as bran, meal, grain, flour or finely divided silica. Finely milled metaldehyde formulations made this way are highly effective molluscicides.</p>		

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METALDEHYDE-CONTAINING PESTICIDES

This invention relates to metaldehyde-containing pesticides, and to ways of formulating the same to increase their effectiveness.

5

Metaldehyde has been known for decades to be an effective molluscicide particularly useful for combating slugs. It has the advantage that it is relatively non-toxic to mammals and highly specific to molluscs. However,
10 conventional "slug pellets" are often ineffective in practice serving only to disable or kill a relatively small proportion of the slug population, and to do so only after a period of several days.

15 Like many pesticides, its efficacy varies substantially with the conditions of application. Pesticides which rely upon ingestion for their activity need to be formulated so that they are attractive to the pests and, in particular, so that ingestion of a small amount of pesticide,
20 particularly an amount insufficient to kill the pest, does not lead to a reaction inhibiting further ingestion, since otherwise the efficacy of the pesticide is severely decreased. This phenomenon may promote tolerance of the pesticide by a pest or even the emergence of pesticide
25 resistant strains.

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Thus it is well known that slugs tend to take a small quantity of metaldehyde and then to be disinclined to take more. Various possible mechanisms have been proposed to explain this phenomenon, including that the initial
5 ingestion tends to paralyse the mouth parts only of the slugs, thus preventing further immediate ingestion and that, particularly in wet conditions, small quantities of acetaldehyde may be released which disinclines the slugs to eat. Similar considerations apply to snails.

10 It is well known to use in pesticide formulations surface active agents, particularly as spray aids to assist in wetting of vegetation by a liquid composition containing an active agent in suspension or solution. It has also
15 been suggested, for example in British Patent Specification 2098869, that the addition of surface active agents in pesticidal compositions may promote absorption of the pesticide or agent by the pest. In that specification, molluscicide compositions are described
20 consisting of a molluscicide and a surface active agent selected from various sorbitol and sorbitan derivatives.

We have now found that the efficiency of pesticidal compositions based on metaldehyde may be very materially
25 improved by formulating them as a finely particulate mix, the particles of which are intimately associated with surface active agent. In a further development, we have found that such pesticidal compositions of even greater improved effectiveness may be made using surface active
30 agent treated finely particulate pesticidal materials combined with a carrier material on to which the particles are bound by an acceptable water soluble or water dispersible polymeric material.

35 Metaldehyde is difficult to provide in finely particulate form, and, in a further aspect, the present invention

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- provides a method of formulating a pesticidal composition based on metaldehyde which comprises milling the metaldehyde in solid form in the presence of a surface active agent until a desired particle size or particle size range is reached, and subsequently applying the milled material so formed to a solid carrier material. Before, during or after milling a polymeric latex may be added.
- 10 Solid carrier material may be an attractive bait for the pests in question, and, in particular, may be an organic material such as bran, grain, flour or meal or a mixture of two or more of these, e.g. bran and flour. Alternatively, it may be an inorganic material, for example finely divided silica. The mixture may have other ingredients added to it at appropriate stages, e.g. other attractants, preservatives, colourants or repellants (to induce selectivity and dissuade non-pest species from ingesting the material). The final pesticide may be used in solid form, e.g. made into granules or pellets, applied to the locus of the pests by scattering, or in a sprayable form, i.e. a suspension of carrier particles in a suitable liquid. For slug and snail control, pellets are preferred, preferably applied at a rate sufficient to provide a good chance that a slug will find a pellet, and with each pellet being of a size and having an active ingredient concentration such that on consuming the pellet, or on taking successive feeds from several pellets, the slug receives a lethal dose of metaldehyde.
- 30 Metaldehyde is generally manufactured in granule form but at a relatively coarse particle size. For example, technical grade metaldehyde tends to have a particle size range around 500 microns or greater, with relatively little material either coarser or very much finer. We have found that by milling together metaldehyde and

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surface active agent, it is possible to reduce the particle size of the metaldehyde, e.g. to a particle size within the range of 5 to 30 microns, to provide a stable very finely particulate metaldehyde which may then be
5 mixed with a polymer latex and applied to a carrier such as those noted above.

Care needs to be taken in selection of surface active agent for use when milling the metaldehyde. We have found
10 that good results may be obtained by the use of cationic surface active agents, particularly ethoxylated amine types.

It is often also preferable first to mill the metaldehyde
15 to a desired small particle size in the presence of a cationic surface active agent and a stabilising amount of a further surface active agent of a non-ionic type. Such stabilisation is often particularly necessary if the polymeric dispersion, preferably a styrene acrylic
20 copolymer dispersion or emulsion, is to be used as binder to cohere the individual particles on to the carrier material.

The proportions of the various ingredients which go to
25 make up the final formulated pesticidal composition may be varied widely and need to be chosen with care to promote effectiveness. In particular, the proportion of polymeric latex material needs to be sufficient to enable the dispersed metaldehyde to be combined with the carrier and,
30 in many cases, to provide a suitably protective effect, e.g. against weathering, but which should not be present in so great an amount that it masks the action of the metaldehyde in use.

35 In particular the amount of polymeric latex should not be so great that, following ingestion, the particles of

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metaldehyde are over-protected and can pass through the target pest effectively without influencing it, i.e. without the metaldehyde exerting its pesticidal activity.

5 We have found that satisfactory pesticidal compositions may be obtained by dispersing 0.5 to 10 parts by weight of metaldehyde and 5 to 50 parts by weight of water and 0.5 to 5 parts by weight of a cationic surface active agent, milling the mixture to reduce the particle size of the
10 metaldehyde to 30 microns or below, and mixing the mixture with 1 to 20 parts by weight of polymer latex emulsion to provide a metaldehyde suspension which may be sprayed on to suitable carrier material and dried to form a final pesticide composition. The amount of coated composition
15 relative to the carrier may be 1.5 to 10 percent by weight. The amount of the active ingredient, metaldehyde, in the final composition is preferably 1 to 6 percent by weight.

20 Using the method of the present invention it is possible to produce molluscicidal compositions, particularly in the form of slug pellets, which are both effective and efficient in use and give enhanced control of slug or snail infestations.

25

In particular, by using the milling to reduce the particle size of the metaldehyde, and by surrounding it with polymeric latex the palatability of the metaldehyde may be improved. In particular, the finely divided metaldehyde
30 can be ingested easily by a slug and an adequate dose of metaldehyde ingested to ensure that the slug dies. The improvement in availability means that less metaldehyde needs to be used per unit area of ground, however large numbers of slug pellets may be used per unit area of
35 ground, materially improving the chances of a slug finding one of them. Obviously the greater the chance that a slug

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will find a pellet, the greater the efficacy of the pelleted pesticidal formulation.

5 It has become clear that by using the formulation techniques according to the present invention, metaldehyde formulations may be produced which are much more satisfactorily targetted to the slug population, and which accordingly leave considerably less residual metaldehyde in the environment, thus reducing environmental stress.

10

The following Examples will serve to illustrate the invention:

Example 1

15

A mixture was made up of:

water	295.8 grams
metaldehyde technical	94.7 grams
antifoaming agent	9.0 grams
20 (Rhodorsil 426R ex Rhone-Poulenc)	
Cationic ethoxylated amine surface	
active agent (Catafor 09 ex ABM Chemicals)	11.3 grams
partially hydrolysed polyvinyl acetate	
(Airvol 203 ex Air Products)	11.3 grams
25 wetting agent (Hyonic PE90 ex Henkel-Nopco)	4.5 grams
antimicrobial agent (Proxel GXL ex ICI)	4.5 grams
Styrene/acrylic latex, 50% polymer	
(Vinacryl 18246 ex Vinamul)	19.0 grams

30 All the components were placed in a ball mill and milled for 21 hours at room temperature to give a suspension in which the particle size of all particles was below 30 microns.

35 Deionised water was then sprayed on to bran, following which 1 part by weight suspension was then sprayed on to 3

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parts by weight dampened bran and the mixture extruded to form pellets.

5 The pellets were allowed to air dry and were then applied at a rate of 100 pellets per square metre to test areas containing known numbers of slugs. It was found that after 24 hours, 90 percent of the slugs were clearly affected and by 96 hours after application all were dead.

10 Example 2

The process was repeated, adding half the milled suspension/latex to bran, to give an active ingredient level of 3%, and tested in the same way as in Example 1.
15 The formulation was still found to be more effective than commercial samples.

Example 3

20 The following ingredients were mixed together to form an extendable paste:

Parts by weight

25	Aqueous metaldehyde suspension	
	(as in Exampe 1)	14.3
	wheatmeal	82.0
	chalk	10.0
	benzoic acid	2.0
30	calcium stearate	3.0
	blue dye	0.2

This paste was extruded to from pellets approximately 2 mm diameter and an average 4 mm long. These proved highly
35 effective at an application rate of 10 Kg/ha at controlling grey field slugs.

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CLAIMS

1. A pesticidal composition comprising a mixture of finely divided particles of solid metaldehyde formulated
5 with a carrier material and wherein the particles of the metaldehyde are intimately associated with surface active agent.
2. A pesticidal composition according to Claim 1,
10 wherein the finely divided metaldehyde is bound by an acceptable water soluble or water dispersible polymeric material on to the carrier material.
3. A pesticidal composition according to Claim 1 or 2,
15 wherein the particle size of the metaldehyde is substantially within the range of 5 to 30 microns.
4. A pesticidal composition according to any one of claim 1 to 3 wherein the carrier is bran, flour or a
20 mixture of these.
5. A pesticidal composition according to any one of claims 1 to 4 in pellet form wherein the average pellet weight is in the range of 10-30 milligrams.
25
6. A pesticidal composition according to any one of claims 1 to 5 wherein the proportion of metaldehyde contained therein is in the range of 1- 6 percent by weight.
30
7. A method of formulating a pesticidal composition based on metaldehyde which comprises milling the metaldehyde in solid form in the presence of a surface active agent until a desired particle size or particle
35 size range is reached and subsequently applying the milled material so formed to a solid carrier material.

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8. A method according to Claim 7, wherein prior to or subsequent to milling, a polymeric latex is added.

9. A pesticidal composition made according to the method
5 of claim 7 or 8.

10. A method of combating pests which comprises applying
to the locus of the pests an effective amount of a
pesticidal composition according to any one of claims 1 to
10 6.

11. A method according to claim 10 wherein the pests are
slugs.

AMENDED CLAIMS

[received by the International Bureau on 17 October 1991 (17.10.91);
original claim 1 amended, original claim 3 cancelled;
claim 2 unchanged;
claims 4-11 amended and renumbered as claims 3-10 (2 pages)]

1. A pesticidal composition comprising a mixture of finely divided particles of solid metaldehyde formulated with a carrier material and wherein the particles of the metaldehyde are intimately associated with surface active agent, and of particle size substantially within the range of 5 to 30 microns.
2. A pesticidal composition according to Claim 1, wherein the finely divided metaldehyde is bound by an acceptable water soluble or water dispersible polymeric material on to the carrier material.
3. A pesticidal composition according to Claim 1 or 2 wherein the carrier is bran, flour or a mixture of these.
4. A pesticidal composition according to any one of Claims 1 to 3 in pellet form wherein the average pellet weight is in the range of 10-30 milligrams.
5. A pesticidal composition according to any one of Claims 1 to 4 wherein the proportion of metaldehyde contained therein is in the range of 1-6 percent by weight.
6. A method of formulating a pesticidal composition based on metaldehyde which comprises milling the metaldehyde in solid form in the presence of a surface active agent until a desired particle size or particle size range is reached and subsequently applying the milled material so formed to a solid carrier material.
7. A method according to Claim 6, wherein prior to or subsequent to milling, a polymeric latex is added.

8. A pesticidal composition made according to the method of Claim 6 or 7.

5 9. A method of combating pests which comprises applying to the locus of the pests an effective amount of a pesticidal composition according to any one of Claims 1 to 5.

10 10. A method according to Claim 10 wherein the pests are slugs.

STATEMENT UNDER ARTICLE 19

The subject matter of original claim 3 has been incorporated into the main claim the better to differentiate the invention from the prior art. The change has no impact on the description.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/00779

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : A 01 N 35/02																	
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="width: 75%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">IPC⁵</td> <td style="border: 1px solid black; padding: 5px;">A 01 N</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁵	A 01 N											
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="width: 60%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">GB, A, 2098869 (UNIVERSITY COLLEGE CARDIFF CONSULTANTS) 1 December 1989 see claims; examples cited in the application --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1-6,10,11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">Central Patents Index, Basic Abstracts Journal, Section C, Week 8351, 22 February 1984, Derwent Publications Ltd., (London, GB), see abstract no. 83-84878351 & SU, A, 242592 (UFA PLANT PROTECT) 8 September 1969 --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1,10,11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border: 1px solid black; padding: 5px;">GB, A, 894431 (BROOK CHEMICALS) 18 April 1962 see claims --</td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">1,10,11</td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;">DE, A, 3612161 (BAYER AG) 15 October 1987 -----</td> <td style="border: 1px solid black;"></td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	GB, A, 2098869 (UNIVERSITY COLLEGE CARDIFF CONSULTANTS) 1 December 1989 see claims; examples cited in the application --	1-6,10,11	X	Central Patents Index, Basic Abstracts Journal, Section C, Week 8351, 22 February 1984, Derwent Publications Ltd., (London, GB), see abstract no. 83-84878351 & SU, A, 242592 (UFA PLANT PROTECT) 8 September 1969 --	1,10,11	X	GB, A, 894431 (BROOK CHEMICALS) 18 April 1962 see claims --	1,10,11	A	DE, A, 3612161 (BAYER AG) 15 October 1987 -----	
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center;">19th July 1991</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center;">02.09.91</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> Danielle van der Haas </div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center;">19th July 1991</div>	Date of Mailing of this International Search Report <div style="text-align: center;">02.09.91</div>	International Searching Authority <div style="text-align: center;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center;"> Danielle van der Haas </div>											
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9100779
SA 47470

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/08/91
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2098869	01-12-82	BE-A- 893266 FR-A, B 2506124	22-11-82 26-11-82
GB-A- 894431		None	
DE-A- 3612161	15-10-87	AU-B- 597639 AU-A- 7146787 EP-A- 0248991	07-06-90 15-10-87 16-12-87