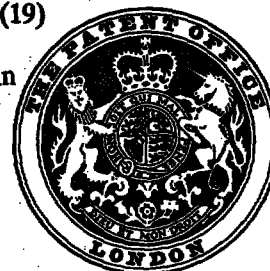


PATENT SPECIFICATION

(11) 1 587 573

- 1 587 573 (21) Application No. 34793/77 (22) Filed 18 Aug. 1977 (19)
 (31) Convention Application No's 10558/76 (32) Filed 19 Aug. 1976
 2718/77 4 Mar. 1977 in
 (33) Switzerland (CH)
 (44) Complete Specification Published 8 Apr. 1981
 (51) INT. CL.³ C07D 251/44
 A01N 43/68



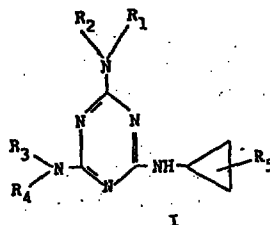
(52) Index at Acceptance

C2C	1173	1341	1410	1562	1652	200	202
	215	225	22Y	246	250	251	252
	255	25Y	28X	29X	29Y	30Y	321
	322	323	32Y	345	364	36Y	456
	45Y	624	630	640	652	660	670
	680	774	775	805	80Y	AA	LH
	LY	NE	ASE	241	248	260	261
	262	265	266	270	273	275	279
	503	510	A				

(54) "2-CYCLOPROPYLAMINO-4,6-DIAMINO-S-TRIAZINE DERIVATIVES AND THEIR USE AS INSECTICIDES"

(71) We, CIBA-GEIGY AG., a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 The present invention relates to 2-cyclopropylamino-4,6-diamino-s-triazine derivatives and salts thereof, to a process for their manufacture and to the use of 2-cyclopropylamino-4,6-diamino-s-triazine derivatives as insecticides. The present invention provides a method of preventing the development of adult insects from larvae or pupae, which comprises applying to the larvae or pupae, a 2-cyclopropylamino-4,6-diamino-s-triazine derivative of the general formula



wherein

- 25 R_1 represents hydrogen, C_{1-4} -alkyl which is unsubstituted or substituted by C_{1-4} -alkoxy or cyano, or represents C_3 - or C_4 -alkenyl, C_3 - or C_4 -alkynyl, cyclopropyl, hydroxyl, methoxy or ethoxy;
 R_2 represents hydrogen, methyl or ethyl or
 R_1 and R_2 together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole heteroatom or which contains a further nitrogen atom or an oxygen atom,
 30 R_3 represents hydrogen, C_{1-4} -alkyl, C_3 -alkenyl, C_3 -alkynyl or cyclopropyl,
 R_4 represents hydrogen, methyl or ethyl, or
 R_3 and R_4 together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole hetero-atom or which contains a further nitrogen atom or an oxygen atom, and
 35 R_5 represents hydrogen or methyl, or an acid addition salt thereof.
 Possible alkyl groups R_1 and R_2 can be straight-chain or branched, unsubstituted or substituted by cyano groups or alkoxy groups of 1 to 4 carbon atoms. Examples of such alkyl groups include: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec- and tert-butyl, 2-methoxyethyl, 1-cyanoethyl, 1-cyanopropyl and 2-cyano-prop-2-yl. Examples of possible alkenyl and alkynyl groups R_1 and R_3 include allyl and propargyl respectively.

The term "acid addition salts" of the 2-cyclopropylamino-4,6-diamino-s-triazine derivatives of the formula I is to be understood as meaning salts with strong mineral acids, for example salts with hydrochloric acid or sulphuric acid.

Preferred compounds on account of their action are those compounds of the formula I in which R_1 represents hydrogen, C_1-C_4 -alkyl which is unsubstituted or substituted by C_1-C_4 alkoxy, or represents C_3 or C_4 -alkenyl, C_3 or C_4 -alkynyl, cyclopropyl, hydroxyl, methoxy or ethoxy; R_2 represents hydrogen, methyl or ethyl, or R_1 and R_2 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, 1-piperazinyl, 1-(4-methyl)-piperazinyl or 1-imidazolyl; R_3 represents hydrogen, C_1-C_4 alkyl, C_3 -alkenyl, C_3 -alkynyl or cyclopropyl; R_4 represents hydrogen, methyl or ethyl, or R_3 and R_4 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, 1-piperazinyl, 1-(4-methyl)-piperazinyl or 1-imidazolyl; and R_5 represents hydrogen or methyl, and the acid addition salts thereof.

Compounds to be singled out for special mention are those in which R_1 represents hydrogen, methyl, ethyl, n-propyl, isopropyl, cyclopropyl, hydroxyl or methoxy; R_2 represents hydrogen, methyl or ethyl, or R_1 and R_2 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl or 1-imidazolyl; R_3 represents hydrogen, methyl, ethyl, n-propyl, isopropyl or cyclopropyl; R_4 represents hydrogen, methyl or ethyl; and R_5 represents hydrogen, and the acid addition salts thereof.

Particularly preferred compounds are those in which R_1 represents hydrogen, ethyl or cyclopropyl; R_2 represents hydrogen; R_3 represents hydrogen or methyl; R_4 represents hydrogen, methyl or ethyl; and R_5 represents hydrogen, whilst at least one of the symbols R_1 , R_3 and R_4 represents hydrogen, and the hydrochlorides thereof, in particular 2-cyclopropylamino-4-amino-6-ethylamino-s-triazine dihydrochloride, 2,4-bis-(cyclopropylamino)-6-amino-s-triazine, 2-cyclopropyl-amino-4-amino-6-methylamino-s-triazine dihydrochloride, 2-cyclopropylamino-4,6-diamino-s-triazine, 2-cyclopropylamino-4-amino-6-dimethylamino-s-triazine, 2-cyclopropylamino-4,6-bis-(ethylamino)-s-triazine dihydrochloride and 2-cyclopropylamino-4-amino-6-(N-methyl-N-ethylamino)-s-triazine.

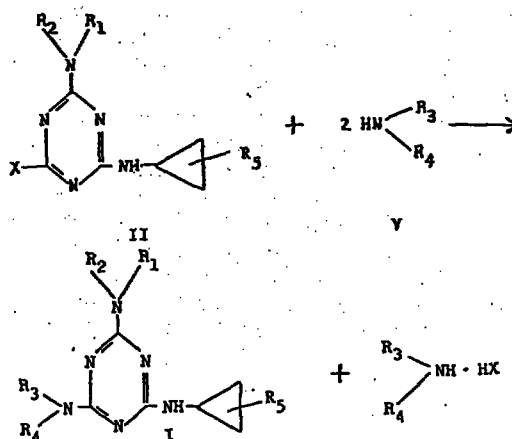
The invention also includes as compounds *per se*, compounds of formula (I) *except* those in which R_1 is butyl, hydroxyl, methoxy or ethoxy, or in which R_3 is butyl and *with the provisos that*:

- (1) R_1 does not represent cyclopropyl when simultaneously
 - (a) R_2 and R_3 represent hydrogen and R_4 represents methyl or ethyl or
 - (b) R_2 and R_4 represent hydrogen and R_3 represents methyl, ethyl, n-propyl or cyclopropyl
- (2) R_3 does not represent cyclopropyl when simultaneously
 - (a) R_1 and R_4 represent hydrogen and R_2 represents methyl or ethyl or
 - (b) R_2 and R_4 represent hydrogen and R_1 represents methyl ethyl, n-propyl or cyclopropyl.

The invention includes also insecticidal compositions comprising such a compound and a carrier.

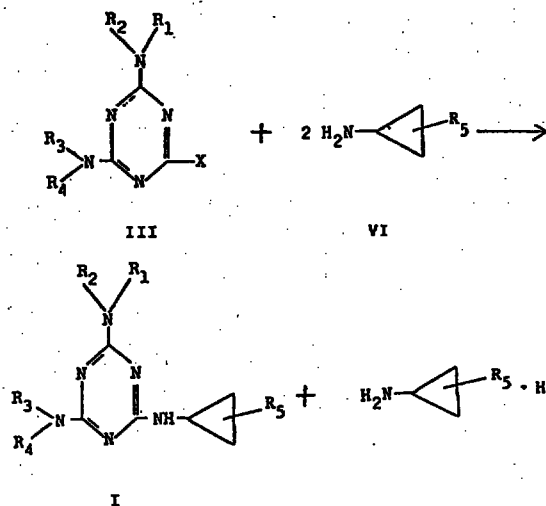
The compounds of the formula I can be obtained by methods which are known *per se*, for example by

- a) reacting a 2-cyclopropylamino-4-amino-6-halogeno-s-triazine of the formula II, in which R_1 , R_2 and R_5 are as defined in formula I and X represents halogen, preferably chlorine, with ammonia or a primary or secondary amine of the formula V, in which R_3 and R_4 are as defined in formula I:



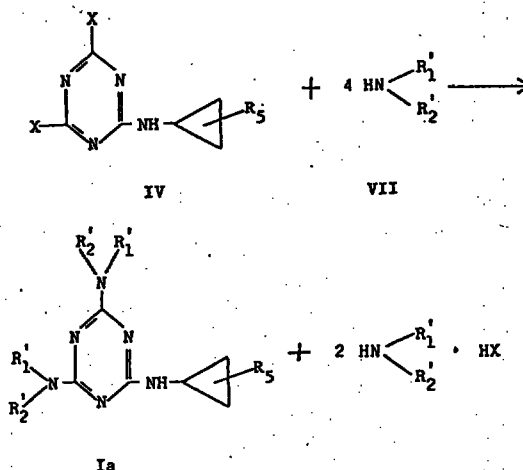
or

b) reacting a 2,4-diamino-6-halogeno-s-triazine of the formula III, in which R_1 , R_2 , R_3 and R_4 are as defined in formula I and X represents halogen, preferably chlorine, with a compound of the formula VI, in which R_5 is as defined in formula I:



or

c) if in the compounds of the formula I R_1 has the same meaning as R_3 and R_2 has the same meaning as R_4 , reacting a 2-cyclopropylamino-4,6-dihalogeno-s-triazine of the formula IV, in which R_5 is as defined in formula I and X represents halogen, preferably chlorine, with ammonia or a primary or secondary amine of the formula VII, in which R'_1 has the meaning of $R_1 = R_3$, as defined in formula I, and R'_2 has the meaning of $R_2 = R_4$, as defined in formula I:



The substitution of the halogen atoms with ammonia or a primary and/or secondary amine of the formulae V, VI and VII can be effected by dissolving the starting material of the formulae II, III and IV in an inert solvent, for example acetone, acetone/water mixtures, methyl ethyl ketone, dioxane or dioxane/water mixtures, and reacting the mixture at normal or, if appropriate, elevated pressure and at a temperature between 20° and 150°C, preferably between 50° and 140°C, with ammonia or a primary and/or secondary amine.

Most of the starting materials of the formulae II, III and IV are known or they can be obtained in accordance with known methods.

Diamino- and triamino-s-triazines are described as chemosterilants for adult houseflies (*Musca domestica*) in US patent specification 3,189,521. The chemosterilising action on insects of 2,4,6-triamino-s-triazine derivatives (melamine derivatives) is also described by S. Nagasawa et al., Botyu-Kagaku 39 (4), 105 (1974). A.B. Borkovec and A.B. DeMilo [J. Med. Chem. 10 (5), 457 (1967)] and G.C. LaBrecque, R.L. Fye, A.B. DeMilo and A.B.

Borkovec [J. Econ. Entomol. 61, (6), 1621 (1968)] also describe the chemosterilising action of, among other compounds, 2-cyclohexylamino-4,6-diamino-s-triazine, 2-cyclohexylamino-4,6-dihexylamino-s-triazine and 2,4,6-tris-cyclohexylamino-s-triazine, and the salts thereof, on adult houseflies (*Musca domestica*).

Surprisingly, it has now been found that the compounds of the formula I possess a marked larvicidal action on insect larvae, preferably on *Diptera* larvae. In contrast to the above mentioned insecticidal chemosterilants, the compounds of the formula I act on the developmental stages of the insects. The action consists in killing the freshly hatched larvae or preventing adults from hatching from the pupae. The mode of action of the compounds of the formula I is not to be compared with that of classical insecticides, chemosterilants or juvenile hormone analogues.

The compounds of the formula I can be used in particular for controlling hygiene pests and animal ectoparasites of the order *Diptera* especially of the families: *Culicidae*, *Simuliidae*, *Tipulidae*, *Muscidae* and *Calliphoridae*.

The compounds of the formula I without any additive or together with suitable carrier(s) and/or additive(s). Suitable carriers and additives can be solid or liquid and can be any conventionally used in the art of formulation of a larvicidal insecticide, for example natural or regenerated substances, solvents and/or dispersants.

The compositions according to the invention can be manufactured in known manner by homogeneously mixing and/or grinding an active substance (compound of the formula I) with a suitable carrier, which can include a dispersants or solvent and which is inert to the active substance.

The active substances may be processed to the following formulations:

Solid formulations:

Dusts, tracking agents and granules (coated granules, impregnated granules and homogeneous granules), premix (feed additive).

Liquid formulations:

a) active substance concentrates which are dispersible in water: wettable powders, pastes and emulsions;

b) solutions: sprays (aerosols).

To manufacture a solid formulation (dusts, tracking agents), the active substance is mixed with a solid carrier. Suitable carriers are, for example: kaolin, talc, bolus, loess, chalk, limestone, ground limestone, attaclay, dolomite, diatomaceous earth, precipitated silica, alkaline earth silicates, sodium and potassium aluminium silicates (feldspar and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic materials, fertilisers, for example ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, ground vegetable products, such as corn meal, bark dust, sawdust, nutshell meal, cellulose powder, residues of plant extractions, activated charcoal etc. These carriers can either be used alone or in admixture with one another.

Granules can be very easily manufactured by dissolving an active substance of the formula I in an organic solvent and applying the solution thereby obtained to a granulated mineral, for example attapulgit, SiO_2 , granicalcium, bentonite etc. and then evaporating the solvent.

Polymer granules can also be manufactured by mixing an active substance of the formula I with polymerisable compounds (urea/formaldehyde; dicyandiamide formaldehyde; melamine/formaldehyde or others), whereupon a mild polymerisation is carried out that does not affect the active substances and in the process of which the granulation is carried out during the gel formation. It is more advantageous to impregnate finished, porous polymer granules (urea/formaldehyde, polyacrylonitrile, polyester or others) which have a specific surface area and a favourable predetermined adsorption/desorption ratio, with the active substances, for example in the form of their solutions (in a low boiling solvent) and to remove the solvent. Polymer granules of this kind in the form of microgranules having preferably a bulk density of 300 g/litre to 600 g/litre can also be manufactured with the aid of atomisers.

It is also possible to obtain granules by compacting the carrier with the active substance and additive(s) and subsequently comminuting the product.

To these mixtures can also be added additives which stabilize the active substance and/or nonionics, anionics and cationics, which, for example, ensure a better wettability (wetting agents) and dispersibility (dispersants). Examples of suitable substances are: olein/chalk mixture, cellulose derivatives (methyl cellulose, carboxymethyl cellulose), hydroxyethyl glycol ethers of monoalkyl and dialkyl phenols having 5 to 15 ethylene oxide radicals per molecule and 8 or 9 carbon atoms in the alkyl moiety, ligninsulphonic acid, the alkali metal and alkaline earth metal salts thereof, polyethylene glycol ethers, fatty alcohol polyethylene glycol ethers having 5 to 20 ethylene oxide radicals per molecule and 8 to 18 carbon atoms in the fatty alcohol moiety, condensation products of ethylene oxide, propylene oxide,

polyvinylpyrrolidone, polyvinyl alcohol, condensation products of urea and formaldehyde and also latex products.

Water-dispersible concentrates, i.e. wettable powders, pastes and emulsifiable concentrates, are compositions which can be diluted with water to the desired concentration. They consist of active substance, carrier, optionally additive(s) which stabilize the active substance, surface-active substance(s) and anti-foam(s) and, if appropriate, solvent(s).

Wettable powders and pastes are obtained by mixing and grinding the active substance with dispersant(s) and pulverulent carrier(s) in suitable devices until homogeneity is attained. Suitable carriers are, for example, those already mentioned for the solid forms of application. In some cases it is advantageous to use mixtures of different carriers. Examples of dispersants are: condensation products of sulphonated naphthalene and sulphonated naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalene sulphonic acids with phenol and formaldehyde, as well as alkali metal, ammonium and alkaline earth metal salts of ligninsulphonic acid, in addition alkylarylsulphonates, alkali metal and alkaline earth metal salts of dibutynaphthalenesulphonic acid, fatty alcohol sulphates such as salts of sulphated hexadecanols, heptadecanols, octadecanols, and salts of sulphated fatty alcohol glycol ethers, the sodium salt of oleyl methyl tauride, ditertiary ethylene glycols, dialkyl-dilaurylammonium chloride and fatty acid alkali metal and alkaline earth metal salts.

Suitable anti-foams are for example silicone oils.

The active substances is so mixed, ground, sieved and strained with the additive(s) mentioned above that, in wettable powders, the solid particle size of 0.02 to 0.04 mm and in pastes, of 0.03 mm, is not exceeded. Emulsifiable concentrates and pastes are manufactured by using dispersants, such as those referred to above, organic solvents, and water. Examples of suitable solvents are: alcohols, dimethyl sulphoxide, and mineral oil fractions which boil between 120 and 350°C. The solvents must be virtually odourless and inert to the active substances.

Furthermore, the compositions of compounds of formula I can take the form of solutions. For this purpose the compound or compounds of the general formula I are dissolved in a suitable organic solvent or mixture of solvents. Aliphatic and aromatic hydrocarbons, chlorinated derivatives thereof, alkylnaphthalenes and mineral oils, singly or in admixture, can be used as organic solvents.

Formulations of the compounds of the formula I are described hereinafter. The parts denote parts by weight.

Dusts:

The following substances are used to manufacture a) a 0.5% and b) a 2% dust:

a) 0.5 part of active substance

99.5 parts of talc

b) 2 parts of active substance

1 part of highly disperse silica

97 parts of talc.

The active substance is mixed with the carrier and ground.

Tracking Agents:

5 parts of active substance are mixed with

95 parts of carbonate of lime and ground to an average particle size of 80µ.

Granules:

5 parts of active substance are dissolved in a solvent, e.g. methylene chloride, and mixed with

2 parts of polyethylene glycol ("Carbowax" Registered Trade Mark)

91.5 parts of calcium carbonate are impregnated with the mixture and

1.5 parts of precipitated silica are admixed.

The solvent is subsequently evaporated.

Wettable Powder:

50 parts of active substance are mixed with

5 parts of a dispersing agent, e.g. sodium ligninsulphonate,

5 parts of a wetting agent, e.g. dibutynaphthalenesulphonic acid

10 parts of silica and

30 parts of China clay

and the mixture is finely ground.

Emulsifiable Concentrate:

20 parts of active substance are mixed with
20 parts of emulsifier, e.g. a mixture of alkylaryl polyglycol ether with alkylarylsulphonates, and
60 parts of solvent
until the solution is completely homogeneous.

By diluting this concentrate with water it is possible to obtain an emulsion of the desired concentrate.

Premix (feed additive):

0.25 part of active substance and
4.75 parts of secondary calcium phosphate, or China clay, "Aerosil" (Registered Trade Mark) or carbonate of lime are homogeneously mixed with
95 parts of an animal feed, e.g. poultry food.

Spray:

The following constituents are used to manufacture a 2% spray:

2 parts of active substance
98 parts of kerosene.

Other biocidal active substances or agents can be admixed with the compositions described hereinabove. Thus in addition to the cited compounds of the general formula I, the compositions of the present invention can obtain, for example, insecticides to broaden the activity spectrum.

The compositions, or the compounds of the formula (I) contained therein, exert their inhibitory action therefore chiefly on the development of larvae or pupae of insects, preferably of the order Diptera.

EXAMPLE 1**2-Cyclopropylamino-4-amino-6-ethylamino-s-triazine**

A mixture of 13.7 g of 2-cyclopropylamino-4-chloro-6-ethyl-amino-s-triazine, 17.4 g of 25% conc. aqueous ammonia and 30 ml of dioxane is heated for 2 hours in an autoclave to 130°C. After cooling, the reaction mixture is poured into water, whereupon the crude product precipitates. After drying, the product is recrystallized from ether/hexane. Melting point: 141-145°C.

EXAMPLE 2**2,4-Bis-cyclopropylamino-6-isopropylamino-s-triazine**

A mixture of 30 g of 2-cyclopropylamino-4-chloro-6-isopropylamino-s-triazine, 15.1 g of cyclopropylamine and 50 ml of dioxane is heated for 10 hours in an autoclave to 130°C. After cooling, the reaction mixture is concentrated to half its volume in vacuo and then poured into 300 ml of water and extracted with ethyl acetate. The extract is dried over sodium sulphate and the ethyl acetate and dioxane are removed in vacuo. The crude product is recrystallised from dioxane/petroleum ether. Melting point: 88°-93°C.

EXAMPLE 3**a) 2-Cyclopropylamino-4-amino-6-morpholino-s-triazine**

9.3 g of 2-cyclopropylamino-4-chloro-6-amino-s-triazine are suspended in a mixture of 45 ml of dioxane and 9 ml of ether. Then 8.7 g of morpholine are added dropwise at room temperature. The reaction is exothermic and the reaction mixture becomes fluid. The reaction mixture is allowed to continue to react for 16 hours at room temperature and the dioxane and ether are then removed in vacuo. The residue is diluted with water and filtered. After drying, the residual crude product is recrystallised from methanol. Melting point: 186°C.

b) 5 g of 2-cyclopropylamino-4-amino-6-morpholino-s-triazine are dissolved in 700 ml of abs. ether and then gaseous hydrogen chloride is introduced at 10°C until the solution is saturated. The precipitated crystals are filtered off and washed with a small amount of methanol. The resultant hydrochloride of 2-cyclopropylamino-4-amino-6-morpholino-s-triazine melts at 250°C.

EXAMPLE 4**2-Cyclopropylamino-4,6-bis-dimethylamino-s-triazine**

123 g of 2-cyclopropylamino-4,6-dichloro-s-triazine are dissolved in 300 ml of dioxane. Then 397 g of 40.8 % aqueous dimethylamine are added dropwise with gentle cooling in such a manner that the internal temperature does not exceed 55°C. The reaction is allowed

to continue for 4 hours at room temperature. The reaction mixture is then taken up in ether and the aqueous phase is separated. The ether and dioxane are removed in vacuo after washing with water and drying over sodium sulphate. The crude product is recrystallised from isopropanol. Melting point: 82-83°C.

The following active compounds of the formula I are also prepared by proceeding as described in Examples 1 to 4:

	No.	Compound	mp. in °C	
10	1	2-cyclopropylamino-4-amino-6-methylamino-s-triazine	159-162	10
	2	2-cyclopropylamino-4,6-bis-(isopropylamino)-s-triazine	119-121	
15	3	2,4,6-tris-(cyclopropylamino)-s-triazine	75-76	15
	4	2-cyclopropylamino-4-amino-6-pyrrolidino-s-triazine	186	
20	5	2-cyclopropylamino-4-ethylamino-6-morpholino-s-triazine	90-91	20
	6	2-cyclopropylamino-4-ethylamino-6-pyrrolidino-s-triazine	169-170	
25	7	2-cyclopropylamino-4-amino-6-morpholino-s-triazine	186	25
	8	2-cyclopropylamino-4-ethylamino-6-morpholino-s-triazine	90-91	
30	9	2-cyclopropylamino-4-amino-6-morpholino-s-triazine hydrochloride	250	30
	10	2-cyclopropylamino-4-amino-6-imidazolo-s-triazine	244-245	
35	11	2-cyclopropylamino-4-amino-6-pyrrolidino-s-triazine dihydrochloride	196-197	35
	12	2-cyclopropylamino-4-amino-6-ethylamino-s-triazine dihydrochloride	199-200	
40	13	2-cyclopropylamino-4-ethylamino-6-pyrrolidino-s-triazine hydrochloride	226-227	40
	14	2-cyclopropylamino-4-ethylamino-6-morpholino-s-triazine hydrochloride	230-231	
45	15	2-cyclopropylamino-4-amino-6-isopropylamino-s-triazine dihydrochloride	172-173	45
	16	2-cyclopropylamino-4-amino-6-allylamino-s-triazine dihydrochloride	183-185	
50	17	2-cyclopropylamino-4-amino-6-propargylamino-s-triazine	225-226	50
	18	2,4-bis-(cyclopropylamino)-6-amino-s-triazine	137-140	
55	19	2,4-bis-(cyclopropylamino)-6-dimethylamino-s-triazine	136-137	55
60				60

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	20	2-cyclopropylamino-4-amino-6-methylamino-s-triazine dihydrochloride	197-199	
5	21	2-cyclopropylamino-4,6-diamino-s-triazine	219-222	5
	22	2-cyclopropylamino-4-amino-6-(2-methoxyethylamino)-s-triazine	154-156	
10	23	2-cyclopropylamino-4-amino-6-dimethylamino-s-triazine	182-184	10
	24	2-cyclopropylamino-4,6-bis-(ethylamino)-s-triazine	(viscous)	
15	25	2-cyclopropylamino-4-methylamino-6-n-propylamino-s-triazine	(viscous)	15
	26	2-cyclopropylamino-4-ethylamino-6-n-propylamino-s-triazine	(viscous)	
20	27	2,4-bis-(cyclopropylamino)-6-diethylamino-s-triazine	76-77	20
	28	2-cyclopropylamino-4-amino-6-(N-methyl-N-ethylamino)-s-triazine	150-152	
25	29	2-cyclopropylamino-4,6-bis-(methylamino)-s-triazine dihydrochloride	158-162	25
	30	2-cyclopropylamino-4-methylamino-6-dimethylamino-s-triazine dihydrochloride	164-165	
30	31	2,4-bis-(cyclopropylamino)-6-ethylamino-s-triazine dihydrochloride	168-170	30
	32	2-cyclopropylamino-4,6-bis-(ethylamino)-s-triazine dihydrochloride	170-172	
35	33	2-cyclopropylamino-4-methylamino-6-n-propylamino-s-triazine dihydrochloride	164-165	35
	34	2-cyclopropylamino-4-ethylamino-6-n-propylamino-s-triazine dihydrochloride	164-165	
40	35	2,4-bis-(cyclopropylamino)-6-n-propylamino-s-triazine dihydrochloride	166-168	40
	36	2,4-bis-(cyclopropylamino)-6-methylamino-s-triazine dihydrochloride	174-176	
45	37	2-cyclopropylamino-4-ethylamino-6-hydroxylamino-s-triazine	198	45
	38	2-cyclopropylamino-4-dimethylamino-6-isopropylamino-s-triazine	140-142	
50	39	2-cyclopropylamino-4-dimethylamino-6-morpholino-s-triazine	148-150	50
	40	2-cyclopropylamino-4-amino-6-diethylamino-s-triazine	128-129	
55	41	2,4-bis-(cyclopropylamino)-6-morpholino-s-triazine	137-138	55
60				60
65				65

	42	2,4-bis-(cyclopropylamino)-6-pyrrolidino-s-triazine	193-196	
5	43	2-cyclopropylamino-4-dimethylamino-6-propargylamino-s-triazine hydrochloride	178-180	5
	44	2-cyclopropylamino-4-dimethylamino-6-morpholino-s-triazine hydrochloride	208	
10	45	2-cyclopropylamino-4-methylamino-6-diethylamino-s-triazine hydrochloride	153-154	10
	46	2-cyclopropylamino-4-ethylamino-6-diethyl-amino-s-triazine hydrochloride	144-145	
15	47	2-cyclopropylamino-4-dimethylamino-6-diethylamino-s-triazine hydrochloride	153-154	15
20	48	2-cyclopropylamino-4-dimethylamino-6-ethylamino-s-triazine hydrochloride	220	20
	49	2-cyclopropylamino-4-dimethylamino-6-pyrrolidino-s-triazine hydrochloride	214	
25	50	2-cyclopropylamino-4-6-bis-(diethylamino)-s-triazine hydrochloride	(oily)	25
	51	2-cyclopropylamino-4-dimethylamino-6-isobutylamino-s-triazine dihydrochloride	190-191	
30	52	2-cyclopropylamino-4-ethylamino-6-isopropylamino-s-triazine	94.5-96	30
	53	2-cyclopropylamino-4-ethylamino-6-dimethylamino-s-triazine	111-112	
35	54	2-cyclopropylamino-4-ethylamino-6-tert-butylamino-s-triazine hydrochloride	261-263.5	35
40	55	2-cyclopropylamino-4-6-bis-(ethylamino)-s-triazine hydrochloride	140-142	40
	56	2-cyclopropylamino-4-ethylamino-6-n-butylamino-s-triazine dihydrochloride	141.5-143	
45	57	2-cyclopropylamino-4-ethylamino-6-isobutylamino-s-triazine dihydrochloride	154-155	45
50	58	2-cyclopropylamino-4-ethylamino-6-sec-butylamino-s-triazine	75-77	50

EXAMPLE 5

55	Test substance:	compounds of the formula I formulated as acetonic solutions	55
	Test subject:	<i>Musca domestica</i>	
	Test material:	CSMA nutrient substrate for maggots	
	Concentration:	0.1%, 0.05%, 0.01% of active substance	
60	Test method:	50 g of freshly prepared CSMA nutrient substrate for maggots are charged into beakers. A specific amount of a 1% acetonic solution of the respective active substance is pipetted onto the nutrient substrate present in the beakers. The substrate is then thoroughly mixed and the acetone subsequently allowed to evaporate over a period of at least 20 hours.	60
65		Then 25 one-day-old maggots of <i>Musca domestica</i> are put into each of the beakers containing the treated nutrient substrate for testing	65

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with each active substance at one of its given concentrations. After 5 days, the pupae are separated from the substrate by flushing them out with water and then deposited in the same beaker. Each batch of flushed out pupae is counted to determine the toxic effect of the active substance on the maggot development. The number of flies which have hatched out of the pupae are then counted after 10 days and any influence on the metamorphosis thereby determined.

The compounds of the formula I exhibit good activity in this test.

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EXAMPLE 6

Test substance:

Test subject:

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Test material:

Concentration:

Test method:

compound of the formula I formulated as acetonic solutions

Aedes aegypti

yoghourt beakers filled with water

10 ppm, 5 ppm, and 1 ppm of active substance

Yoghourt beakers are each filled with 150 ml of water and a specific amount of a 0.1% solution of the active substance in acetone is pipetted onto the surface of the water. After the acetone has evaporated, 30 to 40 two-day-old larvae of *Aedes aegypti* are put into each of the beakers containing the active substance solution. Two beakers per concentration of active substance are used for the test. Then ground dog-biscuit is added to the beakers, which are covered with a copper gauze top.

Evaluation of mortality is made after 1, 2 and 5 days respectively. Subsequently, evaluation is made of the inhibiting action on pupation, metamorphosis, and shedding and emergence to the adult stage.

The compounds of the formula I have a good action in this test.

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EXAMPLE 7

Test substances:

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Test subject:

Concentration:

Test method:

Active substances of the formula I formulated as 25% wettable powder or as aqueous solution or suspension of the hydrochlorides.

Lucilia sericata (blowfly), freshly hatched - larve I

250 ppm of active substance

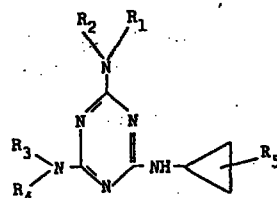
1 ml of an aqueous suspension or solution of the active substance in a concentration of 1000 ppm is added at 50°C to 3 ml of a special culture medium so as to give a homogeneous mixture with an active substance content of 250 ppm. Approx. 30 *Lucilia* larvae are used for each test. Evaluation of mortality is made after 4 days.

In this test, the compounds of formula I exhibit good action.

WHAT WE CLAIM IS:-

1. 2-Cyclopropylamino-4,6-diamino-s-triazines of the formula I

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(I)

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wherein

R₁ represents hydrogen, C₁-C₃-alkyl which is unsubstituted or substituted by C₁-C₄-alkoxy or cyano or represents C₃- or C₄-alkenyl C₃- or C₄-alkynyl or cyclopropyl,

R₂ represents hydrogen, methyl or ethyl or

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R₁ and R₂ together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole hetero-atom or which contains a further nitrogen atom or an oxygen atom,

R₃ represents hydrogen, C₁-C₃-alkyl, C₃-alkenyl, C₃-alkynyl or cyclopropyl,

R₄ represents hydrogen, methyl or ethyl, or

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R₃ and R₄ together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole

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(19)



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with each active substance at one of its given concentrations. After 5 days, the pupae are separated from the substrate by flushing them out with water and then deposited in the same beaker. Each batch of flushed out pupae is counted to determine the toxic effect of the active substance on the maggot development. The number of flies which have hatched out of the pupae are then counted after 10 days and any influence on the metamorphosis thereby determined. The compounds of the formula I exhibit good activity in this test.

EXAMPLE 6

Test substance:
Test subject:
Test material:
Concentration:
Test method:

compound of the formula I formulated as acetonetic solutions
Aedes aegypti
yoghurt beakers filled with water
10 ppm, 5 ppm, and 1 ppm of active substance
Yoghurt beakers are each filled with 150 ml of water and a specific amount of a 0.1% solution of the active substance in acetone is pipetted onto the surface of the water. After the acetone has evaporated, 30 to 40 two-day-old larvae of *Aedes aegypti* are put into each of the beakers containing the active substance solution. Two beakers per concentration of active substance are used for the test. Then ground dog-biscuit is added to the beakers, which are covered with a copper gauze top. Evaluation of mortality is made after 1, 2 and 5 days respectively. Subsequently, evaluation is made of the inhibiting action on pupation, metamorphosis, and shedding and emergence to the adult stage.

The compounds of the formula I have a good action in this test.

EXAMPLE 7

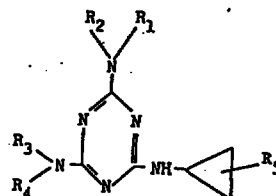
Test substances:
Test subject:
Concentration:
Test method:

Active substances of the formula I formulated as 25% wettable powder or as aqueous solution or suspension of the hydrochlorides. *Lucilia sericata* (blowfly), freshly hatched - larve I
250 ppm of active substance
1 ml of an aqueous suspension or solution of the active substance in a concentration of 1000 ppm is added at 50°C to 3 ml of a special culture medium so as to give a homogeneous mixture with an active substance content of 250 ppm. Approx. 30 *Lucilia* larvae are used for each test. Evaluation of mortality is made after 4 days.

In this test, the compounds of formula I exhibit good action.

WHAT WE CLAIM IS:-

1. 2-Cyclopropylamino-4,6-diamino-s-triazines of the formula I



(I)

wherein

R₁ represents hydrogen, C₁-C₃-alkyl which is unsubstituted or substituted by C₁-C₄-alkoxy or cyano or represents C₃- or C₄-alkenyl C₃- or C₄-alkynyl or cyclopropyl,
R₂ represents hydrogen, methyl or ethyl or
R₁ and R₂ together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole

hetero-atom or which contains a further nitrogen atom or an oxygen atom,
R₃ represents hydrogen, C₁-C₃-alkyl, C₃-alkenyl, C₃-alkynyl or cyclopropyl,
R₄ represents hydrogen, methyl or ethyl, or
R₃ and R₄ together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole



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hetero-atom or which contains a further nitrogen atom or an oxygen atom, and R_5 represents hydrogen or methyl, and the acid addition salts thereof, provided that:

(1) R_1 does not represent cyclopropyl when simultaneously

(a) R_2 and R_3 represent hydrogen and R_4 represents methyl or ethyl or

(b) R_2 and R_4 represent hydrogen and R_3 represents methyl, ethyl, n-propyl or cyclopropyl; and

(2) R_3 does not represent cyclopropyl when simultaneously

(a) R_1 and R_4 represent hydrogen and R_2 represents methyl or ethyl or

(b) R_2 and R_4 represent hydrogen and R_1 represents methyl, ethyl, n-propyl or cyclopropyl.

2. Compounds according to claim 1 wherein R_1 represents hydrogen, C_1-C_3 -alkyl which is unsubstituted or substituted by C_1-C_4 -alkoxy, or represents C_3 - or C_4 -alkenyl, C_3 - or C_4 -alkynyl, cyclopropyl; R_2 represents hydrogen, methyl or ethyl, or R_1 and R_2 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, 1-piperazinyl or 1-(4-methyl)-piperazinyl; R_3 represents hydrogen, C_1-C_3 -alkyl, C_3 -alkenyl, C_3 -alkynyl or cyclopropyl; R_4 represents hydrogen, methyl or ethyl, or R_3 and R_4 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, 1-piperazinyl or 1-(4-methyl)-piperazinyl and R_5 represents hydrogen or methyl.

3. Compounds according to claim 1 wherein R_1 and R_2 , together with the nitrogen atom to which they are attached, represent a 1-imidazolyl group and/or R_3 and R_4 together with the nitrogen atom to which they are attached represent a 1-imidazolyl group and all other symbols are as defined in claim 2.

4. Compounds according to claim 1 wherein R_1 represents hydrogen, methyl, ethyl, n-propyl, isopropyl, or cyclopropyl; R_2 represents hydrogen, methyl or ethyl, or R_1 and R_2 together with the nitrogen atom to which they are attached represent 1-pyrrolidinyl, 1-piperidinyl or 4-morpholinyl; R_3 represents hydrogen, methyl, ethyl, n-propyl, isopropyl or cyclopropyl; R_4 represents hydrogen, methyl or ethyl; and R_5 represents hydrogen.

5. Compounds according to claim 1 wherein R_1 and R_2 together with the nitrogen atom to which they are attached represent an imidazolyl group and all other symbols are as defined in claim 4.

6. Compounds of formula (I) defined in claim 1 wherein R_1 represents hydrogen, ethyl, or cyclopropyl; R_2 represents hydrogen; R_3 represents hydrogen or methyl, R_4 represents hydrogen, methyl or ethyl and R_5 represents hydrogen, but at least one of the symbols R_1 , R_3 and R_4 represents hydrogen, and the hydrochlorides thereof.

7. 2-Cyclopropylamino-4-amino-6-ethylamino-s-triazine dihydrochloride.

8. 2,4-Bis-(cyclopropylamino)-6-amino-s-triazine.

9. 2-Cyclopropylamino-4-amino-6-methylamino-s-triazine dihydrochloride.

10. 2-Cyclopropylamino-4,6-diamino-s-triazine.

11. 2-Cyclopropylamino-4-amino-6-dimethylamino-s-triazine.

12. 2-Cyclopropylamino-4,6-bis-(ethylamino)-s-triazine dihydrochloride.

13. 2-Cyclopropylamino-4-amino-6-(N-methyl-N-ethylamino)-s-triazine.

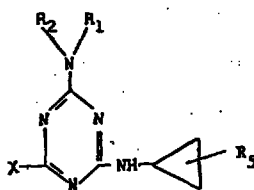
14. 2,4-Bis-cyclopropylamino-6-isopropylamino-s-triazine.

15. 2-Cyclopropylamino-4,6-bis-dimethylamino-s-triazine.

16. Each of the compounds 2, 4, 5 and 6 hereinbefore specifically named.

17. Each of the compounds 8 to 30, 32, 33, 34, 38 to 50, 52, 53 and 55 hereinbefore specifically named.

18. A process for the manufacture of 2-cyclopropyl-amino-4,6-diamino-s-triazines claimed in claim 1, which comprises reacting a 2-cyclopropylamino-4-amino-6-halogeno-s-triazine of the formula II



II

(21)



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in which R_1 , R_2 and R_5 are as defined in claim 1 and X represents halogen, with ammonia or a primary or secondary amine of the formula V

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(V)

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in which R_3 and R_4 are as defined in formula I.

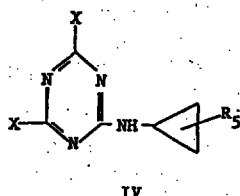
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19. A process according to claim 18 in which X is chlorine.

20. A process for the manufacture of 2-cyclopropylamino-4,6-diamino-s-triazines claimed in claim 1, in which R_1 and R_3 are identical and R_2 and R_4 are identical, wherein a 2-cyclopropylamino-4,6-dihalogeno-s-triazine of the formula IV

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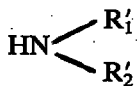
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in which R_5 is as defined in formula I and X represents halogen, is reacted with ammonia or with a primary or secondary amine of the formula VII

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(VII)

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in which R'_1 has the same meaning as R_1 and R_3 and R'_2 have the same meanings as R_2 and R_4 respectively.

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21. A process according to claim 20 wherein X represents chlorine.

22. 2-Cyclopropylamino-4,6-diamino-s-triazines claimed in claim 1 when obtained by a process claimed in claim 18, 19, 20 or 21.

23. An insecticidal composition comprising a 2-cyclopropylamino-4,6-diamino-s-triazine claimed in any one of claims 1 to 17 and a carrier.

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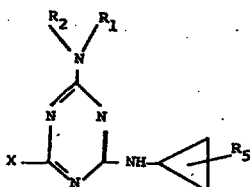
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24. A composition according to claim 23 in the form of a dust, tracking agent, granules, wettable powder, emulsifiable concentrate, animal feed additive or spray.

25. A method of preventing the development of adult insects from larvae or pupae, which comprises applying to the larvae or pupae a 2-cyclopropylamino-4,6-diamino-s-triazine of the formula

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wherein

R_1 represents hydrogen, C_1 - C_4 -alkyl which is unsubstituted or substituted by C_1 - C_4 -alkoxy or cyano or represents C_3 - or C_4 -alkenyl, C_3 - or C_4 -alkynyl, cyclopropyl, hydroxyl, methoxy or ethoxy,

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R_2 represents hydrogen, methyl or ethyl or

R_1 and R_2 together with the nitrogen atom to which they are attached represent a 5- or 6-membered heterocyclic ring in which the nitrogen atom shown is the sole hetero-atom or which contains a further nitrogen atom or an oxygen atom,

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R_3 represents hydrogen, C_1 - C_4 -alkyl, C_3 -alkenyl, C_3 -alkynyl or cyclopropyl,

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- R₄ represents hydrogen, methyl or ethyl, or
R₃ and R₄ together with the nitrogen atom to which they are attached represent a 5- or
6-membered heterocyclic ring in which the nitrogen atom shown is the sole
hetero-atom or which contains a further nitrogen atom or an oxygen atom, and
5 R₅ represents hydrogen or methyl, or an acid addition salt thereof. 5
26. A method according to claim 25 wherein the insects are of the order *Diptera*.
27. A method according to claim 26 wherein the insects are of the families *Culicidae*,
Simuliidae, *Tipulidae*, *Muscidae* and *Calliphoridae* which belong to the order *Diptera*.
10 28. A method according to claim 25, 26 or 27 wherein a compound claimed in any one 10
of claims 2, 4, 7, 8, 9, 14, 15 and 16 is applied.
29. A method according to claim 25, 26 or 27 wherein the compound 3 hereinbefore
specifically named is applied.
30. A method according to claim 25, 26 or 27 wherein a compound claimed in any one
of claims 3, 5, 6, 10 to 13, and 17 is applied.
15 31. A method according to claim 25, 26, or 27 wherein any of the compounds 31, 35 to 15
37, 51, 54 and 56 to 58 hereinbefore specifically named is applied.

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