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METHOD OF COMBATING INSECTS COMPRISING CONTACTING WITH A DICHLORO-1,3,5-TRI-AZINE

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It is known that various derivatives of 1,3,5-triazines are suitable for combating noxious organisms. Reference may, for example, be made to compounds of the general formula:

In this formula Ar designates an aryl-group, n a number of the value 1 or 2 and x a number of the value 0, 1, 2, 3 or 4.

These compounds are said to have a pronounced fungicidal effect and be phytotoxical under particular circumstances.

Other compounds also having a fungicidal effect are 4,6-dichlor-triazines, which are substituted at the position 2 by an aryl-amine-group and of which the aryl-group may have one or more alkyl or negative groups, for example, a chlorine atom or a nitro-group. Reference may furthermore be made to the compounds 2 chloro-4,6(-diarylamino) 1,3,5-triazine and 2,4-dichlor-6-arylamino-1,3,5-tri-azine. These compounds could also be used as fungicides.

Finally we may mention the compound 2-chlor-4,6 bisdiethylamino-1,3,5-triazine. This compound is said to have herbicidal effects, but be free from fungicidal effects. This compound is moreover said to have a slight insecticidal activity.

The present invention relates to a method of producing 50 means for combating noxious organisms, comprising a derivative of 1,3,5-triazine and is characterized in that a compound of the general formula:

wherein X designates —NH, —O— or —S— and R a saturated or an unsaturated, aliphatic or alicyclic hydrocarbon residue containing at least two carbon atoms, is mixed in a dose which is harmful to the organisms to be combated, with solid or liquid, inert carriers.

The compounds referred to in the preceding paragraph are harmful to organisms of different kinds. It has been found, for example, that the said compounds may affect adversely the growth of plants, even if they are in a diluted state, and, moreover, that the compounds in which X is —O— or —S— and R is a saturated or unsaturated,

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aliphatic or alicyclic hydrocarbon residue, have an insecticidal activity.

Of the compounds having a harmful effect on plants we may mention those in which R is an aliphatic hydrocarbon residue containing 2 to 11 carbon atoms. The phytotoxical compounds according to the invention have a particular activity against herbaceous plants, the more ligneous kinds are also affected by the said means, but to a lesser extent. Of the kinds of plants, of which the 10 growth is impeded or terminated by the said phytotoxical compounds, we may mention: starwort (Stellaria media), white goosefoot (Chenopodium album), broad- or narrowleaved waybread (Plantago media and lanceolata), stinging nettle (Urtica ureus), sorrel (Rumex acetosella) and charlock (Raphanus).

From tests with tomatoes and garden beans it was found that of the combating compounds according to the invention particularly the mercapto-compounds have a phytotoxical effect on plants. Of the mercapto-compounds special mention may be made of those, in which the group of R contains 3 to 5 carbon atoms, for example, the n-propyl-, allyl-, n-butyl-, isoamyl-, n-amyl-, isobutyland 3-methylbutyl-derivatives of 2-mercapto-4,6-dichlor 1,3,5-triazines. It has been found that 2 alkylmercapto-25 4,6-dichlor-1,3,5-triazines with a carbon chain having more than 11 carbon atoms has hardly any photytoxical The compounds in which X is -O- and R designates the groups referred to above, were found to have approximately the same phytotoxical effect with tomato- and bean-tests. 2-methoxy-4,6-dichlor-triazine, in a concentration of 1 to 3%, was found to be only slightly effective, as well as those compounds in which the group of R had more than 11 carbon atoms. Of the combating means according to the invention, which are derivatives of 2-oxy-4,6-dichlor-1,3,5-triazine particularly those are important, in which the group of R contains 3 to 11 carbon atoms.

The active compounds or a mixture thereof can be worked up to obtain combating means in a conventional manner. To this end the active compounds are mixed with solid or liquid carriers or, if necessary, dissolved therein, and, if desired, enriched with dispersion agents, emulsifiers or wetting agents. Preparations thus obtained may be sprayed, pulverized or nebulized in air either as such or emulsified or dispersed in a liquid, for example water. Of the various preparations which may be used and which may be obtained by means of the active compounds, mention may be made of the so-called mixable oils, spray powders and atomizing powders. These forms are referred to only by way of example and do not intend to restrict the invention.

In order to produce mixable oils the mixture of active compounds is dissolved in a suitable solvent, which is immiscible with water, and to this solution is added an emulsifier. Suitable solvents are, for example, xylene, toluene dioxane, petroleum distillates rich in aromatic compounds, for example, solvent naphtha, distilled tar oil, furthermore tetraline, cyclohexane or mixtures of these liquids. As emulsifiers may be used alkyl phenoxypoly glycolethers, poly-oxyethylene sorbitane esters of fatty acids or poly oxy-ethylene sorbitol esters of fatty acids. Some of these types of emulsifiers are known under the registered tradename of "Triton," "Tween" and "Atlox."

The concentration of the active compounds in the liquid mixable with water is not subjected to narrow limits. It may vary, for example, between 2 and 50% by weight. When using these solutions, the mixable oils are emulsified in water and this emulsion is sprayed. Usually the concentration of active compounds in these aqueous emulsions lies between 0.01 and 0.5% by weight.

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The spray powders may be produced by mixing the active compounds with a solid, inert carrier, usually in the presence of a dispersion agent and/or wetting agent. Prior to their use the spray powders are dispersed in liquid, preferably in water and this dispersion is sprayed. 5 It is important that the spray powder should consist of small particles in order to prevent the opening of the sprayer from being stopped up. It is therefore advisable to use, as a carrier, a fine powder. If desired, the mixture of the carrier material, the active compounds and 10 any auxiliary substances may in addition be ground.

The carrier material may, for example, be alum earth, diatomaceous earth, kaolin, dolomite, talcum, gypsum, chalk, bentonite, attapulgite, infusorial earth, celite, wood meal, tobacco dust or ground coconut shells. Suitable dispersion agents are lignine sulphonates and naphthalene sulphonates. Wetting agents may be fatty alcohol sulphates, alkyl-aryl-sulphonates or fatty acid condensation products, for example those known under the trade name of "Igepon."

Also with the spray powders the concentration of the active compounds is not subjected to narrow limits. In general, the concentration will be chosen to lie between

10 and 80% by weight.

Atomizing powders may be produced by applying an 2 active compound or mixtures thereof, as such, or dissolved in a solvent, to a solid carrier. When used, the preparation thus obtained is atomized in the air in a dry, finely pulverulent state. These powders may be produced, when suitable light carriers are employed, also 3 in the manner described for the production of spray powders. The carrier material may be the products referred to above for the production of spray powders. Usually, the concentration of active compounds in the atomizing powders is lower than that of the spray powders or mixable oils, but it exceeds the concentration of active compounds in dispersions or emulsions, obtained by diluting spray powders or mixable oils with liquids. The atomizing powders often contain 1 to 20% of active compounds. It may be superfluous to observe that the mixable oils, the spray powders or the atomizing powders according to the invention may be produced by mixing two mixable oils (or spray powders and atomizing powders), each of which contains one of the active compounds.

The compounds according to the invention have a comparatively high chlorine content and are capable of splitting off hydrochloric acid. This may be undesirable. In order to avoid the harmful effect of the hydrochloric acid, a compound may be added to the combating substances, which compound is capable of binding the hydrochloric acid set free. To this end use may be made of propylene oxide. A concentration of about 1 to 5% of this compound usually yields satisfactory results.

The compounds of the invention are fairly stable, when kept in stock; some of them lose their activity rather soon when they are applied to the soil or mixed therein. Owing to this property these compounds, of which we may mention particularly 2n-butylmercapto-, and 2n-butoxy-, -4,6-dichlor-1,3,5-triazine are particularly suitable to destroy weed like plants from agricultural or horticultural fields before the cultural plants have come up. To this end the compounds may be employed in a quantity of 2 to 20 kgs. per hectare. A quantity of about 10 kgs. per hectare often gives satisfactory results.

The phytocidal effect of the compounds of the given formula was determined by tests on tomatoes and garden bean plants in the following manner.

A compound to be examined was dissolved in acetone (concentration 1% by weight). Then this liquid was sprayed on a number of tomato- and garden bean-plants in a quantity which corresponded to 10 kgs. of active substance per hectare. A similar test was made with a

3% acetone solution, which was applied to plants in a 75

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quantity which corresponded to 30 kgs. of active substance per hectare. Each series of tests was carried out on two tomato plants and two garden bean plants, the age of which was 3 to 4 weeks. Ten days after the application it was fixed to what extent the plants had suffered from the treatment. The following standard was fixed:

No traces of burning	0
0 to ½0 part of the surface of the plant burnt	1
1/10-1/3 part of the surface of the plant burnt	2
1/3 to 2/3 part of the surface of the plant burnt	3
2/3 to 9/10 part of the surface of the plant burnt	4
% to 1 part of the surface of the plant burnt :	5
	6

The numerals thus fixed were united in the Tables I, II, III.

TABLE I

Phytotoxic effect of 2-alklymercapto-4,6-dichlor-1,3,5-triazines

30	azines					
		Test plant				
.;	Tested compound	Ton	ato	garden bean		
25	200000 00	concentration		concentration		
		1%	3%	1%	3%	
30	2 - ethyl mercapto - 4,6 - dichlor - 1,3,5 - triazine	1	5	4	6	
	2 - n - propyl mercapto - 4,6 - dichlor - 1,3,5-triazine	4	6	6	6	
. :	2 - iso - propyl mercapto - 4, 6 - di- chlor-1,3,5-triazine	. 1	6	3	6	
95	2 - allyl mercapto - 4, 6 - dichlor - 1,3,5-triazine	4	6	6	6	
35	2 - n - butyl mercapto - 4,6 - dichlor- 1,3,5-triazine	Б	5	. 4	6	
	4.6-dichlor-1.3.5-triazine	1	3	3	5	
٠:	2 - (3'- methyl - butyl) mercapto - 4,6-dichlor-1,3,5-triazine	3	6	. 6	6	
40	2 n - octyl mercapto - 4,6 - dichlor- 1,3,5-triazine	2	3	4	4	
	2 n - amyl mercapto -4,6 - dichlor- 1,3,5-triazine	. 6	6	6	6	
	2 (2' methyl propyl) mercapto - 4,6- dichlor-1,3,5-triazine	6	6	6	6	
	2 (1' methyl propyl) mercapto - 4,6- dichlor-1,3,5-triazine	6	6	6	6	
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TABLE II

Phytotoxic effect of 2-alkyloxy 4,6 dichlor 1,3,5-triazines

	Test plant				
Tested compound	Tomato		garden bean		
20000000	concen	ration	concentration		
	1%	3%	1%	3%	
2 - ethoxy 4,6,- dichlor 1,3,5-triazine 2 n-propoxy 4,6,-dichlor 1,3,5-triazine_	3 5	5 5	3 2 4	4 5 4	
2 iso propoxy 4,6,-dichlor 1,3,5-triazine. 2 (propene-2') oxy-1' 4,6,-dichlor 1,3,5-	4	5	4	4	
triazine	3	6	4	6	
5-triazine	2 3	5	3	5	
2 n-butoxy 4, 6,-dichlor 1,3,5-triazine 2 - (1' - methylpropoxy) 4,6,- dichlor	3	6	3	5	
1,3,5-triazine 2 cyclo hexoxy 4,6,- dichlor 1,3,5-	2	6	3	5	
triazine	3	5	3	5	
2 · octoxy 4,6,-dichlor 1,3,5-triazine 2 (1'- methylheptoxy) 4,6,-dichlor	5	5	3	4	
1,3,5-triazine 2-amyloxy 4,6,-dichlor 1,3,5-triazine	2 5	- 3 6	1 6	. 2	

The insecticidal effect of the compounds of the formula

wherein X designates —O or —S , was found to occur particularly with those compounds, in which R designates an aliphatic residue having 2 to 11 carbon atoms. The insecticidal effect was tested on two kinds of insects i.e. Musca and Sitophilus in two concentrations i.e. of 1000 p.p.m. and of 300 p.p.m. The tests were carried out as follows.

1 cc. of an acetone solution of the compound to be tested in one of the said concentrations was brought into a Petri dish, having a content value of about 64 cc. 10 After the solvent had been evaporated, 10 muscas were introduced into the dishes. With the Sitophilus test both the bottom and the lid of the Petri dish were painted with 1 cc. of an acetone solution and after the solvent had been evaporated, the insects were introduced into the 15 dish. For Musca after 21 hours and for Sitophilus after 5 days is was fixed what percentage of the insects had been killed. Blank tests were carried out in a similar manner. The results of these tests are indicated in the Tables III and IV. The values indicated (percentages of kill) are average values of a series of tests. From these tests it is evident that the insecticidal effect of the mercapto-compounds is slightly greater than that of the oxy-compounds.

TABLE III

Insecticidal effect of 2-alkylmercapto-4,6-dichlor-1,3,5-

	Test insect				
Tested compound	Musca		Sitophilus		
	1,000 p.p.m.	300 p.p.m.	1,000 p.p.m.	300 p.p.m.	35
2-ethyl-mercapto-4, 6-dichlor-1, 3, 5-triazine 2n-propyl mercapto-4, 6-dichlor-1,3, 5-triazine 2n-allyl mercapto-4, 6-dichlor-1, 3, 5-triazine 2n-isopropyl mercapto-4, 6-dichlor-1, 3, 5-triazine 2n-butyl 2(1', 1' dimethylethyl) 2(3'methylbutyl)	100 100 100 100 100 100 100	87 100 97 96 100 94 97	100 100 100 100 100 100 100	100 100 100 100 100 100 100	40

TABLE IV

Insecticidal effect of 2-alkoxy-4,6-dichlor-1,3,5-triazine

	Test insect.				
Tested compound	Musea		Sitophilus		5
	1,000 p.p.m.	300 p.p.m.	1,000 p.p.m.	300 p.p.m.	
2-ethoxy-4, 6-dichlor-1, 3, 5-triazines_2n-propoxy-4, 6-dichlor-1, 3, 5-tria-	100	16	100	8	5
zines	100	100	100	100	
2n;allyloxy 4, 6-dichlor-1, 3, 5-tria- zines2-(propene-2'-oxy-1') 4, 6-dichlor-1, 3,	100	52	100	100	
5-triazines	100	33	100	72	
2-isopropoxy 4, 6-dichlor-1, 3, 5-triazines. 2n-butoxy 4, 6-dichlor-1, 3, 5-triazines. 2(1'-methyl propyl) 4, 6-dichlor-1, 3,	100 100	42 78	100 100	23 100	6
5:triazines 2-actoxy 4, 6-dichlor-1, 3, 5-triazines	100 90	61 71	100 99	84	
2-(1-methyl heptoxy) 4, 6-dichlor 1, 3, 5-triazines	92	67	100	100	_
2-cyclohexoxy. 4, 6-dichlor-1, 3, 5-tria- zines	100	100	100	100	6

It can furthermore be stated that the compounds indicated in table have a "knock-down" effect, particularly with the Musca insects. Also in this respect the mer- 70 capto-compounds proved to have a greater activity than the oxy-compounds. The compounds having an insecticidal effect may be worked up in the manner described for the phytocidal compounds to obtain mixable oils, spray powders or atomizing powders. As an alternative, the 75 acid chloride and the desired aliphatic alcohol or the mer-

compounds may be dissolved in hydrocarbons, for example, mineral oils or coal tar distillates without the addition of auxiliary substances such as wetting agents or dispersion agents. Moreover, the insecticides according to the invention may be dissolved in readily condensable, inert liquids, which are gaseous at room temperature. As such use may be made, for example, of fluorine-chlorine-methanes, for instance "Freon." desired, diluents may be added to these solutions, for example, methylene chloride. These solutions can be readily nebulized.

The compounds of the general formula:

wherein X designates -O or -S and R a saturated or an unsaturated, aliphatic or alicyclic hydrocarbon residue, have not yet been described in the literature. Therefore the invention also relates to a method of producing these compounds.

This part of the invention consists of a method of producing derivatives of 4,6-dichlor-1,3,5-triazines and is characterized in that compounds of the general formula:

wherein X designates —O—, or —S— and R a saturated or an unsaturated or alicyclic hydrocarbon residue, are produced by reacting compounds of the general formula HXR with cyanuric acid chloride, preferably in the presence of an acid binder.

As a solvent use may be made of chloroform, tetrachlorcarbon acetone, aliphatic ethers for instance diethylether, dimethyl-ether, furthermore aromatic hydrocarbons, for instance toluene or benzene. It has been found that in these solvents the presence of water affects adversely the yield of the reaction, so that the reaction is preferably carried out in an anhydrous medium.

As an acid binder use may particularly be made of 2,6-alkyl-substituted pyridine, for instances 2,6-dimethylpyridine, 2,4,6-trimethyl-pyridine, 2 methyl-chinoline, although also other tertiary amines may be used, for instance: dimethyl- or diethyl-aniline.

The compounds according to the invention, wherein X is -0— or -S— are best produced at a temperature between -20 and  $+25^{\circ}$  C.

The said compounds may, as an alternative, be ob-55 tained by causing cyanuric acid chloride to react with a compound of the formula: H-X-R is an excess quantity in the presence of an inorganic acid binder, for instance sodium carbonate, sodium bicarbonate or sodium hydroxide. This reaction may be carried out in an 30 aqueous medium.

The compounds, wherein X designates —O— or —Smay furthermore be produced by reacting cyanuric acid chloride with a compound of the formula: MeX-R, wherein Me designates an alkali atom, for instance 5 sodium ethanolate or potassium methanolate, or an alkali compound of an aliphatic mercaptane. This reaction is carried out preferably in the presence of an excess quantity of the alcohol or the mercaptane. If desired, other organic solvents, for instance, aliphatic or aromatic ethers, such as dimethyl- or diethyl-ether, phenetol anisol, furthermore acetone or benzene and toluene, may be used as diluents.

It should be noted that the compounds are preferably produced by carrying out the reaction between cyanuric 7

captane in the presence of a 2,6-alkyl-substituted pyridine as an acid binder.

EXAMPLE I.—2-METHOXY-4,6-DICHLOR-1,3,5-TRIAZINE

12.3 g. (0.067 mol) of cyanuric chloride was dissolved in 80 mls. of acetone. While being cooled on ice, this solution had added to it 2.13 g. of methanol and 9 mls. of collidine. The deposit of the hydrochloric acid salt of collidine obtained was filtered off after one hour and the filtrate was poured out on ice. The deposit obtained was filtered off sharply and washed with ice-water. The yield was 9.7 g. of 2-methoxy-4,6-dichlor-1,3,5-triazine. The melting range was from 84 to 87° C. After recrystallisation from n-hexane the melting point was 88 to 89° C.

#### EXAMPLE II.—2-ETHOXY-4,6-DICHLOR-1,3,5-TRIAZINE

18.4 g. cyanuric chloride (0.1 mol) was dissolved in 120 mls. of acetone. While being cooled on ice, this solution had added to it in succession, 4.6 g. of ethyl alcohol (0.1 mol) and 13.5 mls. of collidine in a manner such that the temperature of the reaction mixture did not exceed 10° C. The mixture was kept at room temperature for three hours. The hydrochloride acid salt of collidine formed was then filtered off and washed with acetone. The filtrate was then poured out in ice water. 25

The 2-ethoxy-4,6-dichlor-1,3,5-triazine was precipitated in the form on an oil, which was absorbed in diethyl ether. The ethereal solution was washed four to five times with water, dried on sodium sulphate, filtered and evaporated to dryness. The remaining oil was distilled. 30

The yield was 10 g. (52%) of 2-ethoxy-4,6-dichlor-1,3, 5-triazine. Boiling point 14 mm.=114° C.

## EXAMPLE III.—2N-PROPOXY-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 18.41 g. of cyanuric acid chloride (0.1 mol), 6 g. of n-propyl-alcohol and 13.5 mls. of collidine yielded 12.5 g. (60%) of 2-propoxy-4,6-dichlor-1,3,5-triazine. Boiling point 12 mm.=124° C.

## EXAMPLE IV.--2-ISOPROPOXY-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 18.4 g. (0.10 mol) of cyanuric chloride, 6 g. of isopropyl-alcohol and 13.5 mls. of collidine yielded 6.66 45 g. (32%) of 2-isopropoxy 4,6-dichlor-1,3,5-triazine. Boiling point 11 mm.=117° C.

## EXAMPLE V.--2-(PROPENE-2'-OXY-1')-4,6-DICHLOR-1,8,5-TRIAZINE

In the same manner as described in Examples I and II 12.3 g. (0.067 mol) of cyanuric chloride, 3.9 g. of allyl-alcohol and 9 mls. of collidine yielded 7.1 g. (52%) of 2-(propene-2'-oxy-1')-4,6-dichlor-1,3,5-triazine. (Boiling point 11 mm.=126 to 127° C.)

## EXAMPLE VI.—2-(PROPYNYL-2'-OXY 1')-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 18.5 g. (0.10 mol) of cyanuric chloride, 5.6 g. of propargyl-alcohol and 13.5 mls. of collidine yielded 8.6 g. 60 (42%) of 2-(propyn-2'-oxy-1') 4,6-dichlor-1,3,5-triazine. (Boiling point 11 mm.=134 to 135° C.) After some time the substance solidified and melted at 39 to 40° C.

## EXAMPLE VII.—2N-BUTOXY-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 92.2 g. (0.5 mol) of cyanuric chloride, 53.5 g. of n-butyl-alcohol and 67.5 mls. of collidine yielded 95.5 g. (86%) of 2n-butoxy-4.6-dichlor-1,3,5-triazine. Boiling point 12 mm.=139 to 140° C.

#### EXAMPLE VIII.—2-(1'-METHYL PROPOXY)-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and n-propylmercaptane (0.105 mol) and 13.5 mls. of colli-II 12.3 g. (0.067 mol) of cyanuric chloride, 4.95 g. of 75 dine yielded 20.65 g. (92%) of 2n-propylmercapto-4,6-

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butanol and 9 mls. of collidine yielded 9.5 g. (65%) of 2(1' - methyl - propoxy) - 4,6 - dichlor - 1,3,5 - triazine. (Boiling point 12 mm.=127 to 128° C.).

#### EXAMPLE IX.—2-CYCLOHEXOXY-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 12.3 g. (0.067 mol) of cyanuric chloride, 6.7 g. of cyclohexanol and 9 mls. of collidine yielded 10.2 g. (62%) of 2-cyclohexoxy-4,6-dichlor-1,3,5-triazine (boiling point 12 mm.=168 to 169° C.).

#### EXAMPLE X.—2-OCTOXY-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 18.45 g. (0.1 mol) of cyanuric acid chloride, 13 g. of octanol (0.1 mol) and 13.5 mls. of collidine yielded 16.9 g. (61%) of 2-octoxy-4,6-dichlor-1,3,5-triazine (boiling point 0.02 mm.=127 to 130° C.).

## EXAMPLE XI.—2(1'-METHYLHEPTOXY)-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples I and II 18.45 g. (0.1 mol) of cyanuric acid chloride, 13 g. of octanol-2 (0.1 mol) and 13.5 mls. of collidine yielded 13.5 g. (48%) of 2-(1'-methylheptoxy)-4.6-dichlor-1,3,5-triazine. (Boiling point 0.005 mm.=102 to 106° C.)

#### EXAMPLE XII.—2-METHYLMERCAPTO-4,6-DICHLOR-1.3.5-TRIAZINE

55.6 g. (0.2 mol) of methylisothio-urea sulphate was introduced into 80 mls. of 5n-caustic soda. While being carefully heated, the sulphuric acid was bound and the methylisothio-urea was set free. The latter substance is not stable at normal temperature and decomposed into cyanic amide and methyl-mercaptane. The methylmercaptane was introduced into a solution of 18.45 g. of cyanuric chloride, dissolved in 200 mls. of acetone. The temperature of the solution was kept between -25 to -30° C. When all the methylmercaptane had been introduced, the reaction mixture had added to it 13.5 mls. of collidine at the same low temperature. The hydrochloric acid salt of collidine was immediately precipitated. The reaction mixture was kept for one hour at a temperature not rising above 0° C. and was then poured out on ice. The 2-methylmercapto-4,6-dichlor-1,3,5,-triazine was precipitated in the form of a solid substance. After filtering, washing with water and drying on concentrated sulphuric acid in vacuo, 17.5 g. (89%) of 2-methylmercapto - 4,6 - dichlor-1,3,5-triazine was obtained (melting point 57 to 59° C.). Recrystallisation of the substance from petroleum ether (60 to 80) did not raise the melting point.

## EXAMPLE XIII.—2-ETHYLMERCAPTO-4,6-DICHLOR-1,3,5-TRIAZINE

18.45 g. (0.1 mol) of cyanuric chloride was dissolved in 150 mls. of acetone. While being cooled on ice, 10 g. (0.16 mol) of ethyl-mercaptan was added, then 13.5 mls. of collidine. During the reaction the mixture was cooled with ice. The reaction was continued for three hours at a temperature between 20 to 25° C. deposit of the hydrochloride acid salt of collidine was filtered off, washed out with acetone. The acetonic solution was poured out in ice water, in which 2-ethylmercapto-4,6-dichlor-1,3,5-triazine was precipitated in the form of an oil. The oil was dissolved in diethyl ether, the solution was washed with water, dried on sodium sulphate, filtered and inspissated. The remaining oil was distilled in vacuo. Yield 13.5 g. (64%) of 2-ethylmercapto-4,6-dichlor-1,3,5-triazine. (Boiling point 0.07 mm.=79 to 80° C.)

## (86%) of 2n-butoxy-4.6-dichlor-1,3,5-triazine. Boiling 70 EXAMPLE XIV.—2N - PROPYLMERCAPTO-4,6-DICHLOR-

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride, 8 g. of n-propylmercaptane (0.105 mol) and 13.5 mls. of collidine yielded 20.65 g. (92%) of 2n-propylmercapto-4,6-

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dichlor-1,3,5-triazine. After distillation the yield was 78% (boiling point 0.01 mm.=89 to 91° C.).

EXAMPLE XV.—2-ISOPROPYLMERCAPTO 4,6-DÍCHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride, 10 g. (0.13 mol) of isopropylmercaptane and 13.5 mls. of collidine yielded 16.17 (25%) of 2-iso propyl mercapto-4,6-diciller 1,3,5-triazine. (Boiling point 0.2 mm.=81° C.) EXAMPLE XVI.—2-ALLYLMERCAPTO-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride, 10 g. (0.135 mol) of allylmercaptane and 13.5 mls. of collidine yielded 16 g. (72%) of 2-allylmercapto-4,6-dichlor-1,3,5-triazine. (Boiling point 0.25 mm.=111° C.).

EXAMPLE XVII.—2N - BUTYLMERCAPTO-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 92.25 g. (0.5 mol) of cyanuric chloride 45 g. (0.5 mol) of n-butyl-mercaptane and 13.5 mls. of collidine yielded 97.5 g. (81%) of 2n-butylmercapto-4,5-dichlor-1,3,5-triazine. (Boiling point 1.5 mm.=116 to 119° C.)

EXAMPLE XVIII.—2-(1',1'-DIMETHYLETHYL) MER-CAPTO 4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride, 10 g. (0.11 mol) of 1'1-dimethylethyl-mercaptane and 13.5 mls. of collidine yielded 2.7 g. (11%) of 2-(1',1'-dimethylethyl) mercapto - 4,6 - dichlor - 1,3,5 - triazine. (Boiling point 0.01 mm.=80° C.)

EXAMPLE XIX.—2-(3'-METHYLBUTYL) MERCAPTO-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride, 11.0 g. (0.105 mol) of 3-methylbutyl-mercaptane and 13.5 mls. of collidine yielded 19.9 g. (79%) of 3'-methylbutyl-mercapto-4,6-dichlor-1,3,5-triazine. (Boiling point 0.005 mm.=92 to 94° C.)

EXAMPLE XX.—2N-OCTYLMERCAPTO-4,6-DICHLOR-1,3,5-TRIAZINE

In the same manner as described in Examples XII and XIII 18.45 g. (0.1 mol) of cyanuric chloride 18 g. (0.125 mol) of octyl-mercaptan and 13.5 mls. of collidine yielded 23.25 g. (79%) of 2n-octylmercapto-4,6-dichlor-1,3,5-triazine. (Boiling point 0.4 mm.=146 to 148° C.)

#### EXAMPLE XXI

A mixable oil was produced by dissolving 25 g. of 2n-butylmercapto-4,6-dichlor-1,3,5-triazine in 65 g. of xylene and by adding thereto 5 g. of an emulsifier of the type alkylphenoxy-polyglycol ether ("Triton") and 5 g. of propylene oxide the latter substance serving to bind any free hydrochloride acid. Similar mixable oils were produced of 2-isopropylamino-4,6 dichlor-1,3,5-triazine from 2n butoxy-4,6-dichlor-1,3,5-triazine. For practical use these mixable oils were diluted with water in a weight ratio varying between 1:200 and 1:40. The aqueous emulsions were used as weed-killing means in a quantity of about 10 kgs. per hectare.

#### EXAMPLE XXII

An aerosol was produced by dissolving 0.5 g. of 2n-butyl mercapto-4,6-dichlor-1,3,5 triazine in a mixture of 5 g. of xylene, 1 g. of propylene oxide, 40 g. of methylene chloride, 53.5 g. of a fluorine-chlorine-methane compound (a mixture of equal quantities of "Freon-11" and "Freon-12"). A similar aerosol was produced, which contained the same quantity of 2-(3'-methylbutyl)mercapto-4,6-dichlor-1,3,5-triazine and 2-butoxy-4,6-dichlor-1,3,5-triazine. The aerosols were used for combating insects.

What is claimed is:

1. A method of destroying insects comprising contacting said insects with an insecticidal composition containing in an insecticidally effective amount a compound corresponding to the general formula

wherein X designates a member of the group consisting of —O— and —S— and R designates a member of the group consisting of saturated aliphatic hydrocarbon radicals containing from 1 to 11 carbon atoms, the allyl radical and the cyclohexyl radical.

2. A method of destroying insects comprising contacting said insects with an insecticidal composition containing in an insecticidally effective amount a compound corresponding to the general formula:

wherein X designates —S— and R designates a member of the group consisting of saturated aliphatic hydrocarbon radicals containing from 1 to 11 carbon atoms, the allyl radical and the cyclohexyl radical.

3. A method of destroying insects comprising contacting said insects with an insecticidal composition containing in an insecticidally effective amount a compound corresponding to the general formula:

wherein X designates a member of the group consisting of —O— and —S— and R designates a member of the group consisting of saturated aliphatic hydrocarbon radicals containing from 1 to 11 carbon atoms, the allyl radical and the cyclohexyl radical and a solid carrier therefor.

4. A method of destroying insects comprising contacting said insects with an insecticidal composition containing in an insecticidally effective amount a compound corresponding to the general formula:

wherein X designates a member of the group consisting of —O— and —S— and R designates a member of the group consisting of saturated aliphatic hydrocarbon radicals containing from 1 to 11 carbon atoms, the allyl radical and the cyclohexyl radical and a liquid carrier therefor.

5. A method of destroying insects comprising contacting said insects with an insecticidal composition containing 2(n-propylmercapto)-4,6-dichloro-1,3,5-triazine in an insecticidally effective amount.

6. A method of destroying insects comprising contact-75 ing said insects with an insecticidal composition contain-

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ing 2(n-butylmercapto)-4,6-dichloro-1,3,5-triazine in an insecticidally effective amount.

7. A method of destroying insects comprising contacting said insects with an insecticidal composition containing 2(n-alkylmercapto)-4,6-dichloro-1,3,5-triazine in an insecticidally effective amount.

8. A method of destroying insects comprising contacting said insects with an insecticidal composition containing 2(n-propoxy)-4,6-dichloro-1,3,5-triazine in an insecti-

cidally effective amount.

9. A method of destroying insects comprising contacting said insects with an insecticidal composition containing 2(cyclohexyl)-4,6-dichloro-1,3,5-triazine in an insecticidally effective amount.

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