

# PATENT SPECIFICATION

NO DRAWINGS

1.181.023



Date of Application (No. 27286/68) and filing Complete Specification: 7 June, 1968.

Application made in United States of America (No. 647,234) on 19 June, 1967.

Application made in United States of America (No. 728,739) on 13 May, 1968.

Complete Specification Published: 11 Feb., 1970.

Index at acceptance:—C2 C(2D3, 2D25, 20Y, 31Y, 313, 339, 346, 366, 368, 440, 719, MV); A5 E(1C3B1, 1C3B3, 1C4A2, 1C4A3, 1C4A4, 1C4B2, 1C4B3, 1C4B4, 1C5A, 1C17)

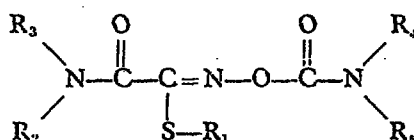
International Classification:—C 07 c 149/00

## COMPLETE SPECIFICATION

### 1-Carbamoyl-N-(Substituted-Carbamoyloxy)-Thioformimidates and their use as Pesticides

We, E. I. DU PONT DE NEMOURS & Co., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, State of Delaware, United States of America, 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:—

This invention relates to chemical pesticides and is more particularly directed to 1 - carbamoyl - N - (substituted carbamoyloxy) thioformimidates of the following formula, and their use as pesticides:



wherein

- R<sub>1</sub> represents alkyl of 1 to 4 carbon atoms or alkenyl of 3 or 4 carbon atoms;
  - R<sub>2</sub> represents hydrogen, methoxy, alkyl of 1 to 4 carbon atoms, alkenyl of 3 or 4 carbon atoms or cycloalkyl of 3 to 5 carbon atoms;
  - R<sub>3</sub> represents hydrogen, alkyl of 1 to 4 carbon atoms, or alkenyl of 3 or 4 carbon atoms; or
  - R<sub>2</sub> and R<sub>3</sub> together represent alkylene of 2 to 6 carbon atoms;
  - R<sub>4</sub> represents alkyl of 1 to 3 carbon atoms, allyl or propargyl;
  - and R<sub>5</sub> represents hydrogen or methyl;
- with the proviso that R<sub>2</sub> and R<sub>3</sub> total not more than 7 carbon atoms.

While there is an evergrowing number of chemical pesticides available to the public [Price 5s. 0d.]

there is also a continuing need for pesticides which possess a desirable combination of physical properties, a desirable combination of pesticidal activities, or a desirable combination of pesticidal activity and good tolerance for plants and mammals. Thus, for example, many of the commercial pesticides are restricted in use because of toxicity to crop plants or to animals or because of low pesticidal activity or low safety margin for the host plant.

We have discovered that the compounds of formula (1) possess a surprisingly advantageous combination of physical properties, good activity towards serious economic pests, and high crop safety margins.

Thus the compounds of formula (1) are useful in preventing the destructive effects of ticks, mites, insects and nematodes in a variety of applications, and are particularly useful in protecting plants from plant predaceous pests. They have demonstrated outstanding activity toward pests such as the boll weevil, *Anthonomus grandis* and the Southern armyworm, *Prodenia eridania*, combined with good safety margins for their host plants. In addition to high levels of safety to seeds, fruits and foliage, the compounds of formula (1) have physical characteristics which permit them to be placed at the site of nematode presence or activity readily and without disturbing plants already established. Additionally the compounds of formula (1) have demonstrated a good margin of safety to mammals and outstanding residual activity.

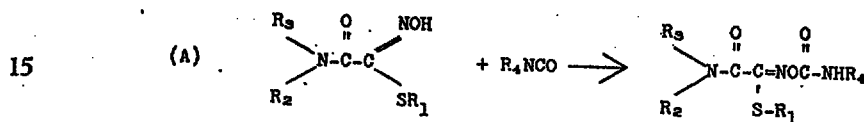
As will be recognized by those skilled in the art, the compounds of formula (1) can exist in the form of either or both of the geometric *syn* and *anti* isomers.

The compounds of formula (1) which have shown the most desirable combination of properties and activity are those wherein R<sub>2</sub> and

$R_3$  are both hydrogen or both methyl. The most preferred compounds of formula (1) are methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimidate and methyl 1 - (dimethylcarbamoyl) - N - methylcarbamoyloxythioformimidate because of their outstanding pesticidal activity and safety margin on crops.

#### PREPARATION

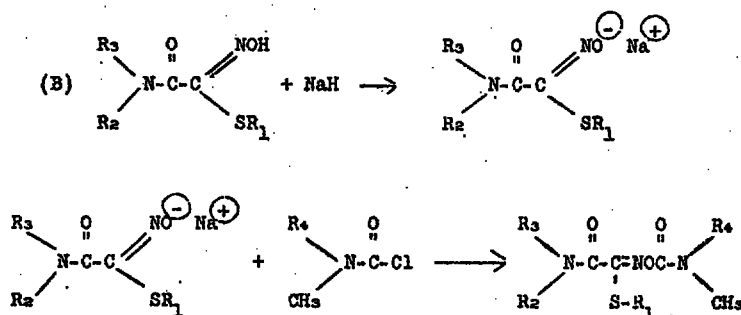
Those compounds of formula (1) wherein  $R_3$  is hydrogen can be prepared by reacting an appropriate 1 - carbamoyl - N - hydroxythioformimidate with a substituted isocyanate in an inert solvent such as acetone. This reaction is illustrated by equation (A):



A trace amount of a catalyst such as triethylamine or dibutyltin dilaurate can be used to advantage in reaction (A) for some of the thioformimidates.

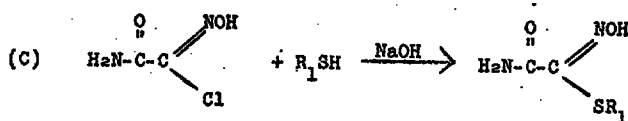
Those compounds of formula (1) wherein  $R_3$  is methyl can be prepared by reacting an

appropriate thioformimidate with sodium hydride in a solvent such as tetrahydrofuran and treating the resulting salt with a substituted carbamoyl chloride. This reaction is illustrated by equation (B):



The thioformimidate starting material for equations (A) and (B), which have both  $R_2$  and  $R_3$  as hydrogen, can be prepared by re-

action of 1-carbamoylformhydroxamyl chloride with a mercaptan in the presence of a base. This reaction is illustrated by equation (C):



The 1-carbamoylformhydroxamyl chloride can be prepared as described in Ber. 46, 2832 (1913).

An alternate procedure for the preparation of the thioformimidate starting materials is by reaction of methoxycarbonylformhydroxamyl chloride with a mercaptan in the presence of a base and then reacting the product with an appropriate amine to form the desired 1 - carbamoyl - N - hydroxythioformimidate.

#### PESTS CONTROLLED

Representative of the pests from which the compounds of formula (1) offer protection are the following insects, ticks, mites and nematodes, named in List X:

#### LIST X

##### Aphids—

Bean aphid — *Aphis fabae*  
Cabbage aphid — *Brevicoryne brassicae*  
Corn leaf aphid — *Aphis maidis*  
Corn root aphid — *Anuraphis maidiradicis*  
Cotton aphid — *Aphis gossypii*  
Green peach aphid — *Myzus persicae*  
Potato aphid — *Macrosiphum solanifolii*  
Woolly apple aphid — *Eriosoma lanigerum*

##### Armyworms—

Fall armyworm — *Laphygma frugiperda*  
Southern armyworm — *Prodenia eridania*

##### Beetles—

Asiatic ga  
Bean leaf  
Cigarette  
Colorado

Japanese  
Mexican  
Squash b  
Sugarcan  
White-fri

Boll weev  
Bollworm

##### Borers—

European  
Peach tre  
Squash v  
Sugarcar

Butterflies—  
Clouded  
Impartea

Caterpillar  
Alfalfa c  
Eastern

Curculio, p  
Earworm, c

Flea beetle  
Corn fle  
Potato f  
Tobacco  
Fleahoppe

##### Flies—

Black fl  
Hessian  
Horn fly  
House f  
Stable f

Fruit flies  
Mediter  
Mexican  
Orienta  
German c

Leaf rolle  
Fruit tr  
Red-ba

Leaf min  
Serpent

Leafhopp  
Beet le  
Potato  
Sugarc

Leafworm

(1) wherein  
d by reacting  
N - hydroxy  
ed isocyanate  
one. This re-  
(A):

h sodium hy-  
drofuran and  
a substituted  
a is illustrated

amyl chloride  
ce of a base.  
ation (C):

brassicae  
is  
maidiradicis

versicae  
solanifolii  
a lanigerum

frugiperda  
na eridania

|                                                           |    |                                                                 |     |
|-----------------------------------------------------------|----|-----------------------------------------------------------------|-----|
| Beetles—                                                  |    | Maggot, seed-corn — <i>Hylemya platura</i>                      |     |
| Asiatic garden beetle — <i>Autoserica castanea</i>        |    | Mealybugs—                                                      |     |
| Bean leaf beetle — <i>Cerotoma trifurcata</i>             |    | Citrus mealybug — <i>Pseudococcus citri</i>                     | 60  |
| Cigarette beetle — <i>Lasioderma serricorne</i>           |    | Pineapple mealybug — <i>Pseudococcus brevipes</i>               |     |
| Colorado potato beetle — <i>Leptinotarsa decemlineata</i> | 5  | Mites—                                                          |     |
| Japanese beetle — <i>Popillia japonica</i>                |    | Citrus red mite — <i>Paratetranychus citri</i>                  |     |
| Mexican bean beetle — <i>Epilachna varivestis</i>         |    | Clover mite — <i>Bryobia praetiosa</i>                          | 65  |
| Squash beetle — <i>Epilachna borealis</i>                 |    | European red mite — <i>Panonychus ulmi</i>                      |     |
| Sugarcane beetle — <i>Euethola regiceps</i>               | 10 | Pacific mite — <i>Tetranychus pacificus</i>                     |     |
| White-fringed beetle — <i>Graphognathus leucoloma</i>     |    | Two-spotted mite — <i>Tetranychus urticae</i>                   |     |
| Boll weevil — <i>Anthonomus grandis</i>                   |    | Mosquitoes—                                                     |     |
| Bollworm — <i>Heliothis zea</i>                           |    | Common malaria mosquito — <i>Anopheles quadrimaculatus</i>      | 70  |
| Borers—                                                   | 15 | Salt-marsh mosquito — <i>Aedes sollicitans</i>                  |     |
| European cornborer — <i>Pyrausta nubilalis</i>            |    | Southern house mosquito — <i>Culex pipiens quinquefasciatus</i> |     |
| Peach tree borer — <i>Sanninoidea exitiosa</i>            |    | Moths— (Damage caused by immature forms called larvae)          | 75  |
| Squash vine borer — <i>Melittia cucurbitae</i>            |    | Clothes moth — <i>Tineola biselliella</i>                       |     |
| Sugarcane borer — <i>Diatraea saccharalis</i>             |    | Codling moth — <i>Carpocapsa pomonella</i>                      |     |
| Butterflies—                                              | 20 | European pine shoot moth — <i>Rhyacionia buoliana</i>           | 80  |
| Clouded sulphur — <i>Colias philodice</i>                 |    | Grape berry moth — <i>Polychrosis viteana</i>                   |     |
| Imparted cabbageworm — <i>Pieris rapae</i>                |    | Gypsy moth — <i>Porthetria dispar</i>                           |     |
| Caterpillars—                                             |    | Melonworm — <i>Diaphania hyalinata</i>                          |     |
| Alfalfa caterpillar — <i>Colias eurytheme</i>             |    | Oriental fruit moth — <i>Grapholitha molesta</i>                |     |
| Eastern tent caterpillar — <i>Malacosoma americanum</i>   | 25 | Pickleworm — <i>Diaphania nitidalis</i>                         | 85  |
| Curculio, plum — <i>Conotrachelus nenuphar</i>            |    | Nematodes—                                                      |     |
| Earworm, corn — <i>Heliothis zea</i> (see bollworm)       |    | Awl nematode — <i>Dolichodorus heterocephalus</i>               |     |
| Flea beetles—                                             |    | Banana nematode — <i>Pratylenchus musicola</i>                  |     |
| Corn flea beetle — <i>Chaetocnema pulicaria</i>           | 30 | Bud and leaf nematodes — <i>Aphelenchoides</i> spp.             | 90  |
| Potato flea beetle — <i>Epitrix cucumeris</i>             |    | Carrot root nematode — <i>Heterodera carotae</i>                |     |
| Tobacco flea beetle — <i>Epitrix hirtipennis</i>          |    | Burrowing nematode — <i>Radopholus similis</i>                  |     |
| Fleahopper, cotton — <i>Psallus seriatius</i>             |    | Coffee root-knot nematode — <i>Meloidogyne exigua</i>           | 95  |
| Flies—                                                    |    | Corn nematode — <i>Pratylenchus zaeae</i>                       |     |
| Black fly (citrus) — <i>Aleurocanthus woglumi</i>         | 35 | Dagger nematodes — <i>Xiphinema</i> spp.                        |     |
| Hessian fly — <i>Phytophaga destructor</i>                |    | Golden nematode — <i>Heterodera rostochiensis</i>               |     |
| Horn fly — <i>Siphona irritans</i>                        |    | Grass nematode — <i>Anguina agrostis</i>                        | 100 |
| House fly — <i>Musca domestica</i>                        |    | Lance nematodes — <i>Hoplolaimus</i> spp.                       |     |
| Stable fly — <i>Stomoxys calcitrans</i>                   |    | Lesion nematodes — <i>Pratylenchus</i> spp.                     |     |
| Fruit flies—                                              | 40 | Northern root-knot nematode — <i>Meloidogyne hapla</i>          |     |
| Mediterranean fruit fly — <i>Ceratitis capitata</i>       |    | Pea root nematode — <i>Heterodera gottingiana</i>               | 105 |
| Mexican fruit fly — <i>Anastrepha ludens</i>              |    | Peanut root-knot nematode — <i>Meloidogyne arenaria</i>         |     |
| Oriental fruit fly — <i>Dacus dorsalis</i>                |    | Pin nematodes — <i>Paratylenchus</i> spp.                       |     |
| German cockroach — <i>Blattella germanica</i>             |    | Potato rot nematode — <i>Ditylenchus destructor</i>             | 110 |
| Leaf rollers—                                             | 45 | Reniform nematode — <i>Rotylenchulus reniformis</i>             |     |
| Fruit tree leaf roller — <i>Archips argyrospila</i>       |    | Rice nematode — <i>Ditylenchus angustus</i>                     |     |
| Red-banded leaf roller — <i>Argyrotaenia velutinana</i>   |    | Ring nematodes — <i>Criconeimoides</i> spp.                     | 115 |
| Leaf miners—                                              |    | Smooth-headed lesion nematode — <i>Pratylenchus brachyurus</i>  |     |
| Serpentine leaf miner — <i>Liriomyza brassicae</i>        | 50 | Southern root-knot nematode — <i>Meloidogyne incognita</i>      |     |
| Leafhoppers—                                              |    |                                                                 |     |
| Beet leafhopper — <i>Circulifer tenellus</i>              |    |                                                                 |     |
| Potato leafhopper — <i>Empoasca fabae</i>                 |    |                                                                 |     |
| Sugarcane leafhopper — <i>Perkinsiella saccharicida</i>   | 55 |                                                                 |     |
| Leafworm, cotton — <i>Alabama argillacea</i>              |    |                                                                 |     |

- Soybean cyst nematode — *Heterodera glycines*  
 Spiral nematodes — *Helicotylenchus* spp.  
 Stem and bulb nematode — *Ditylenchus dipsaci*  
 5 Sting nematodes — *Belonolaimus* spp.  
 Stubby-root nematodes — *Trichodorus* spp.  
 Sugar beet nematode — *Heterodera schachtii*  
 10 Tobacco cyst nematode — *Heterodera tabacum*  
 Tobacco stunt nematode — *Tylenchorhynchus claytoni*  
 Wheat nematode — *Anguina tritici*  
 15 Pink bollworm — *Pectinophora gossypiella*  
 Rootworms—  
 Northern corn rootworm — *Diabrotica longicornis*  
 Southern corn rootworm — *Diabrotica undecimpunctata howardi*  
 20 Western corn rootworm — *Diabrotica virgifera*  
 Thrips—  
 Onion thrips — *Thrips tabaci*  
 25 Tobacco thrips — *Frankliniella fusca*  
 Ticks—  
 American dog tick — *Dermacentor variabilis*  
 Fowl tick — *Argas persicus*  
 30 Rocky Mountain wood tick — *Dermacentor andersoni*  
 Tobacco budworm — *Heliothis virescens*  
 Weevils—  
 Alfalfa weevil — *Hypera postica*  
 35 Granary weevil — *Sitophilus granarius*  
 Rice weevil — *Sitophilus oryzae*  
 Sweetpotato weevil — *Cylas formicarius elegantulus*

#### FORMULATIONS

- 40 Compositions of this invention suitable for practical use as pesticides will include one or more compounds of formula (1) above either individually, in admixture with each other, or in admixture with other pesticides, and  
 45 can include surface-active agents, solid or liquid diluents and other materials as desired to produce e.g. wettable powders, suspensions, emulsifiable concentrates, dusts, solutions, granules, pellets or high-strength compositions.  
 50 **Surfactants**  
 The surface-active agents or surfactants, as they are sometimes called, useful in formulating the compounds of this invention act as wetting, dispersing and emulsifying agents and  
 55 assist dispersion of the active material in a spray. Additionally, the surfactants act as spreaders which aid in obtaining even coverage of the surfaces to be protected from insects and other pests. The surfactants can include such

anionic, non-ionic and cationic agents as have been used heretofore in pesticidal compositions of similar type. A detailed list of such agents is found in "Detergents and Emulsifiers 1967 Annual," (John W. McCutcheon, Inc.).

Anionic and non-ionic surfactants are preferred in formulating compounds of this invention. Among the anionic surfactants, preferred ones are alkali and alkaline earth salts of alkylarylsulfonic acids such as dodecylbenzenesulfonates and alkyl-naphthalenesulfonates, dialkyl sodium sulfosuccinate esters, sodium lauryl sulfate, sodium N-methyl-N-oleoyltaurate, sodium dodecylphenyl ether disulfonate and the oleic acid ester of sodium isethionate. Among the nonionic surfactants, preferred ones include octylphenyl polyethylene glycol ether, didecylphenyl polyethylene glycol ether, sorbitan fatty esters and their polyoxyethylene ethers, polyoxyethylene ethers and thioethers of long-chain alcohols and mercaptans as well as polyoxyethylene esters of fatty acids.

Preferred dispersants are alkali and alkaline earth salts of lignosulfonic acids, salts of polymerized alkylarylsulfonates which are sold under the names "Daxad"® and Darvan, as well as methylcellulose and polyvinyl alcohol. Words followed by a circled R superscript are Trade Marks.

Surfactants are generally used in compositions of this invention in amounts of up to 15% by weight based on the total weight of the resulting insecticidal composition.

#### Diluents

The compositions of this invention can contain, with or without a surfactant, a finely divided solid diluent such as natural silicates, e.g. talc, sepiolite, pyrophyllite; clays, e.g. montmorillonite, kaolinite, attapulgite; diatomaceous earth, synthetic magnesium silicate, synthetic silicas, calcium silicate, calcium sulfate, calcium carbonate, calcium phosphate and flours derived from natural sources such as walnut shell, redwood and cottonseed. The finely divided solids can be used in the compositions of this invention at a concentration of 2 to 98% by weight based on the total weight of the resulting pesticidal composition.

Parts, percentages and ratios in this specification are by weight unless otherwise stated.

These finely divided solid diluents can be used in the preparation of water extendable concentrates containing from 75 to 98% of a compound of this invention; dust-base concentrates of similar strength compounded for easy dilution with dusting diluents; wettable powders containing from 20 to 90% of a compound of this invention; and dusts, usually ranging in active ingredient content from 2 to 25%. Preferred finely divided solid formulations are high-strength compositions and powders containing 2 to 25% of synthetic silica and 75 to 98% active ingredients, with up to approximately 6% of one or more surfactants optionally replacing some silica.

#### Solvents

Organic liquid preparation emulsifiable concentrates in ("Cellosolve Carbitols" (Mark), ketoaffinic hydrocarbons and halogenated hydrocarbons) active compound suspension

Preferred to 30% active ingredient. Preferred amide and

Suspensions from 10 to

vention dispersants

sent to improve of such for

are general active ingredients

than about organic carrier for

soluble compounds

For aerogenated hydrocarbons and

partially refined which act

ordinarily in the range

on the total

**Granules**

Formulations pellets are

positions (1) which

a basic macroscopic

leaching granule or

Suitable origin

pyrophyllites, nut shell

anionic or For the

vention, The first

granules, granular

screened granular

a solution and will

tions up weight. in a volume

nts as have 60  
compositions  
such agents  
isifiers 1967  
ac.).  
its are pre- 65  
of this in-  
stants, pre-  
earth salts  
dodecylben-  
sulfonates, 70  
ers, sodium  
oleoyltau-  
disulfonate  
isethionate.  
ferred ones 75  
lycol ether,  
ether, sor-  
oxyethylene  
thioethers  
ans as well 80  
acids.  
nd alkaline  
lts of poly-  
re sold un-  
an, as well 85  
f alcohol.  
erscript are  
  
r composi-  
of up to 90  
weight of  
l.  
  
n can con-  
; a finely 95  
silicates,  
clays, e.g.  
ite; diato-  
n silicate,  
cium sul- 100  
phate and  
ch as wal-  
The finely  
npositions  
2 to 98% 105  
hr of the  
  
his speci-  
se stated.  
ts can be 110  
xtendable  
98% of a  
e concen-  
nded for  
wetttable 115  
)% of a  
s, usually  
rom 2 to  
formula-  
and pow- 120  
tic silica  
ith up to  
urfactants

### Solvents

Organic liquids which are suitable for the preparation of solutions, suspensions and emulsifiable concentrates of the compounds of this invention include alcohols, glycols, cellosolves ("Cellosolve" is a Registered Trade Mark), Carbitols ("Carbitol is a Registered Trade Mark), ketones, esters, sulfoxides, amides, paraffinic hydrocarbons, aromatic hydrocarbons, and halogenated hydrocarbons. Ordinarily, solvent choice is dictated by the solubility of the active compound to be used and whether a suspension or solution is desired.

Preferred solutions are those containing 5 to 30% active ingredient and 70 to 95% solvent. Preferred solvents are dimethyl formamide and dimethylsulfoxide.

Suspension formulations generally comprise from 10 to 50% of a compound of this invention dispersed in a non-solvent carrier. Dispersants and suspending agents can be present to improve the handling characteristics of such formulations. Suspension formulations are generally preferred if the solubility of the active ingredient in the liquid carrier is less than about 0.1%. In addition to non-solvent organic carriers, water can be used as a carrier for suspension concentrates of water-insoluble compounds of the invention.

For aerosol formulations low-boiling halogenated hydrocarbons are preferred as solvents and propellants, although they can be partially replaced by low boiling hydrocarbons which act as propellants. Aerosol formulations ordinarily contain an organic or aqueous liquid in the range of 80 to 98% by weight based on the total weight of the pesticidal composition.

### Granules and Pellets

Formulations in the form of granules and pellets are physically stable, particulate compositions containing a compound of formula (1) which adheres to or is distributed through a basic matrix of a coherent, inert carrier of macroscopic dimensions. In order to aid leaching of the active ingredient from the granule or pellet, a surfactant can be present.

Suitable carriers can be of mineral or organic origin such as natural clays, some pyrophyllites, vermiculite and gypsum or ground nut shell and corncob. Suitable surfactants are anionic or non-ionic.

For the granule compositions of this invention, most suitable carriers are of two types. The first are porous, absorptive, preformed granules, such as preformed and screened granular attapulgite; heat expanded, granular, screened vermiculite; screened nut shell; or granular corncob. On such preformed granules, a solution of the active agent can be sprayed and will generally be absorbed at concentrations up to 25 weight per cent of the total weight. The active agent is preferably applied in a volatile organic solvent when its solubility

permits. Ordinarily, if an organic solvent is used, it is preferably selected from methylene chloride, methyl Cellosolve and dimethyl formamide.

Preformed granules can also be treated with a melt of active ingredient if the active ingredients melting point is sufficiently below its decomposition temperature. When this means of application is used, the active ingredient in a very finely divided form is deposited on the surface of the granules such as by tumbling in a mixer. The finely divided active agent can if desired contain minor amounts of diluents such as synthetic silicas, natural clays and surface active agents. After the active agent is distributed on the granules the granules are heated to above the melting point of the active agent preferably while tumbling is continued. The granules are then cooled and contain active ingredient within, as well as fixed on, their surfaces.

The second type of carrier suitable for granules as well as pellets is initially in a powder form. Powdered kaolin clays, hydrated attapulgite, bentonite clays such as sodium, calcium and magnesium bentonite or gypsum or plaster of Paris are blended with the active ingredient and the mixtures are then granulated or pelleted. Water soluble salts can be included in the compositions to aid in disintegration of the granules and pellets in the presence of moisture. Granules or pellets can be made containing 15 to 30 weight per cent of active ingredient, but more frequently a concentration of 2 to 20 per cent is preferred for optimum distribution. Such granular compositions are most useful in a size range of 0.25 mm. to 1.4 mm.

The most preferred formulation for granules or pellets is 2 to 20 weight per cent active ingredient, 0 to 5 weight per cent surfactant and 75 to 98 per cent inert mineral carrier.

The above formulations can be prepared by methods generally used for pesticidal compositions of similar type. The solid compositions, with the exception of granules and pellets are prepared in a blending operation and will usually include passage through a grinder such as an attrition mill, a hammer mill or a fluid energy mill.

Solutions can be prepared by stirring the combined ingredients; in some cases warming may speed solution and in others cooling or pressure may be required to prevent evaporation of the solvent. Aqueous and oil suspensions can be prepared by mixing the insoluble active ingredient and other ingredients and ball milling or sand grinding the mixture to produce a concentrated slurry of very finely divided particles.

### Modifiers

Additional modifiers can be used to advantage in the compositions of this invention. Thus, although the compounds of formula (1)

are quite stable under most conditions, the use of a desiccant, buffering agent or materials such as urea, which inactive catalytic sites on diluent particles can prove desirable. Additives which will inhibit corrosion, reduce foam, reduce caking and increase flocculation can also be used. In addition, bactericides, fungicides, bacteriostats and fungistats and other insecticides, acaricides and nematocides are often desirably present in the compositions of this invention, e.g. in amounts of 0.025 to 10 parts by weight for each 1 part by weight of compound of formula (1). Suitable biologically active compounds are well known to those skilled in the art.

Of the biologically active compounds, those which are insecticides and with which compounds of formula (1) are preferably combined include DDT®; TDE; EPN; 3 - (dimethoxyphosphinyloxy) - N,N - dimethyl - cis - crotonamide; toxaphene; "Strobane"® (chlorinated terpenes having a chlorine content of ca. 66%); and endosulfan.

Fungicides and fungistats with which compounds of formula (1) are preferably combined include pentachloronitrobenzene (PCNB); thiram; dodine; maneb; methylmercury 2,3-dihydroxypropyl mercaptide; methylmercury acetate; N-ethylmercury p-toluenesulfonanilide; 1,4-dichloro-2,5-dimethoxybenzene; dimethyl ester of 2-carboxyamino-1-benzimidazolecarboxylic acid; N - trichloromethylthiotetrahydrophthalimide; N - trichloromethylthiophthalimide; sodium and calcium propionate; and 3,3' - ethylene - bis-(tetrahydro - 4,6 - dimethyl - 2H - 1,3,5 - thiadiazine - 2 - thione).

Bacteriostats and bacteriocides with which compounds of formula (1) are preferably combined include tribasic copper sulfate and streptomycin sulfate.

Specific combinations which are preferred and their area of exceptional utility include:

(a) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide and methyl O - (methylcarbamyl)thiocetohydroxamate in ratios ranging from 1:4 to 4:1 for use on cotton plants.

(b) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide or methyl 1 - (dimethylcarbamoyl) - N - methylcarbamoyloxythioformimide and 1,4 - dichloro - 2,5 - dimethoxybenzene (chloroneb) in ratios ranging from 1:6 to 6:1 for use on cotton seed.

The chloroneb can be replaced in these combinations by one of the following compounds, their mixtures with each other or their mixtures with chloroneb: pentachloronitrobenzene, captan; tetramethylthiuran disulfide; 1 - chloro - 2 - nitropropane; 5 - ethoxy - 3 - trichloromethyl - 1,2,4 - thiadiazole; and p - dimethylaminobenzene - diazo sodium sulfonate. Such combinations are useful on seeds other than cotton including both vegetable and

65

agronomic crops.

(c) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide, chloroneb, and 2 - carboxyamino - 1 - benzimidazole - carboxylic acid, dimethyl ester, in ratios ranging from 1:4:4 to 4:1:1, for use on cotton seed and other crop seed.

(d) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide and DDT®, in ratios ranging from 1:6 to 6:1 for use on cotton plants. In other combinations for this use, the DDT can be replaced by one of the following compounds, their mixtures with each other and their mixtures with DDT®; endrin; carbaryl; Malathion®; methyl parathion; parathion; "Guthion"® and toxaphene.

(e) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide and 2 - carboxylamino - 1 - benzimidazolecarboxylic acid, dimethyl ester, in ratios ranging from 1:3 to 3:1, for use on rice plants in seedbed, paddy or field for the control of insects and disease.

(f) Methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide combined with EPN, carbaryl, "Guthion"®, malathion, methyl parathion or parathion, in ratios ranging from 1:4 to 4:1, for use on rice plants.

(g) Methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide combined with DDT®, endrin, EPN, toxaphene, Malathion®, parathion, diazinon, "Guthion"®, carbaryl or methoxychlor in ratios ranging from 1:5 to 5:1, for use on potato plants or cruciferous crops. The methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide can be replaced in this combination by other compounds of formula (1) such as methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide.

(h) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide combined with parathion, aldrin, diazinon or phorate, in ratios ranging from 1:3 to 3:1 for application to soil prior to or during the planting of corn.

The methyl 1 - carbamoyl - N - (methylcarbamoyloxy) - thioformimide can be replaced in this combination by other compounds of formula (1) such as methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide.

(i) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide combined with DDT®, methoxychlor, malathion, parathion, lead arsenate, "Guthion"® carbaryl or dieldrin in ratios ranging from 1:4 to 4:1, for use on apples and other crops.

(j) Methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide combined with DDT®, carbaryl, EPN toxaphene, methoxychlor or diazinon, in ratios ranging from 1:5 to 5:1 for use on corn plants.

(k) Methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide combined with TDE, DDT®, "Guthion"®, Malathion®, diazinon, parathion or carbaryl, in ratios ranging from 1:6 to 6:1, for use on tobacco plants in seedbed or field.

(l) Methyl carbamoyloxy in ratios ranging from 1:4 to 4:1, for use on sugarcane seed of planting.

(m) Methyl carbamoyloxy toxaphene, in ratios ranging from 1:6 to 6:1 for use on sugarcane.

(n) Methyl carbamoyloxy methoxychlor or toxaphene in ratios ranging from 1:4 to 4:1, for use on sugarcane.

(o) Methyl carbamoyloxy chlordane, in ratios ranging from 1:4 to 4:1, for use on sugarcane prior to or during the planting of sugarcane.

The use of the compounds of formula (1) in combination with other compounds of formula (1) is true when the combined volume of a nematodes combination with pesticide dimethoxy carbamate are present.

In applying for pest control applied in desired proportions required to be governed by the time of the and pest is not possible of application factory. It generally rates of a and to which are best suited.

Thus, it is used to control mites by those plants are to be treated. Due and animal of formula without damage to Use rates generally in active ingredient 17 kilograms

- (methyl-  
proneb, and  
azole - car-  
bios ranging  
cotton seed 70

- (methyl-  
DDT®, in  
for use on  
ms for this  
one of the  
s with each  
®; endrin;  
parathion;  
hene. 80

- (methyl-  
2 - car-  
oxylic acid,  
om 1:3 to  
bed, paddy  
nd disease.  
(dimethyl-  
bined with  
malathion,  
atios rang-  
rice plants.  
(dimethyl-  
bined with  
ae, Mala-  
uthion"®,  
es ranging  
o plants or  
arbamoyl -  
rmimide  
n by other  
methyl 1 -  
yloxy)thio- 100

- (methyl-  
bined with 105  
e, in ratios  
lication to  
g of corn.  
methylcar-  
e replaced 110  
pounds of  
urbamoyl -  
rmimide.  
- (methyl-  
bined with 115  
parathion,  
il or diel-  
:1, for use

(dimethyl- 120  
bined with  
methoxy-  
from 1:5

- (methyl- 125  
bined with  
lathion,®  
atios rang-  
cco plants 130

- (l) Methyl 1 - carbamoyl - N - (dimethyl-  
carbamoyloxy)thioformimide and chlordane,  
in ratios ranging from 1:8 to 8:1, for use on  
of planting. 5
- (m) Methyl 1 - carbamoyl - N - (methyl-  
carbamoyloxy)thioformimide combined with  
toxaphene, carbaryl, endrin, or "Guthion"®,  
in ratios ranging from 1:12 to 12:1, for use  
on sugarcane foliage. 10
- (n) Methyl 1 - carbamoyl - N - (dimethyl-  
carbamoyloxy)thioformimide combined with  
methoxychlor, carbaryl, Malathion®, DDT®  
or toxaphene, in ratios ranging from 1:4 to  
4:1, for use on shade trees or forest lands. 15
- (o) Methyl 1 - carbamoyl - N - (methyl-  
carbamoyloxy)thioformimide combined with  
chlordane, DDT®, diazinon or parathion, in  
ratios ranging from 1:5 to 5:1, for use in soil  
prior to or during planting of potatoes. 20
- The use of other agents, such as those men-  
tioned above, in combination with the com-  
pounds of formula (1) can offer an unexpected  
degree of plant protection. This is especially  
true when the compounds of formula (1) are  
combined with a fungicide and applied to the  
locus of a plant where both plant-parasitic  
nematodes and fungi are present. Thus, the  
combination of the compounds of formula (1)  
with pesticides such as 1,4 - dichloro - 2,5 -  
dimethoxy benzene, methyl N - methylthiol-  
carbamate and 1,2 - dibromo - 3 - chloropro-  
pane are particularly preferred combinations. 30

#### APPLICATION

- In applying the compounds of formula (1)  
for pest control, the compound is of course  
applied in an amount sufficient to exert the  
desired pesticidal action. The amounts re-  
quired to give pest control action however are  
governed by such variables as temperature,  
time of the year, moisture, type of application  
and pest species to be controlled. Thus it is  
not possible to state any one method or rate  
of application which would be generally satis-  
factory. It is possible however to describe  
generally some of the various methods and  
rates of application for certain areas of use  
and to which the compounds of formula (1)  
are best suited. 35
- Thus, the compounds of formula (1) can be  
used to control plant-predacious insects and  
mites by distributing the chemical evenly over  
those plant surfaces which are infested or which  
are to be protected from subsequent infesta-  
tion. Due to the margin of safety for plants  
and animals characteristic of the compounds  
of formula (1) such applications can be made  
without danger to the applicator or fear of  
damage to the plant when used as directed. 40
- Use rates for this type of application are gen-  
erally in the range of 0.05 to 34 kilograms of  
active ingredient per hectare. Rates of 0.1 to  
17 kilograms per hectare are preferred and 45

rates of 0.2 to 8 kilograms per hectare are  
most preferred for reasons of convenience and  
economy. This type of application may need to  
be repeated at intervals of 3 to 20 days. Such  
applications can be made with any of a variety  
of widely-available types of equipment ordinari-  
ly used for such applications. 65

Other effective methods of application in-  
clude: 70

a. To the seed of agricultural, horticultural  
and ornamental crops to protect the seed dur-  
ing storage and shipping prior to planting as  
well as to protect the seed and seedlings from  
attack by insects and mites after planting. The  
preferred rates for application to seed are in  
the range of 0.06 gram to 3 kilograms of the  
active compound of this invention per 100  
kilograms of seed. The most preferred rates  
are in the range of 0.6 to 600 grams per 100  
kilograms of seed. 75

b. To soil in which plants are to be  
planted or are growing to protect seed and  
plants from attack by insects and mites. Such  
protection is against both soil insects attack-  
ing the roots and insects and mites attacking  
the above-ground parts of the plants. Preferred  
use rates are in the range of 0.1 to 60 kilo-  
grams of active ingredient per hectare treated.  
The most preferred rates are in the range of  
0.3 to 20 kilograms per hectare. 80

c. To the walls and floors of structures  
such as warehouses, stores, recreation buildings,  
factories, homes, poultry houses and barns to  
control insects, ticks and mites which could  
damage contents as well as attack or annoy  
people or domestic animals. Applications to  
be repeated as needed. 85

d. To insects, ticks and mites that cause  
injury or annoyance, or carry disease to ani-  
mals. The compounds of this invention can be  
applied to the animals to be protected by  
sprays, dusts or dips in such a way as to give  
a more or less uniform coating. Applications  
to be repeated as needed. 90

e. To land areas (including marsh or  
swamp) for the control of insects, ticks or  
mites causing injury or annoyance or dis-  
seminating disease to humans or animals. Pre-  
ferred use rates are in the range of 0.01 to  
10 kilograms of active compound of this in-  
vention per hectare 1 to 5 times a year. The  
most preferred rates are in the range of .03 to  
3 kilograms of active compound per hectare  
on the same schedule. 95

The compounds of formula (1) are also well  
suited to the control of plant-parasitic nema-  
todes inhabiting soil in which the plants are  
planted or are to be planted. The physical  
characteristics of the compounds of formula (1)  
permit them to be placed readily at the site of  
nematode presence or activity without disturb-  
ing already established plants. The physical  
nature of the compounds of formula (1) per-  
mit their movement deep into undisturbed soil  
around plant roots, often the site of nematode 100

attack. The safety margin for plants make practical such application as well as application to soil being prepared for planting and application directly to seeds and growing plants at rates well above those required to control the nematodes.

Use rates for application to soil in which plants are growing are generally the same as those for application to soil being prepared for planting. Such rates range from about 0.15 to 225 kilograms of active ingredient per hectare of surface actually treated. Rates of 0.25 to 55 kilograms per hectare are most preferred for these uses for reasons of convenience and economy.

Other methods of applying the compounds of formula (1) to prevent the destructive effects of plant-parasitic nematodes include: spraying above-ground parts such as stems, leaves or buds in which nematodes are already present or where later attack is possible; dipping or soaking reproductive parts such as seeds, cane pieces or bulbs (which are already infested or are to be planted in infested soil) in a water suspension, solution or emulsion of the active ingredient; or immersing the root system or the entire plant of nursery stock or transplants in a water system to disinfest them or provide protection against subsequent nematode invasion. The rates of active ingredient in the sprays or dips used as noted just above are generally 12 grams to 4.8 kilograms per 100 liters of water. Preferred rates are in the range of 30 grams to 1.2 kilograms per 100 liters.

In all of the applications discussed above,

the distribution of the compounds of this invention may be simplified and made more accurate and economical by use of formulations as discussed previously.

The following Examples further illustrate the invention.

#### EXAMPLE 1

A mixture of 12.3 parts of 1 - carbamoyl-formhydroxamyl chloride, 79.2 parts of methanol and 10 parts of water is cooled to 5°C. and treated with 7 parts of methyl mercaptan. To this mixture is then added gradually at -5 to 0°C., 8 parts of 50% aqueous sodium hydroxide which increases the pH to 8. The sodium chloride formed is filtered off and the filtrate concentrated until crystals form. The mixture is cooled well and filtered to give methyl 1 - carbamoyl - N - hydroxythioformimidate melting at 163—164°C.

To a suspension of 4.5 parts of the methyl 1-carbamoyl-N-hydroxythioformimidate and 2.2 parts of methyl isocyanate in 20 parts of acetone is added a trace of Dabco®, 1,4 - diazabicyclo - [2.2.2] - octane. The reaction temperature rises to 55°C. and then subsides and a white solid forms. After several hours at room temperature the mixture is filtered, giving methyl 1 - carbamoyl - N - (methyl-carbamoyloxy)thioformimidate melting at 162—164°C.

The compounds of Table I are prepared by the procedures of Example 1 using the mercaptans and isocyanates listed in place of the methyl mercaptan and methyl isocyanate of Example 1.

40

45

50

55

60

65

70

TABLE I

## Product

## Isocyanate

## Mercaptan

ethyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimidate

allyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimidate

methyl isocyanate

methyl isocyanate

ethyl mercaptan

allyl mercaptan

of this in-  
made more  
formulations  
r illustrate

carbamoyl-  
is of meth-  
ed to 50°C.  
mercaptan,  
actually at  
us sodium  
to 8. The  
ff and the  
form. The  
d to give  
xythiofor-  
the methyl  
late and  
0 parts of  
; 1,4-di-  
c reaction  
n subsides  
utal hours  
is filtered,  
- (methyl-  
ng at 162  
65  
prepared  
the mer-  
ace of the  
yanate of  
70

TABLE I

| Mercaptan            | Isocyanate           | Product                                                    |
|----------------------|----------------------|------------------------------------------------------------|
| ethyl mercaptan      | methyl isocyanate    | ethyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide      |
| allyl mercaptan      | methyl isocyanate    | allyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide      |
| but-2-enyl mercaptan | ethyl isocyanate     | but-2-enyl 1-carbamoyl-N-(ethylcarbamoyloxy)thioformimide  |
| isopropyl mercaptan  | allyl isocyanate     | isopropyl 1-carbamoyl-N-(allylcarbamoyloxy)thioformimide   |
| methyl mercaptan     | propargyl isocyanate | methyl 1-carbamoyl-N-(propargylcarbamoyloxy)thioformimide  |
| propyl mercaptan     | methyl isocyanate    | propyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide     |
| allyl mercaptan      | allyl isocyanate     | allyl 1-carbamoyl-N-(allylcarbamoyloxy)thioformimide       |
| isopropyl mercaptan  | methyl isocyanate    | isopropyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide  |
| butyl mercaptan      | methyl isocyanate    | butyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide      |
| sec. butyl mercaptan | methyl isocyanate    | sec-butyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide  |
| tert-butyl mercaptan | methyl isocyanate    | tert-butyl 1-carbamoyl-N-(methylcarbamoyloxy)thioformimide |
| methyl mercaptan     | ethyl isocyanate     | methyl 1-carbamoyl-N-(ethylcarbamoyloxy)thioformimide      |
| butyl mercaptan      | ethyl isocyanate     | butyl 1-carbamoyl-N-(ethylcarbamoyloxy)thioformimide       |
| methyl mercaptan     | isopropyl isocyanate | methyl 1-carbamoyl-N-(isopropylcarbamoyloxy)thioformimide  |
| butyl mercaptan      | isopropyl isocyanate | butyl 1-carbamoyl-N-(isopropylcarbamoyloxy)thioformimide   |
| allyl mercaptan      | isopropyl isocyanate | allyl 1-carbamoyl-N-(isopropylcarbamoyloxy)thioformimide   |
| allyl mercaptan      | n-propyl isocyanate  | allyl 1-carbamoyl-N-(n-propylcarbamoyloxy)thioformimide    |
| methyl mercaptan     | allyl isocyanate     | methyl 1-carbamoyl-N-(allylcarbamoyloxy)thioformimide      |
| butyl mercaptan      | allyl isocyanate     | butyl 1-carbamoyl-N-(allylcarbamoyloxy)thioformimide       |
| allyl mercaptan      | propargyl isocyanate | allyl 1-carbamoyl-N-(propargylcarbamoyloxy)thioformimide   |

## EXAMPLE 2

Methyl 1-(dimethylcarbamoyl)-N-(methylcarbamoyloxy)-thioformimide

5 A solution of 206 parts of methylglyoxalate oxime in 1500 parts of water is treated at 0 to -5°C. with 145 parts of chlorine in about 37 minutes. An oil of 1 - (methoxycarbonyl)-formhydroxamyl chloride is formed, which can be isolated by extraction with methylene chloride, evaporation of the methylene chloride and recrystallization from benzene, M.P. 63—65°C.

10 To the suspension of 1 - (methoxycarbonyl)-formhydroxamyl chloride in water as obtained above are added at 0 to -5°C. 105 parts of methyl mercaptan followed by 130 parts of 50% aqueous sodium hydroxide mixed with 330 parts of water. The resulting two-phase reaction mass is then extracted with methylene chloride. Removal of the solvent under reduced pressure leaves the solid methyl 1 - methoxycarbonyl - N - hydroxythioformimide, which can be recrystallized from benzene, M.P. 63—64°C.

25 The crude methyl 1 - methoxycarbonyl - N - hydroxythioformimide obtained above is 250 parts of methanol and 180 parts of anhydrous dimethylamine dissolved in the solu-

tion below 30°C. This solution is allowed to stand at ambient temperature overnight. Removal of excess dimethylamine and the solvent under reduced pressure leaves 240 parts (74%) of methyl 1 - (dimethylcarbamoyl) - N - hydroxythioformimide. 30

To a suspension of 70 part of methyl 1 - (dimethylcarbamoyl) - N - hydroxythioformimide and 1/2 part of Dabco® in 350 parts of acetone at 40°C. is added slowly 27 parts of methyl isocyanate. The temperature of the reaction mixture rises to 58°C. After the temperature of the reaction mass has subsided to 25°C., the solvent is evaporated under reduced pressure, and the resulting residue recrystallized. Recrystallization from benzene gives one isomer of methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide of M.P. 109—110°C. Recrystallization from water gives the other isomer of methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide of M.P. 101—103°C. 35 40 45 50

The compounds of Table II are prepared according to the procedures of Examples 1 and 2 using the mercaptans, amines, and isocyanates listed in place of methyl mercaptan, dimethylamine and methyl isocyanate. 55

is allowed to  
vernigh. Re-  
id the solvent  
1 parts (74%)  
d) - N - hy-  
f methyl 1 -  
xythioformi-  
in 350 parts  
why 27 parts  
rature of the  
fier the tem-  
s subsided to  
nder reduced  
ue recrystal-  
ene gives one  
carbamoyl) -  
formimide  
ization from  
methyl 1 -  
ylcarbamoyl-  
101-103°C.  
are prepared  
amples 1 and  
and isocyan-  
ercaptan, di-  
te.

10

11

1,181,023

11

TABLE II

| Mercaptan           | Amine                      | Isocyanate           | Product                                                                  |
|---------------------|----------------------------|----------------------|--------------------------------------------------------------------------|
| methyl mercaptan    | methylamine                | methyl isocyanate    | methyl 1-(methylcarbamoyl)-N-(methylcarbamoyl-oxy)thioformimide          |
| methyl mercaptan    | butylamine                 | methyl isocyanate    | methyl 1-(butylcarbamoyl)-N-(methylcarbamoyl-oxy)thioformimide           |
| isopropyl mercaptan | cyclopropylamine           | methyl isocyanate    | isopropyl 1-(cyclopropylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide   |
| allyl mercaptan     | N,O-dimethyl-hydroxylamine | ethyl isocyanate     | allyl 1-(N-methoxy-N-methylcarbamoyl)-N-(ethylcarbamoyloxy)thioformimide |
| butyl mercaptan     | allylamine                 | ethyl isocyanate     | butyl 1-(allylcarbamoyl)-N-ethylcarbamoyloxy)-thioformimide              |
| methyl mercaptan    | diallylamine               | allyl isocyanate     | methyl 1-(diallylcarbamoyl)-N-(allylcarbamoyloxy)-thioformimide          |
| ethyl mercaptan     | isopropylamine             | allyl isocyanate     | ethyl 1-(isopropylcarbamoyl)-N-(allylcarbamoyloxy)thioformimide          |
| methyl mercaptan    | ethylamine                 | propargyl isocyanate | methyl 1-(ethylcarbamoyl)-N-(propargylcarbamoyloxy)thioformimide         |
| methyl mercaptan    | diethylamine               | methyl isocyanate    | methyl 1-(diethylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide          |
| methyl mercaptan    | diisopropylamine           | methyl isocyanate    | methyl 1-(diisopropylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide      |
| ethyl mercaptan     | but-2-enylamine            | isopropyl isocyanate | ethyl 1-(2-enylcarbamoyl)-N-isopropylcarbamoyloxy)-thioformimide         |

(2)

TABLE II (Continued)

| Mercaptan        | Amine                      | Isocyanate           | Product                                                                    |
|------------------|----------------------------|----------------------|----------------------------------------------------------------------------|
| methyl mercaptan | aziridine                  | methyl isocyanate    | methyl 1-(aziridinocarbonyl)-N-(methyl-carbamoyloxy)thioformimide          |
| methyl mercaptan | hexahydroazepine           | methyl isocyanate    | methyl 1-(hexahydroazepinocarbonyl)-N-(methyl-carbamoyloxy)thioformimide   |
| methyl mercaptan | pyrrolidine                | methyl isocyanate    | methyl 1-(pyrrolidinocarbonyl)-N-(methyl-carbamoyloxy)thioformimide        |
| methyl mercaptan | methylamine                | allyl isocyanate     | methyl 1-(methylcarbamoyl)-N-(allylcarbamoyloxy)-thioformimide             |
| methyl mercaptan | dimethylamine              | propargyl isocyanate | methyl 1-(dimethylcarbamoyl)-N-(propargyl-carbamoyloxy)thioformimide       |
| methyl mercaptan | allylamine                 | propargyl isocyanate | methyl 1-(allylcarbamoyl)-N-(propargyl-carbamoyloxy)thioformimide          |
| methyl mercaptan | N,O-dimethyl-hydroxylamine | methyl isocyanate    | methyl 1-(N-methoxy-N-methylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide |
| methyl mercaptan | N-methylethylamine         | allyl isocyanate     | methyl 1-(N-methyl-N-ethylcarbamoyl)-N-(allylcarbamoyloxy)thioformimide    |
| ethyl mercaptan  | piperidine                 | allyl isocyanate     | ethyl 1-(piperidinocarbonyl)-N-(allylcarbamoyloxy)-thioformimide           |
| butyl mercaptan  | piperidine                 | methyl isocyanate    | butyl 1-(piperidinocarbonyl)-N-(methyl-carbamoyloxy)thioformimide          |
| methyl mercaptan | N-methylbutylamine         | methyl isocyanate    | methyl 1-(N-methyl-N-butylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide   |
| methyl mercaptan | N-methylallylamine         | methyl isocyanate    | methyl 1-(N-methyl-N-allylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide   |

To a solution of sodium hydride of tetrahydrofuran, a one hour temperature subsidence of dimethylamine at 100°C for one hour.

## EXAMPLE 3

- 5 To a stirred suspension of 48 parts of 50% sodium hydride and mineral oil in 648 parts of tetrahydrofuran is added portion-wise over a one hour period 114 parts of methyl 1 - carbamoyl - N - hydroxythioformimide. The temperature is maintained at 20—30°C. After subsidence of hydrogen evolution, 107.5 parts of dimethylcarbamoyl chloride is added drop-wise at 15—25°C. Stirring is continued for one hour after the completion of addition. The
- 10

inorganic solids are then removed by filtration and the methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide is recovered by removal of the solvent under reduced pressure. 15

The compounds of Table III are prepared according to the procedures of Example 3 using the N-hydroxythioformimidates and carbamoyl chlorides listed in place of methyl 1 - carbamoyl - N - hydroxythioformimide and dimethylcarbamoyl chloride. 20

(methylcarbamoyloxy)thioformimide  
methyl 1-(N-methyl-N-allylcarbamoyl)-N-(methylcarbamoyloxy)thioformimide

methyl isocyanate

N-methylallylamine

methyl mercaptan

TABLE III

| N-hydroxythioformimide                               | Carbamoyl Chloride                     | Product                                                               |
|------------------------------------------------------|----------------------------------------|-----------------------------------------------------------------------|
| methyl 1-carbamoyl-N-hydroxythioformimide            | N-allyl-N-methylcarbamoyl chloride     | methyl 1-carbamoyl-N-(N-allyl-N-methylcarbamoyloxy)thioformimide      |
| methyl 1-carbamoyl-N-hydroxythioformimide            | N-methyl-N-propargylcarbamoyl chloride | methyl 1-carbamoyl-N-(N-methyl-N-propargylcarbamoyloxy)thioformimide  |
| methyl 1-carbamoyl-N-hydroxythioformimide            | N-methyl-N-propylcarbamoyl chloride    | methyl 1-carbamoyl-N-(N-methyl-N-propylcarbamoyloxy)thioformimide     |
| methyl 1-carbamoyl-N-hydroxythioformimide            | N-ethyl-N-methylcarbamoyl chloride     | methyl 1-carbamoyl-N-(N-ethyl-N-methylcarbamoyloxy)thioformimide      |
| methyl 1-methylcarbamoyl-N-hydroxythioformimide      | dimethylcarbamoyl chloride             | methyl 1-(methylcarbamoyl)-N-(dimethylcarbamoyloxy)thioformimide      |
| methyl 1-dimethylcarbamoyl-N-hydroxythioformimide    | dimethylcarbamoyl chloride             | methyl 1-(dimethylcarbamoyl)-N-(dimethylcarbamoyloxy)thioformimide    |
| methyl 1-cyclopentylcarbamoyl-N-hydroxythioformimide | dimethylcarbamoyl chloride             | methyl 1-(cyclopentylcarbamoyl)-N-(dimethylcarbamoyloxy)thioformimide |
| propyl 1-carbamoyl-N-hydroxythioformimide            | dimethylcarbamoyl chloride             | propyl 1-carbamoyl-N-(dimethylcarbamoyloxy)thioformimide              |
| ethyl 1-carbamoyl-N-hydroxythioformimide             | dimethylcarbamoyl chloride             | ethyl 1-carbamoyl-N-(dimethylcarbamoyloxy)thioformimide               |
| butyl 1-carbamoyl-N-hydroxythioformimide             | dimethylcarbamoyl chloride             | butyl 1-carbamoyl-N-(dimethylcarbamoyloxy)thioformimide               |
| methyl 1-piperidinocarbonyl-N-hydroxythioformimide   | dimethylcarbamoyl chloride             | methyl 1-piperidinocarbonyl-N-(dimethylcarbamoyloxy)thioformimide     |
| allyl 1-carbamoyl-N-hydroxythioformimide             | dimethylcarbamoyl chloride             | allyl 1-carbamoyl-N-(dimethylcarbamoyloxy)thioformimide               |
| but-2-enyl 1-carbamoyl-N-hydroxythioformimide        | dimethylcarbamoyl chloride             | but-2-enyl 1-carbamoyl-N-(dimethylcarbamoyloxy)thioformimide          |

14

1,181,023

14

15  
 14  
 13  
 12  
 11  
 10  
 9  
 8  
 7  
 6  
 5  
 4  
 3  
 2  
 1  
 0  
 -1  
 -2  
 -3  
 -4  
 -5  
 -6  
 -7  
 -8  
 -9  
 -10  
 -11  
 -12  
 -13  
 -14  
 -15  
 -16  
 -17  
 -18  
 -19  
 -20  
 -21  
 -22  
 -23  
 -24  
 -25  
 -26  
 -27  
 -28  
 -29  
 -30  
 -31  
 -32  
 -33  
 -34  
 -35  
 -36  
 -37  
 -38  
 -39  
 -40  
 -41  
 -42  
 -43  
 -44  
 -45  
 -46  
 -47  
 -48  
 -49  
 -50  
 -51  
 -52  
 -53  
 -54  
 -55  
 -56  
 -57  
 -58  
 -59  
 -60  
 -61  
 -62  
 -63  
 -64  
 -65  
 -66  
 -67  
 -68  
 -69  
 -70  
 -71  
 -72  
 -73  
 -74  
 -75  
 -76  
 -77  
 -78  
 -79  
 -80  
 -81  
 -82  
 -83  
 -84  
 -85  
 -86  
 -87  
 -88  
 -89  
 -90  
 -91  
 -92  
 -93  
 -94  
 -95  
 -96  
 -97  
 -98  
 -99  
 -100  
 -101  
 -102  
 -103  
 -104  
 -105  
 -106  
 -107  
 -108  
 -109  
 -110  
 -111  
 -112  
 -113  
 -114  
 -115  
 -116  
 -117  
 -118  
 -119  
 -120  
 -121  
 -122  
 -123  
 -124  
 -125  
 -126  
 -127  
 -128  
 -129  
 -130  
 -131  
 -132  
 -133  
 -134  
 -135  
 -136  
 -137  
 -138  
 -139  
 -140  
 -141  
 -142  
 -143  
 -144  
 -145  
 -146  
 -147  
 -148  
 -149  
 -150  
 -151  
 -152  
 -153  
 -154  
 -155  
 -156  
 -157  
 -158  
 -159  
 -160  
 -161  
 -162  
 -163  
 -164  
 -165  
 -166  
 -167  
 -168  
 -169  
 -170  
 -171  
 -172  
 -173  
 -174  
 -175  
 -176  
 -177  
 -178  
 -179  
 -180  
 -181  
 -182  
 -183  
 -184  
 -185  
 -186  
 -187  
 -188  
 -189  
 -190  
 -191  
 -192  
 -193  
 -194  
 -195  
 -196  
 -197  
 -198  
 -199  
 -200  
 -201  
 -202  
 -203  
 -204  
 -205  
 -206  
 -207  
 -208  
 -209  
 -210  
 -211  
 -212  
 -213  
 -214  
 -215  
 -216  
 -217  
 -218  
 -219  
 -220  
 -221  
 -222  
 -223  
 -224  
 -225  
 -226  
 -227  
 -228  
 -229  
 -230  
 -231  
 -232  
 -233  
 -234  
 -235  
 -236  
 -237  
 -238  
 -239  
 -240  
 -241  
 -242  
 -243  
 -244  
 -245  
 -246  
 -247  
 -248  
 -249  
 -250  
 -251  
 -252  
 -253  
 -254  
 -255  
 -256  
 -257  
 -258  
 -259  
 -260  
 -261  
 -262  
 -263  
 -264  
 -265  
 -266  
 -267  
 -268  
 -269  
 -270  
 -271  
 -272  
 -273  
 -274  
 -275  
 -276  
 -277  
 -278  
 -279  
 -280  
 -281  
 -282  
 -283  
 -284  
 -285  
 -286  
 -287  
 -288  
 -289  
 -290  
 -291  
 -292  
 -293  
 -294  
 -295  
 -296  
 -297  
 -298  
 -299  
 -300  
 -301  
 -302  
 -303  
 -304  
 -305  
 -306  
 -307  
 -308  
 -309  
 -310  
 -311  
 -312  
 -313  
 -314  
 -315  
 -316  
 -317  
 -318  
 -319  
 -320  
 -321  
 -322  
 -323  
 -324  
 -325  
 -326  
 -327  
 -328  
 -329  
 -330  
 -331  
 -332  
 -333  
 -334  
 -335  
 -336  
 -337  
 -338  
 -339  
 -340  
 -341  
 -342  
 -343  
 -344  
 -345  
 -346  
 -347  
 -348  
 -349  
 -350  
 -351  
 -352  
 -353  
 -354  
 -355  
 -356  
 -357  
 -358  
 -359  
 -360  
 -361  
 -362  
 -363  
 -364  
 -365  
 -366  
 -367  
 -368  
 -369  
 -370  
 -371  
 -372  
 -373  
 -374  
 -375  
 -376  
 -377  
 -378  
 -379  
 -380  
 -381  
 -382  
 -383  
 -384  
 -385  
 -386  
 -387  
 -388  
 -389  
 -390  
 -391  
 -392  
 -393  
 -394  
 -395  
 -396  
 -397  
 -398  
 -399  
 -400  
 -401  
 -402  
 -403  
 -404  
 -405  
 -406  
 -407  
 -408  
 -409  
 -410  
 -411  
 -412  
 -413  
 -414  
 -415  
 -416  
 -417  
 -418  
 -419  
 -420  
 -421  
 -422  
 -423  
 -424  
 -425  
 -426  
 -427  
 -428  
 -429  
 -430  
 -431  
 -432  
 -433  
 -434  
 -435  
 -436  
 -437  
 -438  
 -439  
 -440  
 -441  
 -442  
 -443  
 -444  
 -445  
 -446  
 -447  
 -448  
 -449  
 -450  
 -451  
 -452  
 -453  
 -454  
 -455  
 -456  
 -457  
 -458  
 -459  
 -460  
 -461  
 -462  
 -463  
 -464  
 -465  
 -466  
 -467  
 -468  
 -469  
 -470  
 -471  
 -472  
 -473  
 -474  
 -475  
 -476  
 -477  
 -478  
 -479  
 -480  
 -481  
 -482  
 -483  
 -484  
 -485  
 -486  
 -487  
 -488  
 -489  
 -490  
 -491  
 -492  
 -493  
 -494  
 -495  
 -496  
 -497  
 -498  
 -499  
 -500  
 -501  
 -502  
 -503  
 -504  
 -505  
 -506  
 -507  
 -508  
 -509  
 -510  
 -511  
 -512  
 -513  
 -514  
 -515  
 -516  
 -517  
 -518  
 -519  
 -520  
 -521  
 -522  
 -523  
 -524  
 -525  
 -526  
 -527  
 -528  
 -529  
 -530  
 -531  
 -532  
 -533  
 -534  
 -535  
 -536  
 -537  
 -538  
 -539  
 -540  
 -541  
 -542  
 -543  
 -544  
 -545  
 -546  
 -547  
 -548  
 -549  
 -550  
 -551  
 -552  
 -553  
 -554  
 -555  
 -556  
 -557  
 -558  
 -559  
 -560  
 -561  
 -562  
 -563  
 -564  
 -565  
 -566  
 -567  
 -568  
 -569  
 -570  
 -571  
 -572  
 -573  
 -574  
 -575  
 -576  
 -577  
 -578  
 -579  
 -580  
 -581  
 -582  
 -583  
 -584  
 -585  
 -586  
 -587  
 -588  
 -589  
 -590  
 -591  
 -592  
 -593  
 -594  
 -595  
 -596  
 -597  
 -598  
 -599  
 -600  
 -601  
 -602  
 -603  
 -604  
 -605  
 -606  
 -607  
 -608  
 -609  
 -610  
 -611  
 -612  
 -613  
 -614  
 -615  
 -616  
 -617  
 -618  
 -619  
 -620  
 -621  
 -622  
 -623  
 -624  
 -625  
 -626  
 -627  
 -628  
 -629  
 -630  
 -631  
 -632  
 -633  
 -634  
 -635  
 -636  
 -637  
 -638  
 -639  
 -640  
 -641  
 -642  
 -643  
 -644  
 -645  
 -646  
 -647  
 -648  
 -649  
 -650  
 -651  
 -652  
 -653  
 -654  
 -655  
 -656  
 -657  
 -658  
 -659  
 -660  
 -661  
 -662  
 -663  
 -664  
 -665  
 -666  
 -667  
 -668  
 -669  
 -670  
 -671  
 -672  
 -673  
 -674  
 -675  
 -676  
 -677  
 -678  
 -679  
 -680  
 -681  
 -682  
 -683  
 -684  
 -685  
 -686  
 -687  
 -688  
 -689  
 -690  
 -691  
 -692  
 -693  
 -694  
 -695  
 -696  
 -697  
 -698  
 -699  
 -700  
 -701  
 -702  
 -703  
 -704  
 -705  
 -706  
 -707  
 -708  
 -709  
 -710  
 -711  
 -712  
 -713  
 -714  
 -715  
 -716  
 -717  
 -718  
 -719  
 -720  
 -721  
 -722  
 -723  
 -724  
 -725  
 -726  
 -727  
 -728  
 -729  
 -730  
 -731  
 -732  
 -733  
 -734  
 -735  
 -736  
 -737  
 -738  
 -739  
 -740  
 -741  
 -742  
 -743  
 -744  
 -745  
 -746  
 -747  
 -748  
 -749  
 -750  
 -751  
 -752  
 -753  
 -754  
 -755  
 -756  
 -757  
 -758  
 -759  
 -760  
 -761  
 -762  
 -763  
 -764  
 -765  
 -766  
 -767  
 -768  
 -769  
 -770  
 -771  
 -772  
 -773  
 -774  
 -775  
 -776  
 -777  
 -778  
 -779  
 -780  
 -781  
 -782  
 -783  
 -784  
 -785  
 -786  
 -787  
 -788  
 -789  
 -790  
 -791  
 -792  
 -793  
 -794  
 -795  
 -796  
 -797  
 -798  
 -799  
 -800  
 -801  
 -802  
 -803  
 -804  
 -805  
 -806  
 -807  
 -808  
 -809  
 -810  
 -811  
 -812  
 -813  
 -814  
 -815  
 -816  
 -817  
 -818  
 -819  
 -820  
 -821  
 -822  
 -823  
 -824  
 -825  
 -826  
 -827  
 -828  
 -829  
 -830  
 -831  
 -832  
 -833  
 -834  
 -835  
 -836  
 -837  
 -838  
 -839  
 -840  
 -841  
 -842  
 -843  
 -844  
 -845  
 -846  
 -847  
 -848  
 -849  
 -850  
 -851  
 -852  
 -853  
 -854  
 -855  
 -856  
 -857  
 -858  
 -859  
 -860  
 -861  
 -862  
 -863  
 -864  
 -865  
 -866  
 -867  
 -868  
 -869  
 -870  
 -871  
 -872  
 -873  
 -874  
 -875  
 -876  
 -877  
 -878  
 -879  
 -880  
 -881  
 -882  
 -883  
 -884  
 -885  
 -886  
 -887  
 -888  
 -889  
 -890  
 -891  
 -892  
 -893  
 -894  
 -895  
 -896  
 -897  
 -898  
 -899  
 -900  
 -901  
 -902  
 -903  
 -904  
 -905  
 -906  
 -907  
 -908  
 -909  
 -910  
 -911  
 -912  
 -913  
 -914  
 -915  
 -916  
 -917  
 -918  
 -919  
 -920  
 -921  
 -922  
 -923  
 -924  
 -925  
 -926  
 -927  
 -928  
 -929  
 -930  
 -931  
 -932  
 -933  
 -934  
 -935  
 -936  
 -937  
 -938  
 -939  
 -940  
 -941  
 -942  
 -943  
 -944  
 -945  
 -946  
 -947  
 -948  
 -949  
 -950  
 -951  
 -952  
 -953  
 -954  
 -955  
 -956  
 -957  
 -958  
 -959  
 -960  
 -961  
 -962  
 -963  
 -964  
 -965  
 -966  
 -967  
 -968  
 -969  
 -970  
 -971  
 -972  
 -973  
 -974  
 -975  
 -976  
 -977  
 -978  
 -979  
 -980  
 -981  
 -982  
 -983  
 -984  
 -985  
 -986  
 -987  
 -988  
 -989  
 -990  
 -991  
 -992  
 -993  
 -994  
 -995  
 -996  
 -997  
 -998  
 -999  
 -1000  
 -1001  
 -1002  
 -1003  
 -1004  
 -1005  
 -1006  
 -1007  
 -1008  
 -1009  
 -1010  
 -1011  
 -1012  
 -1013  
 -1014  
 -1015  
 -1016  
 -1017  
 -1018  
 -1019  
 -1020  
 -1021  
 -1022  
 -1023  
 -1024  
 -1025  
 -1026  
 -1027  
 -1028  
 -1029  
 -1030  
 -1031  
 -1032  
 -1033  
 -1034  
 -1035  
 -1036  
 -1037  
 -1038  
 -1039  
 -1040  
 -1041  
 -1042  
 -1043  
 -1044  
 -1045  
 -1046  
 -1047  
 -1048  
 -1049  
 -1050  
 -1051  
 -1052  
 -1053  
 -1054  
 -1055  
 -1056  
 -1057  
 -1058  
 -1059  
 -1060  
 -1061  
 -1062  
 -1063  
 -1064  
 -1065  
 -1066  
 -1067  
 -1068  
 -1069  
 -1070  
 -1071  
 -1072  
 -1073  
 -1074  
 -1075  
 -1076  
 -1077  
 -1078  
 -1079  
 -1080  
 -1081  
 -1082  
 -1083  
 -1084  
 -1085  
 -1086  
 -1087  
 -1088  
 -1089  
 -1090  
 -1091  
 -1092  
 -1093  
 -1094  
 -1095  
 -1096  
 -1097  
 -1098  
 -1099  
 -1100  
 -1101  
 -1102  
 -1103  
 -1104  
 -1105  
 -1106  
 -1107  
 -1108  
 -1109  
 -1110  
 -1111  
 -1112  
 -1113  
 -1114  
 -1115  
 -1116  
 -1117  
 -1118  
 -1119  
 -1120  
 -1121  
 -1122  
 -1123  
 -1124  
 -1125  
 -1126  
 -1127  
 -1128  
 -1129  
 -1130  
 -1131  
 -1132  
 -1133  
 -1134  
 -1135  
 -1136  
 -1137  
 -1138  
 -1139  
 -1140  
 -1141  
 -1142  
 -1143  
 -1144  
 -1145  
 -1146  
 -1147  
 -1148  
 -1149  
 -1150  
 -1151  
 -1152  
 -1153  
 -1154  
 -1155  
 -1156  
 -1157  
 -1158  
 -1159  
 -1160  
 -1161  
 -1162  
 -1163  
 -1164  
 -1165  
 -1166  
 -1167  
 -1168  
 -1169  
 -1170  
 -1171  
 -1172  
 -1173  
 -1174  
 -1175  
 -1176  
 -1177  
 -1178  
 -1179  
 -1180  
 -1181  
 -1182  
 -1183  
 -1184  
 -1185  
 -1186  
 -1187  
 -1188  
 -1189  
 -1190  
 -1191  
 -1192  
 -1193  
 -1194  
 -1195  
 -1196  
 -1197  
 -1198  
 -1199  
 -1200  
 -1201  
 -1202  
 -1203  
 -1204  
 -1205  
 -1206  
 -1207  
 -1208  
 -1209  
 -1210  
 -1211  
 -1212  
 -1213  
 -1214  
 -1215  
 -1216  
 -1217  
 -1218  
 -1219  
 -1220  
 -1221  
 -1222  
 -1223  
 -1224  
 -1225  
 -1226  
 -1227  
 -1228  
 -1229  
 -1230  
 -1231  
 -1232  
 -1233  
 -1234  
 -1235  
 -1236  
 -1237  
 -1238  
 -1239  
 -1240  
 -1241  
 -1242  
 -1243  
 -1244  
 -1245  
 -1246  
 -1247  
 -1248  
 -1249  
 -1250  
 -1251  
 -1252  
 -1253  
 -1254  
 -1255  
 -1256  
 -1257  
 -1258  
 -1259  
 -1260  
 -1261  
 -1262  
 -1263  
 -1264  
 -1265  
 -1266  
 -1267  
 -1268  
 -1269  
 -1270  
 -1271  
 -1272  
 -1273  
 -1274  
 -1275  
 -1276  
 -1277  
 -1278  
 -1279  
 -1280  
 -1281  
 -1282  
 -1283  
 -1284  
 -1285  
 -1286  
 -1287  
 -1288  
 -1289  
 -1290  
 -1291  
 -1292  
 -1293  
 -1294  
 -1295  
 -1296  
 -1297  
 -1298  
 -1299  
 -1300  
 -1301  
 -1302  
 -1303  
 -1304  
 -1305  
 -1306  
 -1307  
 -1308  
 -1309  
 -1310  
 -1311  
 -1312  
 -1313  
 -1314  
 -1315  
 -1316  
 -1317  
 -1318  
 -1319  
 -1320  
 -1321  
 -1322  
 -1323  
 -1324  
 -1325  
 -1326  
 -1327  
 -1328  
 -1329  
 -1330  
 -1331  
 -1332  
 -1333  
 -1334  
 -1335  
 -1336  
 -1337  
 -1338  
 -1339  
 -1340  
 -1341  
 -1342  
 -1343  
 -1344  
 -1345  
 -1346  
 -1347  
 -1348  
 -1349  
 -1350  
 -1351  
 -1352  
 -1

### A. Water Soluble Powders

It is possible to prepare wettable powders which become solutions rather than dispersions of active material in the spray tank. Then, as these solutions dry out on foliage the crystalline form may be restored. It is often advantageous to inhibit or control crystal growth during the drying step, so that the active ingredient remains in finely divided form. In other cases, larger crystals do not appear to diminish insecticidal activity.

#### EXAMPLE 4

methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide 95%  
synthetic fine silica 5%

A screened fraction of active material of less than 60 mesh is blended with fine silica to prevent agglomeration in storage. When added to water this crystalline form disperses satisfactorily without lumping and dissolves within a few minutes.

This formulation is dissolved in water and applied with conventional spray equipment at a concentration of 120 grams of formulation to 100 liters of water and a rate of 2.5 kilograms of active ingredient per hectare to bush snap beans being attacked by Mexican bean beetle (*Epilachna varivestis*) and the two-spotted mite (*Tetranychus urticae*). The treated bean plants make rapid growth, have deep green leaves without the chewed areas characteristic of bean beetle attack, and produce a good yield of snap beans. In an untreated area nearby, bean plants are stunted, have chlorotic and netted leaves and produce a poor crop.

Methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide formulated in the same manner as above and used in tobacco transplant water at the rate of 15 milligrams of active ingredient per plant, protects the tobacco plants from nematode attack resulting in rapid growth and good tobacco yield.

#### EXAMPLE 5

The water-soluble powder formulation of Example 4 is dissolved at the rate of 80 milligrams per liter of water and is used as transplant water in the amount of 235 milliliters for each tobacco plant being set in a field that is infested with the southern root-knot nematode (*Meloidogyne incognita*), the stunt nematode (*Tylenchorhynchus claytoni*), the lesion nematode (*Pratylenchus brachyurus*) and tobacco wireworm (*Conoderus vespertinus*). The treated tobacco plants develop an extensive root system essentially free of root-knot, make rapid growth and yield well. Tobacco not so treated grows slowly and produces little marketable leaf.

#### EXAMPLE 6

The formulation of Example 4 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thioformimide as the active ingredient is dispersed in water and used to

treat sugarcane seed pieces being planted in muck soil in Florida so that the formulation is used at the rate of 3.5 kilograms of active ingredient per hectare of planted cane. The young plants are protected from the attack of the stunt nematode (*Tylenchorhynchus martini*) and make rapid growth compared to seedlings not protected in this manner.

#### EXAMPLE 7

The formulation of Example 4 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thioformimide as the active ingredient is sprayed on an alfalfa field infested with the alfalfa stem nematode (*Ditylenchus dipsaci*) at the rate of 1.25 kilograms of active ingredient per hectare in a volume of 60 liters per hectare. The treated alfalfa plants make rapid growth and produce deep green foliage while the plants in a nearby untreated area produce distorted growing tips and stems which are easily broken by the wind and have yellowish top growth.

#### EXAMPLE 8

The formulation of Example 4 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thioformimide as the active ingredient is sprayed around young, bearing citrus trees in Florida in a grove infested with the burrowing nematode (*Radopholus similis*). The material is applied at a rate of 4.5 to 9 kilograms of active ingredient per hectare and washed into the soil with overhead irrigation. This application is repeated at three month intervals for a total of 3 applications. The trees are protected from burrowing nematodes, make rapid growth and bear a heavy crop of fruit. Citrus trees in a nearby grove not protected in this manner show a gradual decline in vigor and produce a light crop of fruit.

### B. Wettable Powders

Wettable powders of active ingredient(s) with diluents and dispersing agents can be prepared by blending and grinding. At relatively high spray concentrations the particles of the active ingredient(s) of the invention are in dispersion, but as the concentration is reduced they pass into solution according to their solubility in water.

#### EXAMPLE 9

methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide 75%  
alkyl naphthalene sulfonic acid, Na salt 1%  
partially desulfonated sodium lignin sulfonate 10%  
synthetic fine silica 14%

The above components are blended, micro-pulverized and then air-milled. When used in low volumes of water the active ingredient which fails to dissolve remains dispersed as a fine suspension. In larger volumes it all dis-

solves, but upon drying on foliage the crystal size is controlled by the lignin sulfonate present.

This formulation is dispersed in water and sprayed by means of a tractor-mounted sprayer at a rate of about 1.5 kilograms of active ingredient in 50 liters of water per hectare of cotton. Applications are made on a weekly schedule and finally on a five-day schedule during the latter part of the growing season. The treated cotton is protected from attacking boll weevil (*Anthonomus grandis*) and the bollworm complex including *Heliothis zea* and *Heliothis virescens*. The developing squares and bolls are retained by the plants, and a good yield of cotton fiber is obtained at the end of the season. In a nearby untreated field, the fruit set is markedly reduced by the several pests, and the yield of cotton is greatly reduced.

Even much higher rates than those given above can be used with complete safety to the cotton plants. If infestations are very severe, better control can be obtained by combining the compound of this invention with one of the following: DDT®, carbaryl, dimethyl parathion or the dimethyl phosphate of 3-hydroxy-N-methyl-cis-crotonamide.

The same composition can be used to formulate:

- 30 methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide
- ethyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide
- ethyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide

#### EXAMPLE 10

The formulation of Example 9 is dispersed in water and sprayed at the rate of 10 kilograms of active ingredient in 200 dekaliters of water per hectare of a Zoysia lawn in Florida where the soil is heavily infested with sting nematode (*Belonolaimus longicaudatus*) and lance nematode (*Hoplolaimus* spp.). After spraying, the material is washed into the ground with the equivalent of about 1200 dekaliters of water per hectare. The grass in the treated area develops a deep root system and makes rapid growth, whereas grass in a similar but untreated area grows slowly and develops a shallow root system.

Methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide is formulated as in Example 9 and applied to another plot of Zoysia lawn in Florida similarly infested with nematodes. The formulation is applied in the same manner as above but at a rate of only 2.5 kilograms of active ingredient in 200 dekaliters of water per hectare. The lawn thus treated exhibits similar beneficial effects to those described above.

#### EXAMPLE 11

For the simultaneous control of the root knot nematode and soil fungi as represented by *Pythium* spp. and *Rhizoctonia* spp., the wettable powder formulation of Example 9 is applied in a spray which also contains 1,4-dichloro - 2,5 - dimethoxybenzene. For this type of application, 2.4 kilograms of the active compound of this invention and 4.8 kilograms active of 1,4 - dichloro - 2,5 - dimethoxybenzene is added to 100 liters of water. This mixture is applied as a soil spray by application to a 25 centimeter band over the row in which cotton is to be planted. The application rate in the row is 67.5 kilograms of total active ingredient (22.5 kilograms of the compound of this invention and 45 kilograms of 1,4 - dichloro - 2,5 - dimethoxybenzene) per hectare of area actually treated. The soil is rotovated immediately thereafter to mix the chemicals thoroughly with the soil. Following this, cotton seed is planted in the treated band. The cotton seedlings which develop are protected against root knot nematode (*Meloidogyne incognita*), the reniform nematode (*Rotylenchulus reniformis*) and the fungi *Pythium* spp. and *Rhizoctonia* spp. A healthy stand of cotton plants is obtained and at harvest time, a high yield of cotton. Where no treatment is applied, the stand is poor, growth is slow and lint yield is reduced.

Methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide is formulated as in Example 9 and is applied in a spray along with 1,4 - dichloro - 2,5 - dimethoxybenzene to soil prior to planting with cotton seed in the manner described above. The application rate in the row is 6 kilograms of the compound of this invention and 45 kilograms of 1,4-dichloro-2,5-dimethoxybenzene per hectare of area actually treated. The soil is rotovated immediately thereafter to mix the chemicals thoroughly with the soil. Cotton seed is planted in the treated band. Cotton seedlings are protected from root-knot and reniform nematodes as well as the attack of *Pythium* and *Rhizoctonia* fungi. The plants develop an extensive deep root system and make rapid growth.

Even much higher use rates than those given above can be employed with complete safety to the cotton plants.

#### EXAMPLE 12

The formulation of Example 9 is added to water in an amount to give 45 grams of active ingredient per 100 liters of spray. This solution-dispersion is sprayed on apple trees to the point of run-off by means of a high pressure hydraulic sprayer. Sprays on a weekly schedule provide control of green apple aphid, codling moth, plum curculio and redbanded

leaf  
sectic  
the s  
plicat  
other  
DDT  
arsen

Th  
ampl  
mean  
and  
Amer  
An a  
6 kil  
of an  
pest.

Th  
in w  
root  
spiral  
at a  
hecta  
to wa  
roots.  
contr  
wood  
Simil  
left

n -

dioc  
low  
diato

Th  
ropul  
less  
powd  
exter

Fe

Thes  
cone

TI  
cover  
duste

the f  
ing

aphi  
aphi  
adul

are  
dust  
zate

cont  
carp

27

leaf roller. One or more of the following insecticides in effective amounts can be added to the spray when a longer interval between applications is desired or it is needed to control other especially difficult-to-control pests: DDT®, methoxychlor, Malathion®, lead-arsenate, "Guthion"®, or carbaryl.

## EXAMPLE 13

The wettable powder formulation of Example 9 is dispersed in water and sprayed by means of a conventional sprayer over a lawn and adjacent vegetation infested with the American dog tick (*Dermacentor variabilis*). An amount of the formulation is used to give 6 kilograms of 800 liters of water per hectare of area sprayed which effectively controls the pest.

## EXAMPLE 14

The formulation of Example 9 is dispersed in water, and drenched on the soil over the root zone of boxwood plants infected with the spiral nematode (*Helicotylenchus buxophilus*) at a rate of 3.5 kilograms of active agent per hectare of area treated using enough water to wash the active agent down about the plant roots. Substantially all spiral nematodes are controlled by this treatment, allowing the boxwood plant to develop in a normal manner. Similarly infested boxwood plants which are left untreated grow poorly and finally die.

## EXAMPLE 15

|                                                                              |       |
|------------------------------------------------------------------------------|-------|
| n - propyl - 1 - carbamoyl - N -<br>(methylcarbamoyloxy)thioformi-<br>midate | 50%   |
| dioctylsodium sulfosuccinate                                                 | 1.5%  |
| low viscosity methylcellulose                                                | 2.0%  |
| diatomaceous silica                                                          | 46.5% |

The above composition is blended and micropulverized until substantially all particles are less than 50 microns. The resulting wettable powder can be added to water and sprayed, or extended with heavy diluents to form a dust.

For example:

|                     |     |
|---------------------|-----|
| composition above   | 20% |
| ground pyrophyllite | 80% |

These components are blended in a ribbon or cone blender to form a 10% active dust.

The 10% active dust is applied in thorough coverage by means of a hand crank-operated duster to both the upper and lower surfaces of the foliage of rose bushes still wet with morning dew. Infesting aphids such as the potato aphid (*Macrosiphum euphorbiae*) and the rose aphid (*Macrosiphum rosae*) as well as feeding-adults of the Japanese beetle (*Popillia japonica*) are controlled by this application. The above dust can be formulated to contain 5% "Manzate"® in the finished product to also give control of the disease called black spot (*Dipllo-carpon rosea*), which frequently affects roses.

Roses treated with this combination make good growth, possess shiny deep-colored foliage and produce numerous buds. Adjacent untreated bushes exhibit poor growth, drop numerous yellowed leaves and fail to produce the expected crop of blooms.

## EXAMPLE 16

A wettable powder formulation of Example 15 is prepared using methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thioformimidate as the active ingredient. This formulation is used to treat farm land in Florida infested with the stubby-root nematode (*Trichodorus christiei*) and the lesion nematode (*Pratylenchus zae*). The material is applied as a spray at the rate of 2.25 to 4.5 kilograms of active ingredient per hectare of land and thoroughly mixed with the soil by disking. Sweet corn planted in this treated field develops a deep and extensive root system, makes rapid growth and yields a heavy crop of marketable ears. Corn in a nearby untreated field grows slowly and produces a low yield.

## EXAMPLE 17

The wettable powder formulation of Example 16 is sprayed around young, bearing apple trees in Holland that are infested with lesion nematodes (*Pratylenchus* spp.). Application is made by spraying within the drip line of the trees at the rate of 2.25 to 4.5 kilograms of active ingredient per hectare of area actually treated. The trees make rapid growth as a result of the treatment in contrast to nearby untreated trees.

## EXAMPLE 18

Chickens are temporarily removed from a poultry house and surrounding areas which are heavily infested with the fowl tick (*Argas persicus*). The house and areas are thoroughly dusted with a 10% dust formulated from the dust concentrate of Example 15. The infestation is controlled and the poultry returned to the house soon assumes a healthy appearance and resumes egg-laying at the normal level.

## EXAMPLE 19

The wettable powder formulation of Example 15 is applied in a spray covering a 25 centimeter band over the open furrow as cotton seed are being planted. For this type of application 2.5 kilograms of active ingredient per 10,000 meters of row is applied in 75 liters of water. The active ingredient of this invention moves by means of systemic action from the soil into the cotton seedlings to render them toxic to certain sucking insects. Infestations of aphids, thrips species and plant-sucking bugs are thereby controlled. Plants in the treated area grow rapidly and produce full green foliage. Plants in a similar but untreated area grow slowly and have thickened silvery leaves, the latter due to thrips injury.



When stock so treated is planted it grows well and is of good appearance. Similar stock which is not treated grows poorly, is of poor appearance, and, in many instances, does not survive.

#### EXAMPLE 26

The water-miscible formulation of Example 22 is added to water in an amount to give 90 grams of the active compound per 100 liters. Tobacco plants infested with tobacco budworm (*Heliothis virescens*) and hornworms (*Manduca* spp.) are sprayed with the above material to run-off. Excellent control is obtained by applications made on a 10-day interval.

#### EXAMPLE 27

allyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide 25%  
dimethylsulfoxide 75%  
A clear solution is formed when these components are mixed. When used at the rate of 0.5 pounds active per 100 gallon water a clear solution results.

This composition is diluted with water to give a final concentration of 0.2% active. House flies, *Musca domestica*, and other flies such as stable flies, *Musca autumnalis*, are controlled in farm buildings, barns, and outdoor locations such as pens and corrals by spraying with this preparation as a space spray using a mist blower.

#### E. Oil Suspension

#### EXAMPLE 28

ethyl 1 - carbamoyl - N - (ethylcarbamoyloxy)thioformimide 30%  
polyethylene oxide lauryl ether 8%  
low viscosity white oil (Litetack oil) 62%  
The above components are mixed and sand milled until the active is substantially all below 10 microns. The resulting suspension can be emulsified in water and sprayed or can be diluted with a nonphytotoxic paraffin oil and sprayed. For ultra low volume use the concentrate can be sprayed as it is.

This formulation when diluted with water to give 2.2 kilograms of active ingredient per 230 liters is sprayed at the rate of 230 liters per hectare on corn directing the spray toward the silks of developing ears. When applied in such a manner during the silking period at an interval of 1 to 2 days, an infestation of the corn earworm, *Heliothis zea*, is controlled.

#### EXAMPLE 29

The oil suspension of Example 28 is diluted with a paraffin oil to give 2.4 kilograms active per 100 liters. This is applied as a spray by means of airplane at the rate of 9.4 liters per hectare to marshlands and swampy areas serving as the breeding grounds for various species of mosquitoes. Control of the developing mosquito larva is obtained with this application.

#### F. Aerosol Formulation

#### EXAMPLE 30

methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide 2%  
equal wt. mixture of "Freon® 11" and "Freon® 12" 98%  
The above mixture is cold packed in an aerosol can for flying insect control.

The above aerosol is discharged at the rate of 140 to 350 grams of active ingredient per 1,000 cubic meters of space in a greenhouse in which carnations are growing. Plant injury is prevented by attaching a wand to the aerosol container and discharging the material above the plants. This application controls aphids such as the green peach aphid, *Myzus persicae*, and the leaf-curl plum aphid, *Aphis helichrysi*, infesting the carnation plants.

#### G. Aqueous Dispersion

#### EXAMPLE 31

allyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide 35%  
Carbopol® 934 (a polycarboxylic hydrocarbon polymer) 0.4%  
10% aqueous NaOH 1.00%  
Na<sub>2</sub>HPO<sub>4</sub> 1.00%  
"Elvanol"® 51-05 (polyvinyl alcohol) 1.00%  
sulfated tallow defoamer 0.1%  
water 61.5%

The Carbopol® and Elvanol are first blended dry with the active to avoid lumping. The NaOH and Na<sub>2</sub>HPO<sub>4</sub> are predissolved in the water. The solids and antifoam are then added and the mix sand ground until the active is substantially all below 10 microns.

The aqueous dispersion is diluted with water and sprayed on selected plots in a strawberry field known to be heavily infested with the bud and leaf nematode (*Aphelenchoides besseyi*). The spray solution contains 120 grams active of the composition of this invention per 100 liters of water. The volume of application is such as to provide 2.2 kilograms of the active ingredient per hectare of plot area. All above-ground parts are thoroughly wetted. The strawberry plants in the sprayed plot grow well and give a good yield. In the unsprayed portions of the field the plants are yellow, grow slowly and produce a poor yield.

#### H. Granules

#### EXAMPLE 32

methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide 2%  
dimethylformamide 4%  
granular attapulgite with particles ranging from 0.25 to 0.6 mm. 94%  
The active ingredient is first dissolved in the dimethylformamide at an elevated temperature and is then sprayed upon the attapulgite

while it is being tumbled. Due to low volatility the solvent remains in the granule for an extended time but does slowly evaporate.

The other compounds of formula (1) can be formulated as granules in the same manner.

The above granular formulation, containing methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide as the active component, is applied in the planting furrows of potatoes at the rate of 3 kilograms of active ingredient per 10,000 meters of row. Certain soil-infesting pests of potatoes such as white-fringed beetle larvae, mole crickets and wireworm larvae are greatly reduced in numbers. The potato plants are protected from infestations of potato aphid, *Macrosiphum euphorbiae*, and green peach aphid; *Myzus persicae*, due to the systemic movement of the compound of this invention from the soil up into the potato foliage.

#### EXAMPLE 33

|                                                                |     |
|----------------------------------------------------------------|-----|
| methyl 1 - carbamoyl - N - (dimethylcarbamoyloxy)thioformimide | 5%  |
| polyethylene oxide trimethylnonyl ether                        | 5%  |
| granular vermiculite                                           | 89% |
| synthetic fine silica                                          | 1%  |

The active and fine silica are first mixed and micropulverized. This dust is then mixed briefly with the granular vermiculite and sprayed with the liquid surfactant.

Other compounds of formula (1) can be formulated as granules in the same manner.

The above granular formulation, containing methyl 1 - carbamoyl - N - (methycarbamoyloxy)thioformimide as the active ingredient, is applied in the furrow with cotton seed at the time of planting at the rate of 2.5 kilograms of the active ingredient per 10,000 meters of row. The resulting seedlings are protected from attacking insects due to the systemic movement of the compound of this invention from the soil into the seedling. Infestations of the cotton aphid, *Aphis gossypii*, various thrips species, and the serpentine leaf miner, *Liriomyza brassicae*, are controlled for a period up to 3 or 4 weeks.

#### EXAMPLE 34

The granular formulation of Example 33 containing methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide as the active ingredient is applied as a sidedress treatment to cotton plants at the start of squaring (fruiting) at the rate of 7.5 kilograms of active ingredient per 10,000 meters of row. Adult boll weevils, *Anthonomus grandis*, emerging from hibernation and feeding on the foliage and young fruit buds are controlled due to the systemic movement of the compound of this invention from the soil up into the plant parts.

#### EXAMPLE 35

The granular formulation of Example 33

containing methyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide as the active ingredient is applied in the furrow with corn seed at the time of planting at the rate of 2.5 kilograms of the active ingredient per 10,000 meters of row. Larvae of the northern corn rootworm, *Diabrotica longicornis*, and the western corn rootworm, *Diabrotica virgifera*, hatching from eggs deposited by adult females in the soil the previous autumn and attacking the corn roots are controlled. The corn makes rapid growth, develops a deep root system that prevents the plants from lodging during windy periods and produces a good yield. Plants in a nearby area left untreated develop a shallow root system that causes a goodly percentage of lodged plants and the yield is greatly reduced.

#### EXAMPLE 36

The granular product of Example 33 is applied to soil infested with plant-pathogenic nematodes at a rate of 20 kilograms active agent per hectare using a conventional fertilizer spreader. The active agent is then worked into the soil by disking. This treatment gives substantially complete control of a high population of the sting nematode (*Belonolaimus longicaudatus*) as shown by a nematode count 15 days after treatment. In a similar area that remains untreated, the population of the sting nematode continues at a damaging level.

#### EXAMPLE 37

|                                                             |     |
|-------------------------------------------------------------|-----|
| allyl 1 - carbamoyl - N - (methylcarbamoyloxy)thioformimide | 10% |
| gypsum plus ammonium sulfate                                | 90% |

The above components are blended and granulated by the procedure described in U.S. Patent No. 3,168,437, to give rapidly disintegrated granules ranging in particle size from 0.25 to 1 mm.

The other compounds of formula (1) can be substituted for the active ingredient shown above and the active concentration can range from 2—50% without loss of physical properties.

The above granular formulation is applied at the rate of 20 kilograms of active ingredient per hectare using a conventional fertilizer spreader. The material is then worked into the soil by disking. Tobacco grown subsequently in this field is substantially free from infestation by the lesion nematode (*Pratylenchus brachyurus*) and the southern root knot nematode (*Meloidogyne incognita*). Soil-infesting insects such as mole crickets and wireworm larvae that damage tobacco are also controlled. The tobacco plants in this field make rapid growth and yield well while tobacco on a similar but untreated area grows slowly and produces little marketable leaf.

Methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy) - thioformimide is

form  
App  
the  
per  
lowe  
in t  
lesio  
tode  
grov

10

T  
1 -  
bam  
pon  
acti  
spre  
cyst  
ules  
disk  
vigo  
grov  
have

20

25

T  
1 -  
bam  
pon  
grar  
of r  
nem  
cati  
the  
seed  
pro  
yiel  
near  
that

30

35

40

T  
1 -  
bam  
pon  
cutt  
wit  
App  
of  
izer  
Gra  
fror  
it t  
as

45

50

55

T  
1 -  
bam  
pon  
fest  
chu  
tyle  
of  
hec

60

formulated as a granule in the same manner. Application of this formulation to a field at the rate of 5 kilograms of active ingredient per hectare, with a fertilizer spreader, is followed by disking into the soil. Tobacco grown in this field is protected from attack by the lesion nematode and southern root-knot nematode. As a consequence, the plants make rapid growth and yield well.

#### EXAMPLE 38

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is applied at the rate of 5 kilograms of active ingredient per hectare with a fertilizer spreader to a field infested with the soybean cyst nematode (*Heterodera glycines*). The granules are thoroughly mixed into the soil by disking. Soybeans grown in this field produce vigorous green plants that yield well. Plants grown in a nearby untreated field are small, have yellowish foliage and yield poorly.

#### EXAMPLE 39

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is applied at the rate of 5 to 12.5 kilograms of active ingredient per 10,000 meters of row in a potato field infested with the golden nematode (*Heterodera rostochiensis*). Application is made by dribbling the granules in the open furrow prior to placing the potato seed pieces. The potato plants in this field produce dark-green vigorous plants and a high yield of potatoes at the end of the season. A nearby untreated field produces small plants that yield poorly at the end of the season.

#### EXAMPLE 40

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is used to treat a field in which grape cuttings are to be set and which is infested with the dagger nematode (*Xiphinema index*). Application is at the rate of 4 to 8 kilograms of active ingredient per hectare with a fertilizer spreader followed by disking into the soil. Grape vines grown in this field are protected from the dagger nematode and the virus that it transmits which causes a condition known as "fanleaf".

#### EXAMPLE 41

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is used to treat a field in Hawaii infested with the reniform nematode (*Reniformulus reniformis*) and the pin nematode (*Pratylenchus minutus*). Application is at the rate of 3 to 8 kilograms of active ingredient per hectare with a fertilizer spreader followed by

disking into the soil. Pineapple plants grown in this field develop a deep extensive root system and make good growth. Plants in a nearby untreated field are small and grow slowly due to a poor root system.

#### EXAMPLE 42

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is used to treat celery in Connecticut in land infested with the pin nematode (*Pratylenchus hamatus*). After the small plants are set in the field, the granules are applied as a side-dressing on both sides of the row in the amount of 5 to 12.5 kilograms of active ingredient per 10,000 meters of row. Overhead irrigation is applied to aid in the break-down of the granules and to wash the active ingredient into the soil. The celery plants in this field grow rapidly and develop a deep green color while plants in a nearby untreated field are stunted and chlorotic.

#### EXAMPLE 43

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is applied around young coconut-palm trees infested with the coconut-palm nematode (*Rhadinaphelenchus cocophilus*). The material is applied within the drip-line of the trees at a rate of 5 to 8 kilograms of active ingredient per hectare of area actually treated. The granules are then lightly worked into the soil. Trees so treated continue to grow and bear while nearby untreated trees grow slowly and eventually die.

#### EXAMPLE 44

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is used to treat young tea plants in Ceylon infested with lesion nematodes (*Pratylenchus* spp.). The granules are dribbled along each side of the row of young plants so that 5 to 12.5 kilograms of active ingredient is applied per 10,000 meters of row. The granules are then worked lightly into the soil. Applications are repeated at six-month intervals. Plants treated in this manner grow rapidly and yield early compared to untreated plants.

#### EXAMPLE 45

The formulation of Example 37 with methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thiolformimidate as the active component is applied around young banana plants in Honduras infested with burrowing nematodes (*Radopholus similis*) and lesion nematodes (*Pratylenchus* spp.). The granules are distributed around the young plants to cover the root area at a rate of 2.25 to 5.6 kilograms of active ingredient per hectare of area actually



Thiram fungicide is added to the seed treatment to control seedling blight.

### EXAMPLE 50

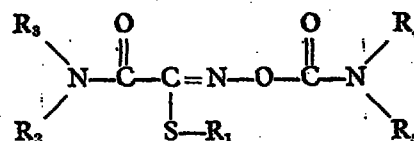
Methyl 1 - (dimethylcarbamoyl) - N - (methylcarbamoyloxy)thioformimidate is applied to a young citrus grove in Arizona infested with the citrus nematode (*Tylenchulus semipenetrans*) by dissolving the chemical in the irrigation water. The equivalent of 4 to 5 kilograms per hectare of land is applied in 2.5 centimeters of irrigation water. The young trees are protected from the injury of the citrus nematode, make rapid growth and begin producing a marketable fruit crop. A nearby grove not treated in this manner has poor growth, less vigorous trees and produces a light crop of small fruit.

### EXAMPLE 51

|                                                                                       |     |
|---------------------------------------------------------------------------------------|-----|
| methyl 1 - (dimethylcarbamoyl) - N -<br>(methylcarbamoxyloxy) - thiol-<br>formimidate | 20% |
| methylthiolcarbamic acid, methyl ester                                                | 80% |

The above formulation is diluted with mineral spirits and applied as a broadcast spray at the rate of 22 kilograms of formulation per hectare in a total volume of 60 liters per hectare to a field in Hawaii infested with the reniform nematode (*Rotylenchulus reniformis*) and the pin nematode (*Paratylenchus minutus*). The soil is then thoroughly mixed by disking. Pineapple plants grown in this field develop a deep extensive root system and make rapid growth. Plants in a nearly untreated field grow slowly due to a poor and shallow root system.

1. A compound of the formula:



wherein

**R<sub>1</sub> represents alkyl of 1 to 4 carbon atoms or alkenyl of 3 or 4 carbon atoms;**

R<sub>2</sub> represents hydrogen, methoxy, alkyl of 1 to 4 carbon atoms, alkenyl of 3 or 4 carbon atoms or cycloalkyl of 3 to 5 carbon atoms;

R<sub>3</sub> represents hydrogen, alkyl of 1 to 4 carbon atoms, or alkenyl of 3 or 4 carbon atoms; or

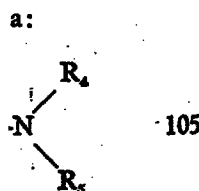
R<sub>2</sub> and R<sub>3</sub> together represent alkylene of 2 to 6 carbon atoms;

1. allyl and with more than 2.
2. where the carbonyl carbon is
3. where the
4. where the
5. is specified
6. is other than methoxythioformyl-N-methoxy carbonyl (cyclobutyl)
7. carbonyl
8. (methoxy)
9. compound and a
10. claim solid.
11. claim
12. claim active
13. claim
14. any compound and
15. claim
16. claim in an
17. claim in an
- 18.

seed in-  
ematode  
f 5 to 10  
ed. Seed  
ous green  
e plants  
ip".  
the seed

) - N -  
te is ap-  
rizona in-  
lenchodus  
emical in  
t of 4 to  
applied in  
The young  
the citrus  
begin pro-  
A nearby  
has poor  
roduces a

N -  
iol-  
20%  
ster 80%  
with min-  
icast spray  
ulation per  
rs per hec-  
d with the  
reniformis)  
is minutus).  
by disk-  
eld develop  
make rapid  
d field grow  
root system.



arbon atoms  
ms;  
xy, alkyl of  
of 3 or 4  
to 5 carbon

f 1 to 4 car-  
or 4 carbon  
alkylene of

23

R<sub>1</sub> represents alkyl of 1 to 3 carbon atoms,  
allyl or propargyl;  
and R<sub>2</sub> represents hydrogen or methyl;  
with the proviso that R<sub>2</sub> and R<sub>3</sub> total not  
more than 7 carbon atoms.

2. A compound according to claim 1  
wherein R<sub>2</sub> represents hydrogen, alkyl of 1 to  
4 carbon atoms, alkenyl of 3 or 4 carbon atoms  
or cycloalkyl of 3 to 5 carbon atoms, or R<sub>2</sub>  
and R<sub>3</sub> together represent alkylene of 2 to 6  
carbon atoms.

3. A compound according to claim 1  
wherein R<sub>2</sub> and R<sub>3</sub> each represents hydrogen.

4. A compound according to claim 1  
wherein R<sub>2</sub> and R<sub>3</sub> each represents methyl.

5. A compound according to claim 1 which  
is specifically named herein.

6. A compound according to claim 5 which  
is other than allyl 1 - (N - methoxy - N -  
methylcarbamoyl) - N - (ethylcarbamoyloxy)-  
thioformimide; methyl 1 - (N - methoxy -  
N - methylcarbamoyl) - N - (methylcarbam-  
oyloxy)thioformimide; methyl 1 - (N -  
methyl - N - allylcarbamoyl) - N - (methyl-  
carbamoyloxy)thioformimide; or methyl 1 -  
(cyclopentylcarbamoyl) - N - (dimethylcar-  
bamoyloxy)thioformimide.

7. Methyl 1 - carbamoyl - N - (methyl-  
carbamoyloxy) - thioformimide.

8. Methyl 1 - (dimethylcarbamoyl) - N -  
(methylcarbamoyloxy)thioformimide.

9. A pesticidal composition comprising a  
compound claimed in any one of claims 1—8  
and a diluent and/or a surface active agent.

10. A pesticidal composition according to  
claim 9 which contains a diluent which is a  
solid.

11. A pesticidal composition according to  
claim 9 which is a suspension.

12. A pesticidal composition according to  
claim 9 which is a solution containing a surface  
active agent.

13. A pesticidal composition according to  
claim 9 which contains also a pesticidal com-  
pound not claimed in claim 1 or a fungicide.

14. A pesticidal composition according to  
any one of claims 9—13 wherein the com-  
pound claimed in any one of claims 1—8 is a  
compound claimed in any one of claims 2—4  
and 6—8.

15. A pesticidal composition according to  
claim 9 substantially as hereinbefore described.

16. A pesticidal composition according to  
claim 9 substantially as hereinbefore described  
in any one of Examples 4—51.

17. A pesticidal composition according to  
claim 9 substantially as hereinbefore described  
in any one of Examples 5, 9, 12—15, and  
18—36.

18. A method for inhibiting pests which  
are infesting or are liable to infest a locus,  
which method comprises applying to the locus  
a pest-inhibiting amount of a compound  
claimed in any one of claims 1—8.

19. A method according to claim 18 where-  
in the compound is applied in the form of a  
composition claimed in any one of claims 9—  
17.

20. A method according to claim 18 or 19  
wherein the pests are insects, acarina or nema-  
todes.

21. A method according to claim 20  
wherein the locus is soil infested with the pests.

22. A method according to claim 20  
wherein the locus is plants.

23. A method according to claim 22  
wherein the compound is applied to soil in  
which the plants are growing.

24. A method according to any one of  
claims 18—23 wherein the pests are of a  
species named herein.

25. A method according to any one of  
claims 18—23 wherein the compound is as  
claimed in any one of claims 2—4 and 6—8.

26. A method according to claim 25 where-  
in the compound is methyl 1 - carbamoyl - N -  
(methylcarbamoyloxy)thioformimide.

27. A method according to claim 25 where-  
in the compound is methyl 1 - (dimethyl-  
carbamoyl) - N - (methylcarbamoyloxy)thio-  
formimide.

28. A method according to claim 25 where-  
in the compound is applied in the form a  
composition claimed in claims 14 or 17.

29. A method according to any one of  
claims 25—28 wherein the pests are of a  
species named in List X herein.

30. A method according to claim 18 per-  
formed substantially as hereinbefore described.

31. A method according to claim 18 per-  
formed substantially as hereinbefore described  
in any one of Examples 4—51.

32. A method according to claim 18 per-  
formed substantially as hereinbefore described  
in any one of Examples 9, 12—15, and 18—  
36.

33. A process for the preparation of a  
compound claimed in claim 1, which process  
is performed substantially as hereinbefore de-  
scribed.

34. A compound claimed in claim 1 when  
prepared by a process claimed in claim 33.

J. A. KEMP & CO.,  
Chartered Patent Agents,  
14 South Square,  
Gray's Inn,  
London, W.C.1.

