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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Novel Synergistic Insecticidal Compositions

We, F. HOFFMANN-LA ROCHE & Co., AKTIENGESELLSCHAFT, a Swiss Company of 124—784 Grenzacherstrasse, Basle, Switzerland, do hereby declare the invention, for which we

5 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:—

10 This invention relates to novel synergistic insecticidal compositions.

The novel compositions provided by the present invention comprise an insecticidal carbamate and a propargyl aryl ether of the general formula



I

wherein *Aryl* represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group which carries one or more halo, lower-alkyl, lower-alkoxy, methylenedioxy, aryl, aryloxy, aralkyl, aralkoxy, nitro, cyano, carboxyl, carboalkoxy, acylamino and/or N,N - di(lower alkyl) - amido substituents, Y represents an oxygen or sulphur atom and X represents a halogen atom.

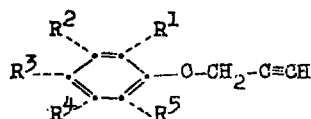
25 As will be evident from the foregoing, the *aryl* group in the foregoing formula can represent any aromatic hydrocarbon group such as phenyl, naphthyl, di- or tetrahydronaphthyl, anthryl, phenanthryl, indenyl or fluorenyl or can represent such an aromatic hydrocarbon group which carries one or more halo, lower-alkyl, lower-alkoxy, methylenedioxy, aryl, aryloxy, aralkyl, aralkoxy, nitro, cyano, carboxyl, carboalkoxy, acylamino and/or N,N - di(lower alkyl) - amido substituents. The term 'halo' and 'halogen' as used in this specification denote chloro, bromo, iodo

and fluoro or chlorine, bromine, iodine and fluorine as the case may be. The term 'lower-alkyl' denotes straight-chain or branched-chain hydrocarbon groups containing from 1 to 7 carbon atoms (e.g. methyl, ethyl, propyl and isopropyl). The term 'lower alkoxy' denotes a lower-alkyl group as defined earlier which is joined to the molecule through an oxygen atom. The term 'aryl' denotes a carbocyclic hydrocarbon group having at least one aromatic ring such as phenyl, naphthyl and dihydronaphthyl and such an aromatic hydrocarbon group in which one or more of the hydrogen atoms has been replaced by a substituent indicated earlier. The term 'aryloxy' denotes an aryl group as defined earlier which is joined to the molecule through an oxygen atom. The term 'aralkyl' denotes a lower-alkyl group which carries an aryl group as defined earlier (e.g. benzyl and phenethyl). The term 'aralkoxy' denotes an aralkyl group which is joined to the molecule through an oxygen atom. The term "acylamino" denotes an amino group in which one of the hydrogen atoms of the amino group has been replaced by an organic acid residue such as, for example, lower-alkanoyl (e.g. acetyl) or aroyl (e.g. benzoyl). Thus, examples of acylamino groups are acetylamino and benzoylamino.

As will be evident from the foregoing, formula I includes both the propargyl aryl ethers (as when Y represents an oxygen atom) and the propargyl aryl thioethers (as when Y represents a sulphur atom). Examples of ethers falling within formula I are the phenyl propargyl ethers such as phenyl propyn-(2)-yl ether, phenyl propyn-(2)-yl thioether and phenyl 3-iodo-propyn-(2)-yl ether, the halo-phenyl propargyl ethers and halo-

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- phenyl propargyl thioethers such as 2,3-dichloro - phenyl propyn - (2) - yl ether, 2,3-dichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2,3 - dibromo - phenyl propyn - (2) - yl ether, 2,4 - dichloro - phenyl propyn - (2) - yl ether, 2,5 - dichloro - phenyl propyn - (2) - yl ether, 2,3,6 - trichloro - phenyl propyn - 2 - yl ether, 2,3,6 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2,3,4 - trichloro - phenyl propyn - (2) - yl ether, 3,4,5 - trichloro - phenyl propyn - (2) - yl ether, 2,3 - dichloro - phenyl propyn - (2) - yl thioether and 2,3 - dichloro - phenyl 3 - iodo - propyn - (2) - yl thioether, alkoxy-phenyl propargyl ethers such as 4 - methoxy-phenyl propyn - (2) - yl ether and 2,6 - dimethoxy - phenyl propyn - (2) - yl ether, methylenedioxy-phenyl propargyl ethers such as 3,4 - methylenedioxy - phenyl propyn - (2) - yl ether, nitro-phenyl propargyl ethers such as 3 - nitro - phenyl propyn - (2) - yl ether, 3 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether and 2 - nitro - phenyl propyn - (2) - yl ether, substituted-phenyl propargyl ethers having mixed substituents such as 2-nitro - 4 - chloro - phenyl propyn - (2) - yl ether, 4 - chloro - 6 - iodo - 2 - nitro - phenyl propyn - (2) - yl ether and 4 - chloro - 6 - iodo - 2 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether and the naphthyl propargyl ethers such as naphthyl - (1) propyn - (2) - yl ether, 2,4 - dichloro - naphthyl - (1) 3 - iodo - propyn - (2) - yl ether.
- 35 The phenyl and substituted phenyl propargyl ethers of the formula



(Ia)

- , wherein the symbols R^1 , R^2 , R^3 , R^4 and R^5 each represent a halogen atom or a nitro, lower-alkyl or lower-alkoxy group or any two of said symbols which are adjacent to one another represent a methylenedioxy group and wherein the broken lines denote that the substituents attached thereby are optional, constitute a preferred class of ethers of formula I. Especially preferred are the dihalo-, trihalo- and mononitro-phenyl propargyl ethers. Of these, 2,4-dichloro-phenyl propargyl ether and the trichloro-phenyl propargyl ethers are especially preferred in terms of activity and availability.

- Any insecticidal carbamate can be used as the carbamate ingredient of the present compositions. The term 'insecticidal carbamate' is well known and encompasses a variety of carbocyclic and heterocyclic carbamates such as, for example, aryl carbamates

[e.g. phenyl carbamates, phenyl N-alkyl carbamates such as phenyl N-methyl carbamate, phenyl N,N-dialkyl carbamates such as phenyl N,N-dimethyl carbamate, substituted-phenyl carbamates such as o-chloro-phenyl N-methyl carbamate, p-fluoro-phenyl N-methyl carbamate, m-bromo-phenyl N-methyl carbamate, p-acetyl-phenyl N-methyl carbamate, alkyl-phenyl N-methyl carbamates such as m-methyl-phenyl N-methyl carbamate, p-ethyl-phenyl N-methyl carbamate, o-cyclohexyl-phenyl N-methyl carbamate, o-iodo-phenyl N-methyl carbamate, 2,3-dimethyl-4-chloro-phenyl N-methyl carbamate and 2,4,6-trichloro-3,5-dimethyl-phenyl N-methyl carbamate, naphthyl carbamates such as naphthyl - (1) N-alkyl carbamates, naphthyl - (2) N-alkyl carbamates and naphthyl - (1) N,N-dialkyl carbamates, substituted-naphthyl carbamates such as 2,4-dichloro-naphthyl - (1) carbamate and 2,4-dichloro-naphthyl - (1) N-methyl carbamate and other carbocyclic carbamates such as hydrogenated naphthyl - (1) N-methyl carbamates, [e.g. 5,6-dihydro-naphthyl - (1) N-methyl carbamate] indanyl carbamates [e.g. indanyl - (4) N-alkyl carbamates, indanyl - (4) N,N-dialkyl carbamates]], heterocyclic carbamates such as pyrazolyl carbamates, (e.g. 1-phenyl-3-methyl-pyrazolyl N,N-dimethyl carbamate and 1-isopropyl-3-methyl-pyrazolyl N,N-dimethyl carbamate) and dithiolane-oximino carbamates (e.g. 2-methylimino-1,3-dithiolane, 2-oximino-1,4-dithiolane, 2-oximino-1,3-oxathiolane, 2-methylcarbamoyloximino-1,3-dithiolane and 2-oximino-5-dithiolane oximino carbamates).

Insecticidal carbamates which are especially well suited for the synergistic compositions of the present invention are the (lower alkyl)-phenyl N-methyl carbamates (e.g. 3-secbutyl-phenyl N-methyl carbamate, 3-tertbutyl-phenyl N-methyl carbamate, 2-tertbutyl-phenyl N-methyl carbamate, 3-isopropyl-phenyl N-methyl carbamate and 3-methyl-5-isopropyl-phenyl N-methyl carbamate), the (lower alkoxy)-phenyl N-methyl carbamates (e.g. 2-isopropoxy-phenyl N-methyl carbamate, o-secbutoxy-phenyl N-methyl carbamate, 2-iso-propoxy-5-methyl-phenyl N-methyl carbamate) o-cyclopentoxy-phenyl N-methyl carbamate, the amino-phenyl N-methyl carbamates [e.g. 3,5-dimethyl-4-dimethylamino-phenyl N-methyl carbamate, 3-methyl-4-dimethylamino-phenyl N-methyl carbamate and the 2-(lower alkyl)-3-amino-phenyl N-methyl carbamates 2-(lower alkyl)-3-alkylamino-phenyl N-methyl carbamates, 2-(lower alkyl)-3-dialkylamino-phenyl N-methyl carbamates and 2-dialkylamino-phenyl

- N - methyl carbamates], the substituted - phenyl N - methyl carbamates, (e.g. 4 - thiocyano - phenyl N - methyl carbamate, 3,5 - dimethyl - 4 - alkylthio - phenyl N - methyl carbamate and 3,4 - dimethyl - 6 - chloro - phenyl N - methyl carbamate), carbocyclic carbamates [e.g. 5,5 - dimethyl - 3 - oxo - cyclohexen - (1) - yl N - methyl carbamate and cyclohexen - (3) - yl - methyl N - methyl carbamate], the naphthyl - (1) N - methyl carbamates [e.g. naphthyl - (1) N - methyl carbamate and 2,4 - dichloro - naphthyl - (1) N - methyl carbamate] and the heterocyclic carbamates [e.g. 1 - isopropyl - 3 - methyl - pyrazolyl - (5) N,N - dimethyl carbamate, 1 - phenyl - 3 - methyl - pyrazolyl - (5) N,N - dimethyl carbamate and 2 - methylcarbamoyloximino - 1,3 - dithiolane].
- It has now been found in accordance with the present invention that the use of an insecticidal carbamate in combination with one of the aforesaid propargyl aryl ethers provides an insecticidal composition of greatly enhanced activity. There is thus provided a means for obtaining a quantitative as well as a qualitative improvement in the insecticidal properties of the carbamates. The synergistic compositions of this invention are capable of achieving faster knockdown and greater lethality resulting in much greater control of insects than has heretofore been obtained by the use of carbamates without synergists or carbamates together with known synergists. One particular advantage of the compositions of this invention is their relative lack of toxicity to warm-blooded animals, particularly to mammals.
- The following table (Table I) illustrates the LD₅₀ for representative carbamates and propargyl aryl ethers which may be present in the compositions of this invention.

TABLE I
Mammalian Toxicity

carbamate and/or ether	LD ₅₀ (mg/kg/p.o.)
naphthyl-(1) N-methyl carbamate	840 (m)
" " "	500—700 (r)
4-dimethylamino-3-,5-xylyl N-methyl carbamate	15—60 (r)
1-isopropyl-3-methyl-pyrazolyl-(5) N,N-dimethyl carbamate	55 (r)
2,3,6-trichloro-phenyl propyn-(2)-yl ether	950 (m)
2,3,6-trichloro-phenyl 3-iodopropyn-(2)-yl ether	1250 (m)
naphthyl-(1) N-methyl carbamate and 2,3,6-trichloro-phenyl propyn-(2)-yl ether (1:5)	450 (m)
naphthyl-(1) N-methyl carbamate and 2,3,6-trichloro-phenyl 3-iodopropyn-(2)-yl ether (1:5)	800 (m)

In Table I (m) indicates LD₅₀ in mice and (r) indicates LD₅₀ in rats.

- The exact proportions of the carbamate and other components in the novel compositions of this invention as an insecticidal formulation will vary with the type of intended use in which the insecticide is employed, the method of application, the nature of insect to be controlled and other factors similarly encountered in the insecticidal art. The ratio of carbamate to propargyl aryl ether can vary between wide limits. However, practical considerations limit the amount of propargyl aryl ether used to 0.1 to 10 parts by weight per part of carbamate present in the composition. In a preferred composition, from 1 to 5 parts by weight of 3,4 - methylenedioxy - phenyl propyn - (2) - yl ether are present per part by weight of the insecticidal carbamate.
- The total concentration of these ingredients in a final insecticidal composition will vary with the form of application and type of intended use. The compositions of this invention can be formulated as concentrates, as granules or with carriers as sprays, aerosols

or dusts. For some purposes it is preferred that the carriers include emulsions or solutions or organic solvents and ancillary suspending and wetting agents. Solid carriers may also be employed including chalk, talc, bentonite, kaolin, diatomaceous earth, silica, Fuller's earth, lime, gypsum, flours derived from various organic wastes and similar powders. In general, the techniques used in formulating insecticidal compositions of naphthyl - (1) N - methyl carbamate described in Farm Chemicals, Vol. 128, p. 52 *et seq.* can also be employed in formulating the synergistic insecticidal compositions of the present invention.

The compositions may also contain other additives such as emulsifying agents, wetting agents and masking agents or they can be combined with other known insecticides such as pyrethrins. In these forms the concentrations of active ingredients and the vehicles are adjusted so that flying insects are exposed to lethal amounts of space-sprays or aerosols and crawling, chewing and hopping insects are exposed to surfaces that have been coated with lethal amounts of this composition in dust or in spray form. The compositions of this invention may be made up in the form of concentrates suitable for storage or transport and containing, for example, from 40 to 80 per cent by weight of the insecticidal carbamate and propargyl aryl ether. These concentrates can be diluted with the same or a different carrier to give a concentration of active ingredients for final application. In particular, concentrations of 2 to 20 per cent by weight of the active ingredients based on the total weight of the composition are satisfactory, although lower or higher concentrations can be applied depending upon the mode of application.

The synergistic compositions of this invention can be used to destroy insects by any of the usual techniques such as contact or ingestion and can be applied as a single composition or, alternatively, the active ingredients can be applied serially in any order at time intervals of up to 8 hours or longer. They are active against a wide variety of insects. They are active, for example, against *Diptera* such as houseflies, fruit flies, mosquitoes, stable flies and face flies, *Lepidoptera* such as cabbage loopers, spruce budworms, gypsy moths, corn earworms and armyworms and *Coleoptera* such as alfalfa weevils and flour beetles.

The following tables summarize the results obtained in a series of experiments using

direct topical application of various synergistic compositions of this invention.

Table II hereinafter illustrates the activity of representative combinations of insecticidal carbamate and propargyl aryl ether against houseflies. A susceptible, stable strain (NAIDM) of houseflies (*Musca domestica*) is maintained in the laboratory under the standard conditions prescribed by the CSMA (see: Soap and Chemical Specialties Blue Book).

The test consists in the topical application to the flies of a known amount of candidate insecticidal carbamate, propargyl aryl ether or a composition in a standard volume of acetone (1 mcl). Only adult female flies 4—6 days old are used for testing. Three replicates of ten flies each are run for every insecticidal carbamate, propargyl ether or composition and every concentration:

Testing is carried out in the following manner:

A cage of flies holding approximately 500 individuals is briefly exposed to an atmosphere of CO₂ in a specially constructed chamber to anesthetize the animals. They are then transferred to several porcelain table-type BUCHNER funnels through which a slow stream of CO₂ is maintained and sorted out by sex, the males being discarded. Ten female flies are placed on a filter paper into the top of a disposable plastic petri dish (diameter 100 mm, height 20 mm). A cotton wick soaked with reconstituted non-fat powdered milk is placed into the dish to serve as source of moisture and food. Exactly 1.0 mcl of an acetone solution of the test insecticidal carbamate, propargyl aryl ether or composition as measured by an ISCO micro-applicator, is applied to the thoracic region of each fly (the micro-applicator, which is available commercially from Instrumentation Specialties Co. Lincoln, Nebraska, is essentially a synchronous motor-driven microsyringe with a timed relay). After application of the test solution, the bottom of the petri dish, into which about 10 small holes had been pierced to allow for air circulation, is placed in position. The assembled petri dishes holding the test insects are then placed in a holding room at 78°—80°C for a period of 24 hours. Knockdown is checked at short time intervals for up to 4 hours following application, mortality is checked at 24 hours at which time the test is terminated. Untreated and acetone-treated controls are included with all series.

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TABLE II
Synergistic Effect of Insecticidal Compositions
Containing x MCG of Naphthyl N-Methyl Carbamate
and y MCG of a Propargyl Aryl Ether Applied
Topically to Houseflies

Propargyl aryl ether	x=0 y=10	x=10 y=0	Per Cent Kill			
			x=0.2 y=1.0	x=0.4 y=2.0	x=1.0 y=5.0	x=2.0 y=10.0
2,3,6-trichlorophenyl propyn-(2)-yl ether	0	0	84	100	—	—
2,3,6-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	90	100	—	—
2,3,4-trichlorophenyl propyn-(2)-yl ether	0	0	91	100	—	—
2,4,5-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	53	100	—	—
3,4,5-trichlorophenyl propyn-(2)-yl ether	0	0	88	100	—	—
2,4,5-trichlorophenyl propyn-(2)-yl ether	0	0	47	97	—	—
2,3,5-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	23	97	—	—
2,3,4-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	20	97	—	—
2,4,6-trichlorophenyl propyn-(2)-yl ether	0	0	17	93	—	—
3,4,5-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	13	97	—	—
2,3,5-trichlorophenyl propyn-(2)-yl ether	0	0	13	87	—	—
2,4,6-trichlorophenyl 3-iodopropyn-(2)-yl ether	0	0	0	53	—	—
2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	13	97	100	100
2,5-dichloro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	10	73	—	—
2,3-dichloro-phenyl propyn-(2)-yl ether	0	0	0	0	33	90
2,3,4,6-tetrachlorophenyl 3-iodo-propyn-(X2)-yl ether	0	0	10	90	100	100
2,3,4,5,6-pentachlorophenyl 3-iodo-propyn-(2)-yl ether	0	0	0	0	0	50

TABLE II (Continued)

Propargyl aryl ether	x=0, y=10	x=10, y=0	Per Cent Kill			
			x=0.2, y=1.0	x=0.4, y=2.0	x=1.0, y=5.0	x=2.0, y=10.0
4-methoxy-phenyl propyn-(2)-yl ether	0	0	—	17	—	—
4-methoxy-phenyl 3-iodo-propyn-(2)-yl ether	0	0	—	17	—	—
2,3-dichloro-phenyl 3-bromo-propyn-(2)-yl ether	0	0	—	—	27	100
2,3-dichloro-phenyl propyn-(2)-yl thioether	0	0	—	0	13	—
2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl thioether	0	0	—	13	87	—
3,4-dichloro-phenyl propyn-(2)-yl thioether	0	0	—	0	7	—
2,4,5-trichlorophenyl propyn-(2)-yl thioether	0	0	—	0	43	—
4-nitro-phenyl propyn-(2)-yl ether	0	0	7	77	—	—
3-nitro-phenyl propyn-(2)-yl ether	0	0	83	100	—	—
2-nitro-phenyl 3-iodopropyn-(2)-yl ether	0	0	70	100	—	—
2-nitro-4-chloro-phenyl propyn-(2)-yl ether	0	0	83	100	—	—
4-chloro-2-nitrophenyl 3-iodo propyn-(2)-yl ether	0	0	60	100	—	—
2,4-dibromo-phenyl propyn-(2)-yl ether	0	0	67	100	100	—
2,4-dichloro-phenyl propyn-(2)-yl ether	0	0	20	100	100	—
2,4-dichloronaphthyl-(1) propyn-(2)-yl ether	0	0	57	100	100	—
2-nitro-phenyl propyn-(2)-yl ether	0	0	3	73	97	—
3-nitro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	0	17	100	—
phenyl 3-iodo-propyn-(2)-yl ether	0	0	0	0	57	—
3-methyl-6-isopropyl-phenyl propyn-(2)-yl ether	0	0	0	0	3	—
4-fluoro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	0	3	90	—

TABLE II (Continued)

Propargyl aryl ether	x=0, y=10	x=10, y=0	Per Cent Kill			
			x=0.2, y=1.0	x=0.4, y=2.0	x=1.0, y=5.0	x=2.0, y=10.0
2-chloro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	0	43	100	—
4-chloro-6-iodo-2-nitro-phenyl propyn-(2)-yl ether	0	0	17	76	97	—
4-chloro-6-iodo-2-nitro-phenyl 3-iodo-propyn-(2)-yl ether	0	0	3	6	40	—
2,3-dibromo-phenyl propyn-(2)-yl ether	0	0	13	97	100	—

Table IIA illustrates the insecticidal activity of compositions containing representative insecticidal carbamates and 3,4-methylenedioxy-phenyl propyn-(2)-yl ether or 3,4-methylenedioxy-phenyl 3-iodo-propyn-(2)-yl ether. 5

TABLE IIA

3,4-methylenedioxy-phenyl propyn-(2)-yl ether (mcg/fly)	naphthyl-(1) N-methyl-carbamate (mcg/fly)	Per Cent Kill
10.0	—	0
—	10.0	0
1.0	0.2	83
2.0	0.4	100
3,4-methylenedioxy-phenyl propyn-(2)-yl ether (mcg/fly)	1-isopropyl-3-methyl-pyrazolyl-(5) N,N-dimethylcarbamate (mcg/fly)	Per Cent Kill
—	0.5	0
—	1.0	0
—	2.0	20
—	3.0	50
—	6.0	100
0.5	0.1	50
1.0	0.2	90
2.0	0.4	100
3,4-methylenedioxy-phenyl propyn-(2)-yl ether (mcg/fly)	4-dimethylamino-3,5-xylol N-methyl-carbamate (mcg/fly)	Per Cent Kill
—	0.4	0
—	0.8	15
—	1.0	43
—	2.0	100
0.5	0.1	0
1.0	0.2	70
2.5	0.5	100
3,4-methylenedioxy-phenyl 3-iodo-propyn-(2)-yl ether (mcg/fly)	naphthyl-(1) N-methyl carbamate (mcg/fly)	Per Cent Kill
1.0	0.2	83
2.0	0.4	100

Table III hereinafter illustrates the synergistic effect of a number of representative insecticidal carbamates in combination with a representative propargyl aryl ether.

5 Tables IV and V hereafter illustrate the insecticidal activity of a number of propargyl aryl ethers combined with a representative insecticidal carbamate at various ratios of carbamate to propargyl aryl ether. The carbamate/ether ratio is varied between two parts of carbamate per part of ether and one part of carbamate per five parts of ether.

15 Tables VI, VII and VIII hereafter illustrate the synergistic effect of the compositions of this invention when applied in insecticidal amounts to representative species of *Diptera*, *Lepidoptera* and *Coleoptera*.

Table IX hereinafter illustrates the insecticidal activity of a representative synergistic

composition against the fruit fly. In this test an insecticidal carbamate and/or propargyl aryl ether in specified amounts in 1.0 ml of acetone was used to saturate a filter paper of 9 cm diameter which was dried and then placed in a covered petri dish. Ten 5-day old female fruit flies (60 flies per replicate) were then placed on the treated filter paper and left for one-half, one or two hours, respectively (contact time). After contact with the treated filter paper, the flies were transferred to a clean petri dish where they were held for a 24-hour period after which the number of dead flies was counted. In both dishes the flies had free access to a square of untreated nutrient media. The results are expressed as the per cent of flies killed for the various synergistic compositions at each of the three contact times.

TABLE III

Insecticidal Activity of Various Carbamate/Propargyl Aryl Ether Combinations

1-isopropyl-3-methyl-pyrazolyl-(5) N,N-dimethyl carbamate	2,3,6-trichloro-phenyl propyn-(2)- yl ether	Per Cent Kill
1.0	—	17
2.0	—	30
4.0	—	80
8.0	—	100
0.04	0.2	10
0.06	0.3	50
0.08	0.4	87
0.1	0.5	100
—	10.0	0
4-dimethylamino-3,5-xylyl N-methyl carbamate	2,3,6-trichloro-phenyl propyn- (2)-yl ether	Per Cent Kill
0.4	—	20
0.8	—	73
1.0	—	100
0.1	0.5	13
0.2	1.0	77
0.4	2.0	100
—	10.0	0
N,N-dimethyl carbamate of (3-hydroxy-phenyl) dimethyl amine hydrochloride	2,3,6-trichloro-phenyl 3-iodo- propyn-(2)-yl ether	Per Cent Kill
10.0	—	10
1.0	5.0	87
—	10.0	0

TABLE IV
Synergist Ratio Test; Topical Application to the Housefly
[x Mcg. of Naphthyl-(1) N-Methyl Carbamate and y Mcg
of Propargyl Aryl Ether]

Propargyl aryl ether	Per Cent Kill (24 hours)			
	x=0.2, y=0.1	x=0.2, y=0.2	x=0.2, y=0.4	x=0.2, y=1.0
2,3,6-trichloro-phenyl propyn-(2)-yl ether	12	38	77	84
2,3,6-trichloro-phenyl 3-iodo-propyn-(2)-yl ether	3	13	68	90
2-nitro-phenyl 3-iodo-propyn-(2)-yl ether	10	20	53	70
2-nitro-4-chloro-phenyl propyn-(2)-yl ether	0	13	30	83
3-nitro-phenyl propyn-(2)-yl ether	0	7	13	83
2,4,5-trichloro-phenyl propyn-(2)-yl ether	0	0	10	47
2,3,4-trichloro-phenyl propyn-(2)-yl ether	0	23	27	91
3,4,5-trichloro-phenyl propyn-(2)-yl ether	3	16	23	88

TABLE V
Synergist Ratio Test; Topical Application to the Housefly
[x Mcg. of Naphthyl-(1) N-Methyl Carbamate and y Mcg.
of Propargyl Aryl Ether]

Propargyl aryl ether	Per Cent Kill (24 hours)			
	x=0.4, y=0.2	x=0.4, y=0.4	x=0.4, y=0.8	x=0.4, y=2.0
2-nitro-phenyl 3-iodopropyn-(2)-yl ether	77	70	100	100
2,3,6-trichloro-phenyl propyn-(2)-yl ether	75	93	97	100
2-nitro-4-chloro-phenyl propyn-(2)-yl ether	47	67	80	100
2,4,5-trichloro-phenyl propyn-(2)-yl ether	17	43	83	100
2,3,4-trichloro-phenyl propyn-(2)-yl ether	37	56	97	100
3,4,5-trichloro-phenyl propyn-(2)-yl ether	16	70	93	100
2,3,6-trichloro-phenyl 3-iodo-propyn-(2)-yl ether	40	90	97	100
3-nitro-phenyl propyn-(2)-yl ether	20	87	100	100

TABLE VI
Alfalfa Weevil (*Hypera Postica*)

Topical Application to Larvae (mcg/Larva)
30 Larvae (Last Instar) Per Replicate

Carbamate	Dose	Propargyl aryl ether	Dose	Per Cent Kill (72 hours)
naphthyl-(1) N-methyl carbamate	2.0	—	—	7
„	5.0	—	—	27
„	0.2	2,4,5-trichlorophenyl propyn-(2)-yl ether	1.0	3
„	0.4	„	2.0	60
„	0.8	„	4.0	97
„	1.0	„	5.0	97
—	—	„	10.0	3
—	—	—	—	0 (control)

TABLE VII
Flour Beetle (*Tribolium Confusum*)

Feeding Test (Flour and Glucose Tablet)
Dosage in Mg per 500 Mg Tablet. Two Tablets per Jar of 30 Beetles.
Two Replicate Jars for each Concentration
Experiment Repeated 3 Times with Similar Results

Carbamate	Dose	Propargyl aryl ether	Dose	Per Cent Kill (8 days)
naphthyl-(1) N-methyl carbamate	0.5	—	—	7
„	5.0	—	—	60
„	0.5	2,4,5-trichlorophenyl-propyn-(2)-yl ether	2.5	97
—	—	„	5.0	17
—	—	—	—	0 (control)

TABLE VIII
Cabbage Looper (*Trichoplusia Ni*)
Topical Application to Larvae (Mcg/Larva) 30
Larvae (4th to 5th Instar) per Replicate)

Carbamate	Dose	Propargyl aryl ether	Dose	Per Cnet Kill (40 hours)
1-isopropyl-3-methyl- pyrazolyl-(5) N,N-di- methyl -carbamate	0.5	2,4,5-trichloro-phenyl propyn-(2)-yl ether	2.5	0
”	1.0	”	5.0	0
”	2.0	”	10.0	65
”	4.0	—	—	10
—	—	2,4,5-trichlorophenyl. propyn-(2)-yl ether	10.0	5
—	—	—	—	0 (control)

TABLE IX
Effect of Synergistic Combination of Naphthyl-(1)
N-Methyl Carbamate and 2,4,5-Trichloro-phenyl propyn-
(2)-yl Ether on the Fruit Fly
(*Drosophila Melanogaster*)

Mg Toxicant per 9cm filter paper		Per Cnet Kill at 24 hours		
Naphthyl-(1) N-methyl carbamate	2,4,5-Trichlorophenyl propyn-(2)-yl ether	Contact Time 30 minutes	Contact Time 60 minutes	Contact Time 120 minutes
0.4	2.0	2	3	35
0.8	4.0	18	23	75
1.6	8.0	13	58	93
2.0	10.0	33	93	100
10.0	—	—	2	2
—	10.0	—	2	2
—	—	—	—	0

The propargyl aryl ethers of formula I hereinbefore can be prepared, for example, by condensing the appropriate aromatic alcohol with a halo-propyne to form the terminal acetylenic compounds and, where the terminal halo compounds are desired, by subsequently halogenating the terminal acetylenic carbon atom. The propargyl aryl thioethers of formula I can be prepared by condensing the appropriate aromatic thiol with a mono- or dihalopropyne.

In order that the invention may be more easily understood and readily carried into effect, the following Examples illustrating the preparation of a representative number of propargyl aryl ethers of formula I will now be given:

EXAMPLE 1

2,3,4 - trichloro - phenyl propyn - (2) - yl ether

To a 250 ml three-neck round bottom flask equipped with a stirrer and reflux condenser there were charged 13.5 g (0.068 mol) of 2,3,4 - trichloro - phenol, 8.9 g (0.075 mol) of 3 - bromo - propyne, 10.4 g (0.75 mol) of potassium carbonate and 125 ml of acetone. After the resulting mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60°C. The residue was recrystallized from 100 ml of ethanol and dried in a vacuum oven at 60°C to yield 2,3,4 - trichloro - phenyl propyn - (2) - yl ether of melting point 78°—80°C.

By a procedure analogous to that described in the preceding paragraph, the following compounds were also prepared: 2,3,6 - trichloro - phenyl propyn - (2) - yl ether of melting point 63°—65°C; 3,4,5 - trichloro - phenyl propyn - (2) - yl ether of melting point 64°—65°C; 2,4,5 - trichloro - phenyl propyn - (2) - yl ether of melting point 63°—64°C; 2,4,6 - trichloro - phenyl propyn - (2) - yl ether of melting point 99°—100°C; 2,3,5 - trichloro - phenyl propyn - (2) - yl ether of melting point 62°C; 2,3 - dichloro - phenyl propyn - (2) - yl ether of melting point 47°—49°C; 4 - methoxy - phenyl propyn - (2) - yl ether of boiling point 118°—120°C/7 mm; 4 - nitro - phenyl propyn - (2) - yl ether of melting point 114°—116°C; 3 - nitro - phenyl propyn - (2) - yl ether of melting point 67°—69°C; 2 - nitro - 4 - chloro - phenyl propyn - (2) - yl ether of melting point 82°—84°C; 2,4 - dibromo - phenyl propyn - (2) - yl ether of melting point 67.2°—67.8°C; 2,4 - dichloro - naphthyl - (1) propyn - (2) - yl ether of melting point 100°—100.8°C; 2 - nitro - phenyl propyn - (2) - yl ether of melting point 74°—76°C; 3 - methyl - 6 - isopropyl - phenyl propyn - (2) - yl ether of boiling point 69°C/0.04mm; 4 - chloro - 6 - iodo - 2 - nitro - phenyl propyn - (2) - yl ether of melting point 91°—93°C; 2,3 - dibromo - phenyl propyn - (2) -

yl ether of melting point 49°—50°C and phenyl propyn - (2) - yl ether of boiling point 92°C/25 mm.

EXAMPLE 2

2,3,6 - trichloro - phenyl propyn - (2) - yl ether and 2,3,6 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether

To a 250 ml three-neck round bottom flask equipped with a stirrer and reflux condenser there were charged 19.8 g (0.1 mol) of 2,3,6 - trichloro - phenol, 13.1 g (0.11 mol) of 3 - bromo - propyne, 15.2 g (0.11 mol) of potassium carbonate and 150 ml of acetone. After the resulting mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60°C. The residue was recrystallized from 100 ml of ethanol and dried in a vacuum oven at 50°C to yield 2,3,6 - trichloro - phenyl propyn - (2) - yl ether of melting point 63°—65°C.

To a 500 ml three-neck round bottom flask equipped with a stirrer, a dropping funnel and a thermometer there were charged 8.5 g (0.036 mol) of 2,3,6 - trichloro - phenyl propyn - (2) - yl ether and 75 ml of methanol. To the vigorously stirred solution there were simultaneously added over a period of 15 minutes 12 g (0.048 mol) of iodine (in small portions) and 45 ml of a 10% aqueous solution of sodium hydroxide (0.11 mol) (dropwise), the reaction temperature being kept between 20°C and 25°C by means of an ice-water bath. After stirring for a further hour at room temperature, the mixture was diluted with 100 ml of water and chilled in an ice-water bath. The crystals which formed were filtered off and dried in a vacuum oven at 60°C to yield 2,3,6 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 88°—89°C.

By a procedure analogous to that described in the two preceding paragraphs, the following compounds were also prepared: 2,4,5 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 111°—113°C; 2,3,5 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 98°—100°C; 2,3,4 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 107°—110°C; 3,4,5 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 107°—110°C; 2,4,6 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 102°C; 2,3 - dichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 59°—60°C; 2,5 - dichloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 86°—88°C; 2,3,4,6 - tetrachloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 104°—105°C; 2,3,4,5,6 - pentachloro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 140°—141°C; 4 - methoxy - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 44°—45°C; 2,3 - dichloro - phenyl 3 - bromo - propyn - (2) -

- yl ether of melting point 68°—69°C; 2-nitro-phenyl 3-iodo-propyn-(2)-yl ether of melting point 96°—98°C; 4-chloro-2-nitro-phenyl 3-iodo-propyn-(2)-yl ether of melting point 116°—117°C; 3-nitro-phenyl 3-iodo-propyn-(2)-yl ether of melting point 88°—90°C; phenyl 3-iodo-propyn-(2)-yl ether of boiling point 90°C/0.05 mm; 4-fluoro-phenyl 3-iodo-propyn-(2)-yl ether of boiling point 37°C/0.075 mm; 2-chloro-phenyl 3-iodo-propyn-(2)-yl ether of boiling point 97°C/0.03 mm and 4-chloro-6-iodo-2-nitro-phenyl 3-iodo-propyn-(2)-yl ether of melting point 115°—116°C.

EXAMPLE 3

2-nitro-4-chloro-phenyl propyn-(2)-yl thioether

- To a 500 ml three-neck round bottom flask equipped with a stirrer and dropping funnel there were charged 20 g (0.1 mol) of 2-nitro-4-chloro-thiophenol and 55 ml (0.14 mol) of a 10% aqueous solution of sodium hydroxide. To the stirred solution there were added dropwise over a period of 15 minutes 13 g (0.11 mol) of propargyl bromide, the reaction temperature being kept between 25°C and 30°C. After stirring for 1 hour at room temperature, the precipitate was filtered off, washed with 200 ml of water and dried in a vacuum oven at 60°C to yield 2-nitro-4-chloro-phenyl propyn-(2)-yl thioether of melting point 134°—136°C.

- By a procedure analogous to that described in the preceding paragraph, the following compounds were also prepared: 2,3-dichloro-phenyl propyn-(2)-yl thioether of melting point 59°—60°C; 3,4-dichloro-phenyl propyn-(2)-yl thioether of boiling point 98°C/0.04 mm and 2,4,5-trichloro-phenyl propyn-(2)-yl thioether of melting point 76°—77°C.

EXAMPLE 4

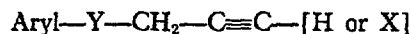
2,3-Dichloro-phenyl 3-iodo-propyn-(2)-yl thioether

- To a 250 ml three-neck round bottom flask equipped with a stirrer and a reflux condenser there were charged 8.9 g (0.05 mol) of 2,3-dichloro-thiophenol, 14.7 g (0.06 mol) of 1-iodo-3-bromo-propyne, 8.3 g (0.06 mol) of potassium carbonate and 150 ml of acetone. After the resulting mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60°C. The residue was taken up in 250 ml of petroleum ether (30°—60°C) and chromatographed on 150 g of silica gel. After taking a total of 1 litre of petroleum ether (30°—60°C) eluates, which were discarded, the column was eluted with eight 200 ml portions of a 1:10 mixture of benzene and petroleum ether. These eluates were pooled and evaporated. The residue was crystallized from 50

ml of petroleum ether (30°—60°C) to give 2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl thioether of melting point 72°—74°C.

WHAT WE CLAIM IS:—

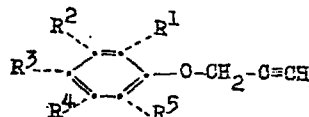
1. A synergistic insecticidal composition comprising an insecticidal carbamate and a propargyl aryl ether of the general formula



wherein Aryl represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group which carries one or more halo, lower-alkyl, lower-alkoxy, methylenedioxy, aryl, aryloxy, aralkyl, aralkoxy, nitro, cyano, carboxyl, carboalkoxy, acylamino and/or N,N-di(lower alkyl)-amido substituents, Y represents an oxygen or sulphur atom and X represents a halogen atom.

2. A composition as set forth in claim 1, wherein from 0.1 to 10 parts by weight of propargyl aryl ether are present for each part by weight of insecticidal carbamate.

3. A composition as set forth in claim 1 or claim 2, wherein the propargyl aryl ether is a propargyl aryl ether of the formula



wherein the symbols R¹, R², R³, R⁴ and R⁵ each represent a halogen atom or a nitro, lower alkyl or lower alkoxy group or any two of said symbols which are adjacent to one another represent a methylenedioxy group and wherein the broken lines denote that the substituents attached thereby are optional.

4. A composition as set forth in claim 1, claim 2 or claim 3, wherein the propargyl aryl ether is a dihalo-phenyl propyn-(2)-yl ether, a trihalo-phenyl propyn-(2)-yl ether or a mononitro-phenyl propyn-(2)-yl ether.

5. A composition as set forth in claim 4, wherein the propargyl aryl ether is 2,3,6-trichloro-phenyl propyn-(2)-yl ether, 2,3,6-trichloro-phenyl 3-iodo-propyn-(2)-yl ether, 2,3,4-trichloro-phenyl propyn-(2)-yl ether, 2,4,5-trichloro-phenyl 3-iodo-propyn-(2)-yl ether, 3,4,5-trichloro-phenyl propyn-(2)-yl ether, 2,4,5-trichloro-phenyl propyn-(2)-yl ether, 2,3,5-trichloro-phenyl 3-iodo-propyn-(2)-yl ether, 3,4,5-trichloro-phenyl 3-iodo-propyn-(2)-yl ether, 2,3,5-trichloro-phenyl propyn-(2)-yl ether, 2,4-dichloro-phenyl propyn-(2)-yl ether, 2,3-dichloro-phenyl 3-iodo-propyn-(2)-yl ether, 2-nitro-4-chloro-phenyl propyn-(2)-yl ether, 4-chloro-2-nitro-phenyl



yl ether of melting point 68°—69°C; 2 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 96°—98°C; 4 - chloro - 2 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 116°—117°C; 3 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 88°—90°C; phenyl 3 - iodo - propyn - (2) - yl ether of boiling point 90°C/0.05 mm; 4 - fluoro - phenyl 3 - iodo - propyn - (2) - yl ether of boiling point 37°C/0.075 mm; 2 - chloro - phenyl 3 - iodo - propyn - (2) - yl ether of boiling point 97°C/0.03 mm and 4 - chloro - 6 - iodo - 2 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether of melting point 115°—116°C.

EXAMPLE 3

2 - nitro - 4 - chloro - phenyl propyn - (2) - yl thioether

To a 500 ml three-neck round bottom flask equipped with a stirrer and dropping funnel there were charged 20 g (0.1 mol) of 2 - nitro - 4 - chloro - thiophenol and 55 ml (0.14 mol) of a 10% aqueous solution of sodium hydroxide. To the stirred solution there were added dropwise over a period of 15 minutes 13 g (0.11 mol) of propargyl bromide, the reaction temperature being kept between 25°C and 30°C. After stirring for 1 hour at room temperature, the precipitate was filtered off, washed with 200 ml of water and dried in a vacuum oven at 60°C to yield 2 - nitro - 4 - chloro - phenyl propyn - (2) - yl thioether of melting point 134°—136°C.

By a procedure analogous to that described in the preceding paragraph, the following compounds were also prepared: 2,3 - dichloro - phenyl propyn - (2) - yl thioether of melting point 59°—60°C; 3,4 - dichloro - phenyl propyn - (2) - yl thioether of boiling point 98°C/0.04 mm and 2,4,5 - trichloro - phenyl propyn - (2) - yl thioether of melting point 76°—77°C.

EXAMPLE 4

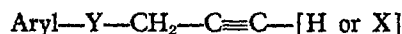
2,3 - Dichloro - phenyl 3 - iodo - propyn - (2) - yl thioether

To a 250 ml three-neck round bottom flask equipped with a stirrer and a reflux condenser there were charged 8.9 g (0.05 mol) of 2,3 - dichloro - thiophenol, 14.7 g (0.06 mol) of 1 - iodo - 3 - bromo - propyne, 8.3 g (0.06 mol) of potassium carbonate and 150 ml of acetone. After the resulting mixture had been stirred and heated at reflux for 8 hours, the solids were filtered off and the filtrate was evaporated *in vacuo* at 60°C. The residue was taken up in 250 ml of petroleum ether (30°—60°C) and chromatographed on 150 g of silica gel. After taking a total of 1 litre of petroleum ether (30°—60°C) eluates, which were discarded, the column was eluted with eight 200 ml portions of a 1:10 mixture of benzene and petroleum ether. These eluates were pooled and evaporated. The residue was crystallized from 50

ml of petroleum ether (30°—60°C) to give 2,3 - dichloro - phenyl 3 - iodo - propyn - (2) - yl thioether of melting point 72°—74°C.

WHAT WE CLAIM IS:—

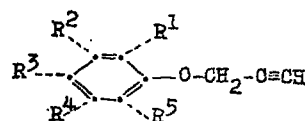
1. A synergistic insecticidal composition comprising an insecticidal carbamate and a propargyl aryl ether of the general formula



wherein Aryl represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group which carries one or more halo, lower-alkyl, lower-alkoxy, methylenedioxy, aryl, aryloxy, aralkyl, aralkoxy, nitro, cyano, carboxyl, carboalkoxy, acylamino and/or N,N - di(lower alkyl) - amido substituents, Y represents an oxygen or sulphur atom and X represents a halogen atom.

2. A composition as set forth in claim 1, wherein from 0.1 to 10 parts by weight of propargyl aryl ether are present for each part by weight of insecticidal carbamate.

3. A composition as set forth in claim 1 or claim 2, wherein the propargyl aryl ether is a propargyl aryl ether of the formula



wherein the symbols R¹, R², R³, R⁴ and R⁵ each represent a halogen atom or a nitro, lower alkyl or lower alkoxy group or any two of said symbols which are adjacent to one another represent a methylenedioxy group and wherein the broken lines denote that the substituents attached thereby are optional.

4. A composition as set forth in claim 1, claim 2 or claim 3, wherein the propargyl aryl ether is a dihalo - phenyl propyn - (2) - yl ether, a trihalo - phenyl propyn - (2) - yl ether or a mononitro - monohalo - phenyl propyn - (2) - yl ether.

5. A composition as set forth in claim 4, wherein the propargyl aryl ether is 2,3,6 - trichloro - phenyl propyn - (2) - yl ether, 2,3,6 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2,3,4 - trichloro - phenyl propyn - (2) - yl ether, 2,4,5 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 3,4,5 - trichloro - phenyl propyn - (2) - yl ether, 2,4,5 - trichloro - phenyl propyn - (2) - yl ether, 2,3,5 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2,3,4 - trichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2,3,5 - trichloro - phenyl propyn - (2) - yl ether, 2,4 - dichloro - phenyl propyn - (2) - yl ether, 2,3 - dichloro - phenyl 3 - iodo - propyn - (2) - yl ether, 2 - nitro - 4 - chloro - phenyl propyn - (2) - yl ether, 4 - chloro - 2 - nitro - phenyl

- 3 - iodo - propyn - (2) - yl ether, 2,4 - di-bromo - phenyl propyn - (2) - yl ether, 2 - chloro - phenyl 3 - iodo - propyn - (2) - yl ether or 2,3 - dibromo - phenyl propyn - (2) - yl ether. 40
- 5 6. A composition as set forth in claim 3, wherein the propargyl aryl ether is 2,3,4,6 - tetrachloro - phenyl 3 - iodo - propyn - (2) - yl ether, 3 - nitro - phenyl propyn - (2) - yl ether, 2 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether, 3 - nitro - phenyl 3 - iodo - propyn - (2) - yl ether or phenyl 3 - iodo - propyn - (2) - yl ether. 45
- 10 7. A composition as set forth in claim 1 or claim 2, wherein the propargyl aryl ether is 2,4 - dichloro - naphthyl - (1) propyn - (2) - yl ether. 50
- 15 8. A composition as set forth in claim 5, wherein the propargyl aryl ether is 2,4 - dichloro - phenyl propyn - (2) - yl ether. 55
- 20 9. A composition as set forth in claim 5, wherein the propargyl aryl ether is 2,4,5 - trichloro - phenyl propyn - (2) - yl ether.
- 25 10. A composition as set forth in claim 5, wherein the propargyl aryl ether is 2 - nitro - 4 - chloro - phenyl propyn - (2) - yl ether.
- 30 11. A composition as set forth in claim 3, wherein the propargyl aryl ether is 3,4 - methylenedioxy - phenyl propyn - (2) - yl ether. 65
- 35 12. A composition as set forth in claim 11, wherein from 1 to 5 parts by weight of 3,4 - methylenedioxy - phenyl propyn - (2) - yl ether are present per part by weight of the insecticidal carbamate.
13. A composition as set forth in any one of claims 1 to 12 inclusive, wherein the insecticidal carbamate is 2 - isopropoxy - phenyl N - methyl carbamate, 4 - (N,N - dimethyl - amino) - 3,5 - xylyl N - methyl carbamate, a 2 - (lower alkyl) - 3 - (N,N - dialkyl - amino) - phenyl N - methyl carbamate, 3,5 - dimethyl - 4 - alkylthio - phenyl N - methyl carbamate, 5,5 - dimethyl - 3 - oxo - [cyclohexen - (1) - yl] N - methyl carbamate, naphthyl - (1) N - methyl carbamate, 1 - isopropyl - 3 - methyl - pyrazolyl - (5) N,N - dimethyl carbamate or 1 - phenyl - 3 - methyl - pyrazolyl - (5) N,N - dimethyl carbamate. 50
14. A composition as set forth in claim 13, wherein the insecticidal carbamate is naphthyl - (1) N - methyl carbamate, 4 - (N,N - dimethyl - amino) - 3,5 - xylyl N - methyl carbamate or 1 - isopropyl - 3 - methyl - pyrazolyl - (5) N,N - dimethyl carbamate. 55
15. A process for enhancing the effectiveness of insecticides containing insecticidal carbamates by incorporating in said insecticides a propargyl aryl ether as set forth in claim 1. 60
16. A method of rendering materials infested with insects or subject on such infestation free from or resistant to infestation, which method comprises treating such materials with a lethal amount of a composition as set forth in claim 1. 65

W. D. WHITAKER,

Patent Agent,

for F. Hoffmann-La Roche & Co.,
Aktiengesellschaft.

