

PATENT SPECIFICATION

NO DRAWINGS

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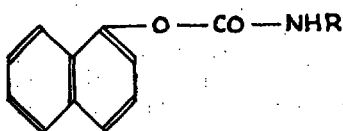
COMPLETE SPECIFICATION

Naphthyl Esters of N-Alkyl-Substituted Carbamic Acids and Insecticidal Compositions containing the same

5 We, UNION CARBIDE CORPORATION (formerly known as Union Carbide and Carbon Corporation), of 30, East 42nd Street, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of JOSEPH AUGUSTINE LAMBRECH), 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:—

10 This invention relates to methods for preparing new chemical compounds, and to insecticidal compositions containing such compounds.

15 The compounds of this invention may be represented by the general formula:



20 wherein R is an alkyl radical having from 1 to 7 carbon atoms.

25 Examples of compounds represented by that formula are: 1-naphthyl N-methyl-carbamate, 1-naphthyl N-ethyl-carbamate, 1-naphthyl N-n-propyl-carbamate, 1-naphthyl N-isopropyl-carbamate, 1-naphthyl N-n-butyl-carbamate, 1-naphthyl N-isobutyl-carbamate, 1-naphthyl N-pentyl-carbamate, 1-naphthyl N-hexyl-carbamate.

30 The compounds of this invention may be

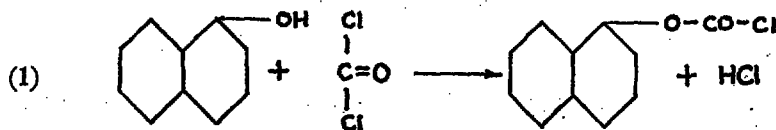
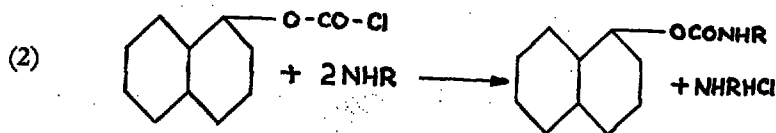
prepared, generally, by reacting 1-naphthol with phosgene to form the corresponding chloroformate and reacting the chloroformate with a primary amine to form the corresponding carbamate and hydrogen chloride. If desired, sodium 1-naphthoxide may be used in place of the 1-naphthol, in which case sodium chloride instead of hydrogen chloride is the reaction product. In the formation of the chloroformate, the phosgene is dissolved in toluene or benzene or other suitable organic solvent and then added to the water solution of the hydroxy compound or its sodium salt at a temperature of from about -30°C . to 20°C . The reaction is slightly exothermic so that some external cooling is usually necessary. The chloroformate separates in the organic phase which is separated from the aqueous phase carrying the hydrogen chloride or sodium chloride. The chloroformate may then either be isolated by distillation or used without further purification.

The reaction involving the addition of the chloroformate to the amine is carried out in the presence of inert solvents for the amine such as water or dioxane. The reaction temperature is preferably in the range from 10°C . to 50°C . Below 10°C . the reaction proceeds but the rate is too slow and above 50°C . the reaction rate is so rapid that loss of low boiling amines may occur and some decomposition may take place.

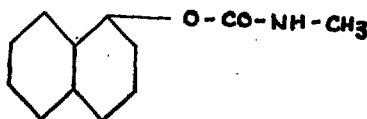
The products of this invention are crystalline solids which are isolated by filtration or centrifugation and dried.

The above described reactions may be represented graphically by the following general equations:





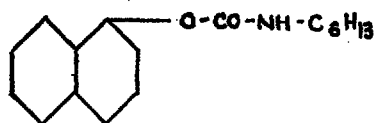
EXAMPLE I
Preparation of 1-naphthyl N-methyl-carbamate.



Following the general procedure, 1-naphthyl N-methyl-carbamate was prepared by first preparing sodium 1-naphthoxide by reacting a mixture of 144 parts of 1-naphthol, 400 parts of water and 44 parts of sodium hydroxide at 85°C. for one hour and then cooling to 20°C. A mixture of 96 parts of phosgene and 300 parts of toluene was then added dropwise. After the addition of the phosgene the reaction mixture was agitated at 25°C. for one hour. The organic phase of the reaction mixture was separated from the salt solution and distilled. 1-Naphthyl chloroformate boils at 96°C. to 100°C. at 2 mm. Hg.

1-Naphthyl N-methyl-carbamate was prepared by slowly adding 103 parts of 1-naphthyl chloroformate to a mixture of 100 parts of a 39 per cent water solution of methylamine and 100 parts of water at 25°C. After the addition of the 1-naphthyl chloroformate the reaction mixture was agitated at 25°C. for one hour. The solid which separated was filtered, washed with water and dried. 1-Naphthyl N-methyl-carbamate is a white crystalline solid which melts at 142°C. Elemental analysis: carbon found 71.2 per cent; theory 71.6 per cent, hydrogen found 5.6 per cent; theory 5.5 per cent.

EXAMPLE II
Preparation of 1-naphthyl N-n-hexyl-carbamate.



1-Naphthyl chloroformate was prepared following the procedure of Example I.

1-Naphthyl N-n-hexyl-carbamate was prepared by slowly adding 103 parts of 1-naphthyl chloroformate to a mixture of 101 parts n-hexylamine and 600 parts dioxane at 20°C. After the addition of the 1-naphthyl chloroformate the reaction mixture was agitated at 40°C. for thirty minutes. The mixture was cooled to 20°C. and the n-hexylamine hydrochloride was removed by filtration. The dioxane was then removed by distillation and the 1-naphthyl N-hexyl carbamate residue dissolved in ethyl ether and washed with water. Ethyl ether was then removed by distillation leaving 1-naphthyl N-n-hexyl-carbamate as a residue product. 1-Naphthyl N-n-hexyl-carbamate is an amber colored liquid which has a specific gravity of 1.064 at 20°C./20°C. and a nitrogen analysis of 5.12 per cent (theory 5.1 per cent).

The compounds of this invention are useful as insecticides and many of them are more potent than rotenone in insecticidal activity. They are stable in the presence of light and air and in the presence of alkaline materials and are thus superior to rotenone, which is oxidized on exposure to air, the oxidation being catalyzed by light and by alkalies, for instance nicotine, lime, lime-sulfur, Bordeaux mixture and alkaline materials which are used as dust diluents.

Experiments were conducted using the following compounds. Compound Nos. 1—5, representing the present invention, were evaluated as insecticides, Compound Nos. 6—13 were tested for comparison.

No. 1—1 - Naphthyl N-methyl-carbamate
The M.P. is 142°C.

No. 2—1-Naphthyl N-ethyl-carbamate —
The M.P. is 102°C.

No. 3—1-Naphthyl N-n-hexyl-carbamate—
The specific gravity is 1.064 at 20°/20°C.

No. 4—1-Naphthyl N-isopropyl-carbamate —
The M.P. is 112°C.

No. 5—1-Naphthyl N-n-butyl-carbamate—
The M.P. is 67°C.

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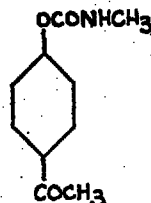
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activity

- No. 6—1-Naphthyl N,N-dibutyl-carbamate —The B.P. is 184°C. at 1.5 mm. Hg.
 No. 7—1-Naphthyl N - (N¹,N¹ - Dimethyl-amino)ethyl-carbamate — The B.P. is 158—164°C. at 3 mm. Hg.
 No. 8—1-Naphthyl N - 1 - naphthyl-carbamate—The M.P. is 260°C.
 No. 9—1-Naphthyl N - (*alpha* - methyl)-benzyl-carbamate—The M.P. is 125°C.
 No. 10—para-Acetylphenyl N-methyl-carbamate—The B.P. is 130—135°C. at 3 mm. Hg.



- No. 11—Phenyl N,N-dimethyl-carbamate—The M.P. is 45°C.
 No. 12—Para-tertiary - butyl - phenyl N,N-dimethyl-carbamate—The B.P. is 110°C. at 15 mm. Hg.
 No. 13—2,3,5-Trimethyl-phenyl N-phenyl-carbamate—The M.P. is 175—176°C.

In one series of tests of the above listed compounds, Mexican bean beetle larvae (*Epilachna varivestis* Muls.) was chosen as a representative test insect and tender green bean plants as a representative test plant. Aqueous suspensions of chemicals Nos. 1 to 13, inclusive, were prepared at the rates of 0.25 gram of the chemical dissolved in 10 milliliters (10 per cent of the final volume of the suspension) of acetone in which was dissolved 0.025 g. (10 per cent of the weight of the chemical) of a non-ionic wetting and emulsifying agent which solution was added to sufficient water to give 100 ml. of the suspension upon agitation. The specific emulsifier used was "Tergitol (Registered Trade Mark) Dispersant NPX" a proprietary non-ionic alkyl phenyl polyethylene glycol ether. The suspensions thus prepared and containing 0.25 per cent of the chemical were sprayed on the bean plants to run-off, the plants being on a revolving turn-table so that all parts of the plants were sprayed. After the plants were dry (about one hour after spraying) each plant was infested with a given number of fourth instar Mexican bean beetle larvae and then the leafy portion of the plant and the larvae were enclosed in a spherical wire mesh cage; and 72 hours after the infestation observations were made of the damage to foliage

by the feeding larvae. The results of the tests are given in the following Table I.

TABLE I.

Compound No.	Mexican Bean Beetle 72 hour rating	
1	A	55
2	A	
3	A	
4	A	
5	A	
6	C	60
7	E	
8	E	
9	E	
10	E	
11	E	65
12	E	
13	E	

The letter ratings in Table I are:

A=excellent control — little feeding (less than 10% foliage consumed)

C=fair control — moderate feeding (10% to 50% of foliage consumed)

E=poor control — severe feeding (51% to 100% foliage consumed)

In tests made on Mexican bean beetle in a similar manner with varying concentrations of compound No. 1, as well as with a known insecticide (rotenone) and the kill of beetles noted and plotted, the amount of toxicant giving a 95 per cent kill (LD 95) was found to be 1.3, and 15.0 milligrams of toxicant in 100 milliliters of suspension, for compound No. 1 and rotenone respectively.

Tests were also conducted on bean aphid (*Aphis rumicis*), using the compounds listed in Table II. For the bean aphid test nasturtium plants growing in small clay pots were infested with about 100 to 150 aphids, and then sprayed in the manner previously stated with spray compositions containing 0.25 gram of the test compound, 10 milliliters of acetone, 0.025 gram of "Tergitol Dispersant NPX" and water to 100 milliliters. After spraying, the plants were placed on their sides in a Petri dish on a piece of white paper which had previously been ruled into squares to facilitate counting. The paper was ringed with tanglefoot glue to prevent the test insects from escaping. Counts of the insects which fell to the paper and those left on the plant were made 24 hours after the spray application.

The results of the tests are given in the following Table II.

TABLE II

Compound No.	Bean aphid 24 hour rating
1	A
2	A
6	C
7	E
8	E
9	E
10	E
11	E
12	E
13	E

The letter ratings in Table II are:

15 A=excellent control (80% to 100% mortality)

C=fair control (30% to 79% mortality)

E=poor control (0% to 29% mortality)

20 In making the tests previously described it was noted that the sprays were not phytotoxic to the plants at the concentrations of the chemicals used. However, it was desired to test compound No. 1 in the field for phytotoxicity on the representative plants corn, bean, tomato, 25 cabbage and broccoli. For this purpose dusts were prepared containing 2.5 and 5.0 parts of compound No. 1 in sufficient inert particulate carrier to give 100 parts by weight. The carrier used was a finely divided pyrophyllite as representative of such inert carriers as infusorial 30 earth, clay, talc, pumice, bentonite diatomaceous earth, cotton seed flour and walnut shell flour. Aqueous suspensions of compound No. 1 were also prepared from a wettable powder 35 consisting of 25 parts by weight of compound 1 in sufficient inert particulate carrier and wetting agent to give 100 parts by weight. The aqueous suspensions were formulated to contain 4, 2 and 1 pounds of the wettable powder 40 per 100 gallons of water. Three applications of the dust and suspensions of compound No. 1 were made at approximately 10 day intervals. The dusts were applied so that complete coverage of the foliage was obtained and the 45 aqueous suspensions were sprayed on the plants to run-off. Notations as to phytotoxicity were made seven days after each application of the spray and dust. Slight phytotoxicity was evident to the bean plants treated with the four 50 pound dosage of compound No. 1 following the third application; lower rates of application to beans showed no phytotoxicity. There was no phytotoxicity at any time to any of the cabbage, broccoli, corn or tomato plants dusted or sprayed with compound No. 1. 55

60 The toxicants or insecticides contemplated herein, i.e. the compounds of this invention, are not deleteriously affected by suitable adjuvants and additives for instance blood albumin or skimmed milk, nor are the phytotoxic properties of the toxicants affected by such agents; and, as distinguished from

rotenone, the properties of the toxicants contemplated herein are not affected by alkaline 65 spray materials such as nicotine, hydrated lime, lime-sulfur, Bordeaux mixture nor alkaline dust extenders with all of which materials the toxicants contemplated herein have been found to be compatible. However, the toxicants are preferably not applied to plants in solution in 70 non-volatile solvents, for instance, oils of the type which are, of themselves, phytotoxic although such oil solutions may be used in treating paper or cardboard. It is a feature of the invention that the toxicants contemplated herein are so chemically inert that they do not 75 react with the various agents nor do they react chemically with the foliage or other parts of the plant or seed, either with or without the additive agents, in a deleterious manner. 80

For application to those parts of the plant which are above ground, the toxicants are preferably applied as water base sprays, the sprays containing the toxicants in finely divided condition, this condition easily being obtained 85 by mixing a solution of the toxicant in a water soluble solvent, for instance acetone, into a larger volume of water whereupon the toxicants are thrown out of solution in the finely divided substantially colloidal condition. In the final 90 spray, the acetone is present in only minute amount and that amount quickly volatilizes as the spray dries. Where the toxicants are used as insecticides in grain or seed treatments, they may be applied to the grain or seeds as a dust, 95 preferably with an adhesive adjuvant, merely being tumbled with the seeds or grain. To obtain a dust, either a concentrate or a dilute composition, having the toxicant in extremely finely divided form or a solution of the toxicant 100 in a volatile solvent, may be mixed into a particulate extender, for instance talc or an adhesive adjuvant, and then dried. The volatilization of the solvent deposits the toxicant on the extender in substantially colloidal sized 105 particles. Regrinding may be necessary to obtain correct particle size. Aqueous spray compositions may also be prepared by grinding the toxicants in water to make a concentrated dispersion, or even with so little water as to make 110 a paste which is then incorporated at the point of use with sufficient additional water to give a spray wherein the toxicant has the desired concentration. The concentrates, either in the form of solutions, concentrated aqueous suspensions, pastes or dusts, may contain such 115 other components of the spray as are desirable, for instance nicotine sulfate or other insecticides or fungicides.

The concentrates from which the ultimate 120 aqueous sprays or dusts are to be prepared preferably contain between 10 and 70 parts by weight of the toxicant with sufficient additional material either inert or active (for instance a contact insecticide or a fungicide) to make 100 125 parts by weight. The ultimate sprays or dusts are prepared by adding a convenient amount

of additional material including inert materials and such addends, for instance nicotine sulfate or other insecticide or fungicide, as may be desired in the spray or dust schedule and as the agriculturist is in the habit of using, so that when the crop plants are thoroughly dusted or sprayed, the toxicants herein contemplated are applied at rates of from 1/32 to 50 lbs. per acre of active toxicant. Whether the toxicants are applied in dust formulations or as aqueous sprays, they are preferably applied in finely divided form. Aqueous sprays prepared by mixing a solution of the toxicants into water are, in general, preferred as the toxicants precipitate in the water in substantially colloidal form and when such a slurry or suspension is applied to the plant the foliage of the plant is thoroughly but adequately covered with the toxicant and the minute particles of the toxicant firmly lodge in the irregularities of the plant surface so that the toxicant is not dislodged by rain nor the flexing of the plant by wind. Satisfactory sprays for general use contain from about 1/2 to 4 pounds of the toxicant to be applied per acre.

Emulsifying agents or suspending agents may be used if desired; in general if the spraying device has mechanism for continually agitating the spray compositions, little or no emulsifying agent need be used but where it is desired to maintain the toxicants in suspension for several hours without agitation a higher amount of emulsifying agent is desirable. The amount of emulsifying agent preferably runs from about 1 pound to 10 pounds per 100 pounds of toxicant but desirably as little emulsifying agent is used as is possible consistent with the desired emulsion characteristics of the spray, so that rain does not emulsify the toxicant after it is applied to the plant and wash it off of the plant.

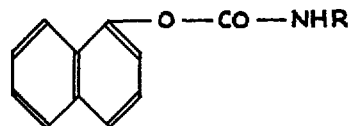
For general use the toxicants are applied as homogeneous aqueous dispersions by the use of surface active agents. These agents cause the toxicants easily to be dispersed in water to give the aqueous sprays. The surface active agents employed may be anionic, cationic or non-ionic and include, for example, sulfonated animal, vegetable and petroleum oils, sodium lauryl sulfate, glycerol monostearate, ethylene oxide condensation products with octyl phenol, lauryl pyridinium bromide and cetyldimethylbenzyl ammonium chloride. The surface active agent can comprise from 1 per cent to 15 per cent by weight of the concentrate.

The insecticides contemplated herein prevent attack by insects upon plants or other material to which the insecticides are applied and they have high residual toxicity. With respect to plants they have a high margin of safety in that, when used in sufficient amount to kill or repel the insects, they do not burn or injure

the plant and they resist weathering which includes wash-off caused by rain, decomposition by ultra violet light, oxidation or hydrolysis in the presence of moisture or, at least, such decomposition, oxidation and hydrolysis as materially decrease the desirable insecticidal characteristics of the toxicants or impart undesirable characteristics, for instance phytotoxicity, to the toxicants. As previously stated the toxicants are so chemically inert that they are compatible with substantially any other constituents of the spray schedule. The low water solubility of the toxicants enable them to be used in the soil upon seeds or the roots of plants without injuring either the seeds, roots or plants by imbibition or root-uptake and they have such low mammalian toxicity that when applied to either the foliage of a plant or the parts of a plant which are below the surface of the soil, for instance tubers and the like, either humans or animals consuming the plants are not injured although, with respect to insects, they kill where the insects imbibe them either through food or, as in the case of the mosquito larvae, through imbibition from the environment.

WHAT WE CLAIM IS:—

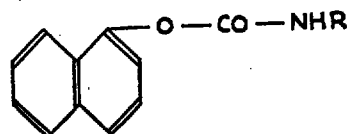
1. Compounds having the formula:



wherein R is an alkyl radical having from 1 to 7 carbon atoms.

2. 1-Naphthyl N-methyl-carbamate.
3. 1-Naphthyl N-ethyl-carbamate.
4. 1-Naphthyl N-*iso*-propyl-carbamate.
5. 1-Naphthyl N-n-butyl-carbamate.
6. 1-Naphthyl N-n-hexyl-carbamate.

7. An insecticide comprising an extender and, as an active insect toxicant, a compound having the formula:



wherein R is an alkyl radical having from 1 to 7 carbon atoms.

8. An insecticide comprising an extender and, as an active insect toxicant, 1-naphthyl N-methyl-carbamate.

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of additional material including inert materials and such addends, for instance nicotine sulfate or other insecticide or fungicide, as may be desired in the spray or dust schedule and as the agriculturist is in the habit of using, so that when the crop plants are thoroughly dusted or sprayed, the toxicants herein contemplated are applied at rates of from 1/32 to 50 lbs. per acre of active toxicant. Whether the toxicants are applied in dust formulations or as aqueous sprays, they are preferably applied in finely divided form. Aqueous sprays prepared by mixing a solution of the toxicants into water are, in general, preferred as the toxicants precipitate in the water in substantially colloidal form and when such a slurry or suspension is applied to the plant the foliage of the plant is thoroughly but adequately covered with the toxicant and the minute particles of the toxicant firmly lodge in the irregularities of the plant surface so that the toxicant is not dislodged by rain nor the flexing of the plant by wind. Satisfactory sprays for general use contain from about 1/2 to 4 pounds of the toxicant to be applied per acre.

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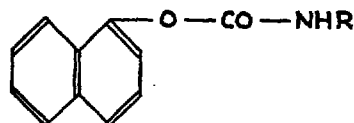
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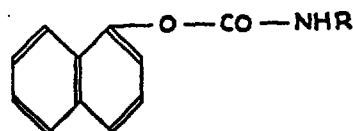
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