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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

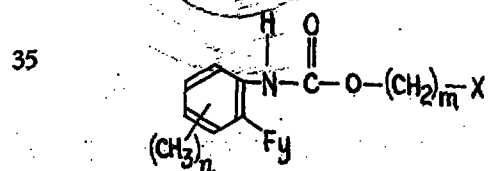
Compounds and Compositions for Controlling Growth of Annual Grasses

We, E. I. DU PONT DE NEMOURS AND COMPANY, 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 concerns certain carbanilic acid esters which are useful for selectively controlling the growth of annual grasses.

It is well recognized by lawn owners that crabgrass is one of the most difficult weeds to eliminate from a lawn as its branching root system firmly anchors the plant in the soil. Minerals and water needed by lawn grasses are used for the growth of the crabgrass plants and the development of lawn grasses in the immediate area of the crabgrass is slowed. The planting of perennial grass seed in the spring therefore, usually results in the crowding out of the perennial grasses before they can become established by the crabgrass which as an annual plant begins its growth in the spring. We have now found that the growth of crabgrass and other annual weed grasses can be selectively controlled by the application of certain carbanilic acid esters.

These carbanilic acid esters are compounds of the formula:



[Price 4s. 6d.]

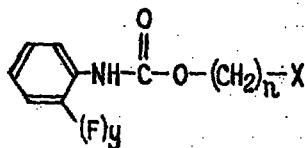
wherein X is saturated cyclo alkyl of 5 to 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, or monohalomonomethyl-saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, saturated bicycloalkyl of 7 or 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, and monohalomonomethyl-saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms, monoethyl- or diethyl-saturated cyclohexyl, with the limitation that when X is cycloalkyl of 5, 7 and 8 carbon atoms and bicycloalkyl of 7 or 8 carbon atoms, (CH₃)_n must be in the *meta* position; and each of m, n and y are 0 or 1. The use of cyclohexanol ester of carbanilic acid (m, n and y are each 0 and X cyclohexyl) is the subject of divisional application No. 35,240/66, Serial No. 1,058,382, and compositions containing this compound and the use of this compound do not form part of the present invention.

We have discovered that by applying the carbanilic acid esters defined above to an area in which there is growing crabgrass, foxtail, German millet, barnyard grass, cheatgrass or Bermudagrass from seed and Johnsongrass from seed there results a marked growth retardation of the seedling grass plants. The esters retard the growth of crabgrass and like annual weed grasses by exerting an effect on the grass root system. The root system fails to grow and develop in a normal manner. Broadleaf plants such as dichondra and established perennial turf grasses such as *Poa pratensis*, Kentucky bluegrass; *Poa* spp., other bluegrasses; *Agrostis* spp., bentgrasses; and *Festuca* spp., fescues show no injury. Therefore, undesirable annual grasses, such as crabgrass, growing in a lawn treated with a compound used in this invention are soon crowded out by desirable plants

or destroyed by lack of an adequate supply of water, oxygen and minerals necessary to sustain life.

5 An additional advantage derived from the use of the esters is that annual grasses are selectively destroyed without disrupting the ecology of the surrounding area. This is accomplished because of the low rate of chemical needed to destroy the annual grasses and the absence of harmful effects on desirable plants from compounds used in this invention even at high rates. Furthermore, the treated crabgrass growing in a well-watered lawn remains green until the desirable lawn grasses take over, so that the lawn owner is not plagued with objectionable brown patches which mar the beauty of his lawn. Previous methods of removing crabgrass, such as with pre-emergence or post-emergence crabgrass herbicides and hand picking, have not been able to accomplish this unexpected result.

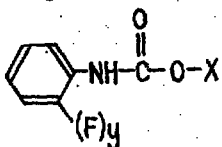
25 The bicycloalkyl or cycloalkyl esters of carbanilic acids of the following formula cause especially marked growth retardation of crabgrass growing in established lawns containing perennial grasses.



II

30 wherein n is 0 or 1; y is 0 or 1; and X is methyl or dimethyl saturated cycloalkyl in which each cycloalkyl has 6 to 8 carbon atoms, saturated bicycloalkyl or cycloalkyl of 7 or 8 carbon atoms or methyl norbornyl.

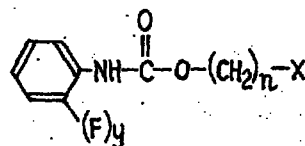
35 The cycloalkyl and alkyl-substituted cycloalkyl esters of carbanilic acids of the following formula exhibit outstanding selectivity in retarding the growth of crabgrass around dicotyledonous plants.



III

40 wherein y is 0 or 1; and X is saturated cycloalkyl of 7 to 8 carbon atoms, saturated bicycloalkyl of 7 or 8 carbon atoms, 2-methylcycloalkyl or 3-methylcycloalkyl in which the cycloalkyl has 5 to 8 carbon atoms.

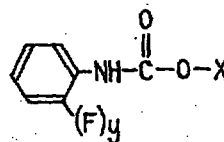
45 The halo substituted cycloalkyl esters of carbanilic acid of the following formula cause especially marked growth retardation of crabgrass growing in established lawns containing perennial grasses.



IV

wherein n is 0 or 1; y is 0 or 1; and X is monohalo- or dihalo- saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, monohalo-, or dihalo- saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms.

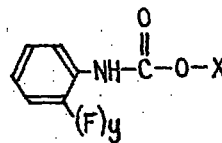
The halo-substituted cycloalkyl esters of carbanilic acid of the following formula exhibit outstanding selectivity in retarding the growth of crabgrass around dicotyledonous plants.



V

wherein y is 0 or 1; and X is monohalo- or dihalo- saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, or monohalo or dihalo- saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms.

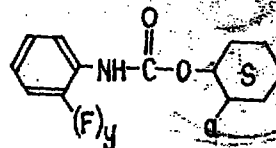
The following compounds are particularly safe to use on Kentucky bluegrass, bentgrass and fescues when retarding crabgrass.



VI

wherein y is 0 or 1; and X is 2-(monohalo)-saturated cycloalkyl of 6 to 8 carbon atoms, 5-halonorbornyl or 6-halonorbornyl.

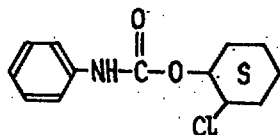
Particularly outstanding annual grass retarding effect is achieved with the *cis* or *trans* isomer of a compound of the formula:



VII

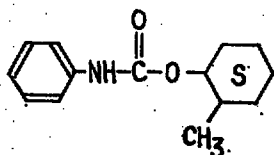
wherein y is 0 or 1; and a is CH₃, Cl or Br.

A particularly preferred compound because of its extended persistence in soil is the *cis* or *trans* isomer of:



VIII

- 5 A particularly preferred compound because of its post-emergence retardation activity on annual weed foliage is the *cis* or *trans* isomer of:



- 10 Mixtures of isomers of the compounds used in this invention can be employed in the procedures of this invention. The most economical means of preparing the cyclo-
15 alkanols, such as 2- or 3-methylcyclohexanol results in a mixture of *cis* and *trans* isomers and this may be used without separation.

For the purposes of this specification and claims *Digitaria* spp., crabgrass; *Setaria* spp. foxtail and German millet; *Echinochloa* spp., barnyard grass; *Bromus secalinus*, cheatgrass; and related genera as well as *Sorghum halepense*, Johnsongrass and *Cynodon dactylon*, Bermudagrass growing from seeds are considered to be annual grass weeds.

- 25 The compositions of the invention contain a compound as defined above together with an inert carrier, e.g. a solid, an oil or a liquid other than an oil, with the proviso that when the carrier consists of a liquid other than an oil, the composition also contains one or more surface-active agents and/or one or more compounds known for use as a plant nutrient, fertilizer, insecticide, fungicide, herbicide or nematocide. The compositions preferably contain a surface-active agent in any case.

- 30 The surface-active agents, also known as surfactants, which can be used in this invention, can be wetting, dispersing, or emulsifying agents. They may act as wetting agents for wettable powders and dusts, as dispersing agents for wettable powders and suspensions, as emulsifying agents for emulsifiable concentrates and may also enhance the biological activity of the carbanilic acid esters of this invention. Such surfactants, can include anionic, cationic and non-ionic agents as have heretofore been generally employed in plant control compositions of similar type, but anionic and non-ionic surfactants are preferred. Suitable surface-active

agents are set out, for example, in Searle United States Patent No. 2,426,417; Jones United States Patent No. 2,412,510; Lenher United States Patent No. 2,139,276; and British Specifications Nos. 691,403 and 692,589. A detailed list of such agents is set forth in "Detergents and Emulsifiers Annual—1963" by John W. McCutcheon, Inc., and Bulletin E-607 of the Bureau of Entomology and Plant Quarantine of the United States Department of Agriculture.

Suitable surfactants for use in compositions of this invention include polyethylene glycol esters with fatty acids and rosin acids, polyethylene glycol ethers with alkylated phenols or with long-chain aliphatic alcohols, polyethylene glycol ethers with sorbitan fatty acid esters, polyoxyethylene thioethers, amine alkali and alkaline earth salts of alkylaryl sulphonic acids, amine alkali and alkaline earth salts of fatty alcohol sulphates, dialkyl esters of alkali metal sulphosuccinates, fatty acid esters of amine alkali and alkaline earth isethionates, and taurates, amine alkali and alkaline earth salts of lignin sulphonic acids, methylated or hydroxyethylated cellulose, polyvinyl alcohols, amine alkali and alkaline earth salts of polymerised alkyl naphthalene sulphonic acids, and long-chain quaternary ammonium compounds.

Preferred wetting agents are sodium alkyl naphthalene sulphonates, sodium dioctylsulphosuccinate, sodium dodecylbenzene sulphonate, ethylene oxide condensates with alkylated phenols such as octyl, nonyl or dodecylphenol, sodium lauryl sulphate, and trimethylnonyl polyethylene glycol. Preferred dispersing agents are sodium, calcium and magnesium lignin sulphonates, low viscosity methyl cellulose, polymerised sodium alkyl naphthalene sulphonate, sodium *N*-oleoyl or *N*-lauryl isethionates, sodium *N*-methyl-*N*-oleoyl taurate, sodium dodecylphenyl-oxide disulphonate, and polyethylene oxide adducts to mixed fatty and rosin acids.

Preferred emulsifying agents are ethylene oxide adducts to lauric, oleic, stearic or palmitic acid esters of sorbitol, polyethylene glycol esters with lauric, oleic, stearic, palmitic or rosin acids, oil soluble alkylaryl sulphonates, oil soluble polyoxyethylene ethers with octyl-, nonyl-, and dodecylphenol, polyoxyethylene adducts to long-chain mercaptans and mixtures of these surfactants.

In general, up to 10% by weight of the surfactant will be used in compositions of this invention and ordinarily the amount of surfactant will be 1–5% but may even be less than 1% by weight.

Additional surfactants can be added to the above formulation to increase the ratio of surfactant:active agent up to as high as 5:1 by weight, so as to increase the growth retardant effect of the active compounds. When used at these higher rates it is preferred



isethionates

that the surfactant be present in the range of one-fifth to five parts surfactant for each one part of active agent.

5 Plant growth retardant compositions of this invention can contain, with or without a surfactant, finely divided inert diluents such as talcs, natural clays including attapulgite clay and kaolinite clay, pyrophyllite, diatomaceous
10 earths, synthetic fine silicas, calcium silicate, carbonates, calcium phosphates, sulphur, lime and such flours as walnut shell, wheat, redwood, soybeans and cottonseed. The amount of the finely divided inert solid diluent can vary widely but will generally
15 range from 10 to 98% by weight of the growth retardant compositions. The particle size can vary considerably but will ordinarily be somewhat under 50 microns in the finished formulation.

20 Compositions containing such finely divided diluents and one or more of the above-mentioned surfactants can be in the form of wettable powders. Such wettable powders are prepared by mixing the cycloalkyl esters of carbanilic acid, surfactants, diluents and
25 other optional ingredients such as corrosion inhibitors, antifoam agents and pigments, in a blender, followed by grinding to obtain a product of fine particle size, suitable for dilution in water and subsequent application as a finely atomized aqueous spray. Such
30 wettable powders can contain 20 to 90% active ingredient, 1/2 to 10% of surface-active agents, plus diluents and optional formulative additives. An active ingredient content of 35 to 85% is preferred.

35 When the composition contains a pulverulent solid and no surfactant, as in dusts or granules, the amount of active ingredient is limited to 0.5% to 10% by weight of the composition. However, if mixtures of the active ingredients are to be processed into extruded pellets, higher active ingredient levels, for example as high as 50%, can
40 be used.

45 Compositions containing an active compound and inert solid diluent can also be formulated into granules and pellets. In such compositions the diluent will generally range from 65 to 99% by weight and the active ingredient can range from 1 to 35% by weight. It should be understood that it will not be necessary to include a surfactant in the granular composition. To prepare granules the active compound can be dissolved in a solvent and this solution can be sprayed over, e.g. pre-formed clay granules or expanded vermiculite to distribute the active ingredient over and throughout the granular
50 mass. Such granules can range in particle size of from +60 mesh to +4 mesh. An active ingredient content of 1 to 6% is preferred. It is also possible to make such granules by mixing the finely divided diluent and finely divided active ingredient, for in-
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stance by grinding together, and then forming granules by adding water, tumbling and drying the resulting product. In another embodiment the active ingredient can be included in granular fertilizer compositions. In addition to the diluents, granular compositions can contain additives such as binders and surfactants.

The cycloalkyl esters of carbanilic acids can also be formulated as densified pellets. For such compositions the active ingredient is mixed with a suitable clay or other binders, the mixture is ground and then compacted in a pug mill, screw extruder, briquetting or tableting machine, and the densified product is broken up into pellets of desired size. If water is added to give the mass suitable plasticity for compaction, as is often desirable when pelleting clays are used and pellets are formed in a screw extruder or pug mill, a drying step is needed. Such compositions may include water soluble salts or surface-active agents to aid the disintegration of pellets and release of active ingredient after application. The active ingredient content of such pellet may range from 5 to 75%, 15-50% being preferred.

In addition to the formulation described above, sand ground formulations can be prepared using the method described in Hochberg U.S. Patent 2,581,414, issued August 19, 1948. Using the methods described in this patent, fine particles of the active compounds within the scope of this invention will be dispersed evenly in a diluent.

100 Emulsifiable oil solutions can also be employed with one or more of the cycloalkyl esters of carbanilic acids used in this invention. In these plant growth regulant compositions, the surface active agent and an oil form a liquid which can be conveniently poured and measured. Such solutions can be mixed with water at the point of application to form an emulsion containing the herbicides and the surface-active agent. Such compositions have the advantage that the oil will often act as a foam inhibitor and thus reduce the tendency for large amount of surfactants to form objectionable foam. The oil used, such as toluene, kerosene, Stoddart solvent, xylene, alkylated naphthalenes, diesel oil and isophorone should be preferably water immiscible and be of a type in which the active agent will be soluble in the amounts used in particular formulations.

110 In the emulsifiable oil concentrations, the cycloalkyl carbanilic acid ester will be present in amounts ranging from 10 to 35% by weight. Precise concentrations of active agent, of course, will depend on the intended use of the composition. When mixed with water at the point of application, the oil concentration will be diluted so that in the final formulation the active agent will be present
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in amounts ranging from 0.5% to 2% by weight.

It is, of course, also possible to use such oil solutions of cycloalkyl esters of carbanilic acids by extending them with other oils, for example, diesel oil and herbicidal oil.

Application.

The esters of formula I above are applied directly to the soil in pre-emergence or post-emergence treatment to foliage or they can be mixed intimately with the soil. Rates of application can be in the range of 1/2 to 20 pounds per acre and preferably will be used as the rate of 1 to 15 pounds per acre. Rates as high as 20 pounds have been used on tests on established turf grasses without undesirable injury.

More specifically, as a pre-emergence application on crop lands 2 to 8 pounds per acre of the compound used in this invention will retard the growth of annual grass weeds. There is a good safety margin to crop plants such as tobacco, corn, cotton, potatoes, flax, eggplants, red clover, ryegrass, tomatoes, peppers, soybeans, red beets, sugar beets, carrots, peanuts, okra, wheat and oat. After treatment, annual grass weeds usually emerge from the ground but then fail to develop showing symptoms of severe growth retardation.

As a directed post-emergence application on crop lands at any time from the moment the weeds emerge to the 3-leaf stage, the plants being approximately 2.5 to 4 inches high, 4 to 10 pounds per acre of active ingredient will prevent the further development of such grasses as crabgrass, Bermudagrass from seed, foxtail, German millet, and barnyard grass. There is a good safety margin to crop plants such as cotton, potatoes, flax, beans, corn, eggplant, red clover, tomatoes, peppers, soybeans, red beets, sugar beets, tobacco, carrots, peanuts and okra.

In particular, the compounds of this invention can be applied at the rate of 2 to 6 pounds per acre to a field of fall seeded wheat in order to give excellent pre-emergence growth retardation of cheatgrass.

As an application on established growing lawns before crabgrass appears, growth of the undesirable crabgrass is retarded with 2 to 10 pounds of active ingredient per acre. There is no injury to established Kentucky bluegrass, bentgrasses or fescues. Crabgrass makes an appearance above the soil and then fails to develop.

As an application on lawn areas either before or after seeding lawn grasses such as bluegrass, bentgrass or fescue and before the lawn grasses and crabgrass have emerged, 2 to 8 pounds of active ingredient per acre prevents the development of crabgrass. There is no undesirable effect on the development of the lawn grasses.

As an application on newly-seeded lawns after such lawn grasses as bluegrass, bentgrass, fescues and crabgrass have appeared 2 to 8 pounds of active ingredient will prevent the further development of crabgrass. There is no perceptible injury to the desirable lawn grasses.

As an application on established lawns after the crabgrass appears at emergence to the 3-leaf stage, 3 to 16 pounds per acre of the active ingredient will prevent the further development of crabgrass without injury to the established grasses.

The esters can also be applied admixed or in common solution with other chemicals which are used in agronomic and horticultural management and are compatible with these esters. Such chemicals may be, but are not restricted to, the classes of chemicals commonly known as plant nutrients, fertilizers, insecticides, fungicides, herbicides and nematocides. Typical of the insecticides that can be used are:

1,2,3,4,10,10 - hexachloro - 6,7 - epoxy - 1,4,4a,5,6,7,8,8a - octahydro - 1,4,5,8 - dimethanonaphthalene (Dieldrin),
1,2,4,5,6,7,8,8 - octachloro - 4,7 - methano - 3a,4,7,7a - tetrahydroindane (Chlordane),
1,1,1 - trichloro - 2,2 - bis(p - methoxyphenyl)ethane (Methoxychlor)
1,1,1 - trichloro - 2,2 - bis(p - chlorophenyl)ethane and
1 - naphthyl - N - methylcarbamate.

Based on the weight of the carbanilic acid ester, 0.02 to 10 parts by weight of insecticide will be present.

Fungicides that can be used in conjunction with the compounds of this invention include one or more of the following:

p - dimethylaminobenzenediazo sodium sulfonate;
quinone oxyaminobenzoxyhydrazone;
tetraalkyl thiuramsulfides such as tetramethyl thiuram monosulfide or disulfide and tetraethyl thiuram monosulfide or disulfide;
metal salts of ethylene bisdithiocarbamic acid, e.g. manganese, zinc, iron and sodium salts;
pentachloronitrobenzene;
dodecylguanidine acetate;
N - trichloromethylthio tetrahydrophthalimide (captan);
phenylmercury acetate;
2,4 - dichloro - 6 - (o - chloroanilino) - s - triazine;
N - methylmercury p - toluenesulfonanilide;
chlorophenol mercuri hydroxides;
nitrophenol mercuri hydroxides;
ethyl mercury acetate;
ethyl mercury 2,3 - dihydroxypropyl mercaptide;
methyl mercury acetate;

- methyl mercury 2,3 - dihydroxypropyl mercaptide;
 3,3' - ethylenebis(tetrahydro - 4,6 - dimethyl - 2H - 1,3,5 - thiadiazine - 2 - thione);
 5 methyl mercury dicyandiamide;
 N - ethyl mercury p - toluenesulfonanilide;
 metal (e.g. iron, sodium and zinc), ammonium and amine salts of dialkyldithiocarbamic acids;
 10 tetrachloronitroanisole;
 hexachlorobenzene;
 methyl mercury nitrile;
 tetrachloroquinone; and
 N - trichloromethylthiophthalimide.

Generally, one can use 0.02 to 10 parts of fungicide by weight based on the carbanilic acid ester. 15

The control of crabgrass with these cycloalkyl esters of carbanilic acid often can be advantageously accomplished together with the use of conventional herbicides in situations where crabgrass is growing with weeds controlled by the second herbicide. 20

Illustrative of herbicides that can be used in conjunction with the active compounds in sprays and granular formulations to take weeds out of other desirable plants are the following. 25

Lbs/acre	Herbicide	Desirable Plants
1—3	2,4-dichlorophenoxy-acetic acid	sugar cane and roadside turf grasses
0.3—1	2,4,5-trichlorophenoxyacetic acid	roadside turf grasses
0.5—1.5	2,4,5-trichlorophenoxypropionic acid	roadside turf grasses
2—4	3-amino-2,5-dichlorobenzoic acid	soybeans
1—4	2,4-bis(isopropylamino)-6-methylmercapto-s-triazine	soybeans, cotton and sugar cane
1—4	1-n-butyl-3-(3,4-dichlorophenyl)-1-methylurea	ornamentals and lawn turf grasses
1—3	2-chloro-4,6-bis-(ethylamino)-s-triazine	ornamentals
1—4	2-chloro-4-ethylamino-6-isopropylamino-s-triazine	sugar cane and pineapples
1—4	3-(p-chlorophenyl)-1,1-dimethylurea	pineapple and sugar cane
0.5—2	4-(2,4-dichlorophenoxy)-butyric acid	alfalfa and other legumes
0.5—2	2-methyl-4-chlorophenoxy-butyric acid	alfalfa and other legumes
1—4	3-(3,4-dichlorophenyl)-1,1-dimethylurea	sugar cane, pineapple, grass seed crops and alfalfa
1—4	N-(3,4-dichlorophenyl)-methacrylamide	cotton
1—3	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea	soybeans

Lbs/acre	Herbicide	Desirable Plants
1—4	1,2-dihydropyridazine-3,6-dione	roadside turf grasses
1—4	2-ethylamino-4-isopropylamino-6-methylmercapto-s-triazine	sugar cane
1—3	sodium 2,4-dichlorophenoxyethylsulfate	soybeans

Where the added herbicides are acids, they may be in the form of salts or non-volatile ester formulations. Also contact herbicides may be included, such as cacodylic acid, potassium cyanate, dinitro - sec. - butyl phenyl, 1,1' - ethylene - 2,2' bipyridylum dibromide (diquat), 1,1' - dimethyl - 4,4' - bipyridylum dichloride (paraquat), disodium methylarsonate, amine methylarsonates and others well known in the art.

Granular compositions of the invention can also include mixtures of the active ingredient on or in fertilizer granules such as are conventionally used for dry application to lawns and golf courses (e.g. fairways and greens). In such compositions the active ingredient content can range from 0.5 to 10% by weight and can be applied to the surface of previously granulated fertilizer or distributed throughout the fertilizer mass prior to granulation. As an example, a conventional 20:10:10 turf food on vermiculite can be treated with a spray containing a solution of the retardant at a rate to give 4% to 8% by weight of active ingredient in the finished product. This yields a composition application in standard lawn spreaders at a rate, for example, of 25 pounds per 5,000 square feet to provide a simultaneous fertilization and long term crabgrass control.

It is understood that the compounds and compositions used in this invention are applied to the "locus" of the grass growth. The term "locus" as used herein and in the claims attached hereto means the plant itself when visible above the ground or the immediate area of soil where the grass plant itself is developing.

It will be apparent to one skilled in the art that certain of the secondary herbicides listed above cannot be applied where it is necessary to preserve the life of desirable grasses.

The following Examples, in which all percents unless otherwise specified are by weight, illustrate the invention.

EXAMPLE 1

A solution of 22.4 parts by weight of 2-methylcyclohexanol in 150 ml. of toluene with 0.1 parts of triethylenediamine is treated with 23.8 parts by weight of phenylisocyanate for 12 minutes. After standing overnight traces of 1,3-diphenylurea by product are filtered from the mixtures and the filtrate is diluted with n-pentane to precipitate the desired product. The product obtained is 40 parts by weight of pure carbanilic acid, 2-methylcyclohexyl ester, m.p. 105—106.5°C.

EXAMPLE 2

The following wettable powder is suitable for any of the compounds described which melt above 90°C.

carbanilic acid, 2-methylcyclohexyl ester	50%	
diatomaceous silica	48%	
coconut acid ester of sodium isethionate	1%	70
sodium lauryl sulfate	1%	

The ingredients are blended and micro-pulverized to pass a 60-mesh screen.

This wettable powder formulation in the amount of four pounds of active ingredient is added to 80 gallons of water in a spray tank. A surfactant such as trimethyl nonyl ether of polyethylene glycol with ethylene oxide, is added to this mixture at the rate of six pounds. This tank spray mixture is applied to one acre of Kentucky 31 fescue lawn which is infested with crabgrass in the one to two leaf stage. Excellent retardation of crabgrass is obtained. It turns dark green, shows very slow growth, and the root system fails to develop normally. The crabgrass offers poor competition and is crowded out by the Kentucky 31 fescue. The fescue shows a slightly reduced rate of growth without injury.

EXAMPLE 3

The following wettable powder formulation is prepared

5	carbanilic acid, 2-methylcyclohexyl ester	52.6%
	Pikes Peak clay	44.4%
	sodium dioctyl sulfosuccinate	1.5%
	sodium lignin sulfonate	1.5%

The above components are blended and micropulverized until homogeneous and then reblended.

A sufficient quantity of the above composition is extended with water so that three pounds per acre of active ingredient is applied in 40 gallons of water to crabgrass and foxtail when they have just emerged to the 3-leaf stage before tobacco is transplanted. A tractor-mounted sprayer designed to spray a blanket application to the prepared soil surface is used for the treatment. After application is made, the tobacco plants are transplanted in the normal manner. This post-emergence treatment results in the control of crabgrass and foxtail during the growing season without injury to the crops.

EXAMPLES 4-5

The following compounds are substituted one at a time for the carbanilic acid, 2-methylcyclohexyl ester of Example 3 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

Ex.	
35	4. carbanilic acid, cis 2-methylcyclohexyl ester
	5. carbanilic acid, 2,2-dimethylcyclohexyl ester

EXAMPLE 6

A formulation example for carbanilic acid, 3-methylcyclohexyl ester follows:

	carbanilic acid, 3-methylcyclohexyl ester	25.00%
	hydrated attapulgite	1.75%
	Na ₂ HPO ₄	0.80%
45	sodium pentachlorophenate	0.60%
	sodium lignin sulfonate	15.00%
	water	56.85%

The above composition is mixed with an equal volume of Ottawa sand of 20-30 mesh and sandmilled for 45 minutes to yield a stable aqueous suspension which may be diluted with water for spray application.

This liquid dispersion is applied at the rate of four to eight pounds of active ingredient per acre in 40 gallons of water for the regulation of crabgrass growth in a planting of arbor-vitae and privet. Crabgrass treated in the one to three leaf stage is retarded markedly.

This formulation has utility for the regulation of crabgrass growth in an established Kentucky 31 fescue lawn. A rate of three to four pounds of active ingredient per acre gives excellent retardation of crabgrass when treated in the two leaf stage.

A further use for this formulation consists of the selective directed post-emergence control of crabgrass and barnyard grass seedlings in young stands of peanuts and soybeans. Application is made by mixing the dispersions at the rate of four to six pounds of active ingredient in 60 gallons of water and spraying at a volume of 60 gallons per acre. The grass weeds substantially cease further growth and eventually are overshadowed by the normally growing crops.

EXAMPLES 7-12

The following compounds are substituted one at a time for the carbanilic acid, 3-methylcyclohexyl ester in Example 6 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

Ex.	
7.	carbanilic acid, 3,4-dimethylcyclopentyl ester
8.	carbanilic acid, 2,4-dimethylcycloheptyl ester
9.	carbanilic acid, 4-methylcyclooctyl ester
10.	carbanilic acid, 2-methylcyclopentyl ester
11.	carbanilic acid, 2-(5,6-dimethyl-norbornyl)methyl ester
12.	carbanilic acid, 2-norbornylmethyl ester

EXAMPLE 13

The following wettable powder can be diluted with water and applied as a post-emergence spray or it can be made up as a tank mix in conjunction with 0.2-5 parts of trimethyl nonyl polyethylene glycol ether per part of active ingredient

	3-methylcarbanilic acid, 2-methylcyclohexyl ester	84%
	montmorillonite clay	13%
	dioctyl sodium sulfosuccinate	2%
	partially desulfonated sodium lignin sulfonate	1%

This wettable powder formulation is applied at the rate of six pounds of active ingredient in conjunction with four pounds of surfactant in 40 gallons of water as a directed post-emergence spray to crabgrass, foxtail and barnyard grass seedlings in a field of cotton when the cotton is eight inches high. Excellent retardation of the growth of the weedy grasses is obtained. Upon examination of the weeds, a severe retardation of the root system is noted. The cotton shows normal growth.

EXAMPLE 14

The following emulsifiable oil can be extended with either oil or water

carbanilic acid, cyclooctyl ester	20%
a blend of polyoxyethylene ethers and oil soluble sulfonates	5%
alkylated naphthalene (principally α -methyl naphthalene)	75%

The above components are blended and agitated until a homogeneous mixture is obtained.

This emulsifiable formulation is extended with 40 gallons of diesel oil and applied at the rate of eight pounds of active ingredient per acre to a brick walk infested with young crabgrass. Excellent growth regulation of crabgrass is obtained.

EXAMPLE 15

The following wettable powder is applicable to the low melting solids described in the examples as well as all the high melting solid compounds of this invention.

carbanilic acid, cycloheptyl ester	25.00%
alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms	1.00%
low viscosity methyl cellulose	0.25%
attapulgitic clay	73.75%

The above components are blended and micropulverized until homogeneous and then reblended.

The formulation described above is applied early post-emergence at the rate of six pounds active ingredient per acre in 80 gallons of water for the control of growth of crabgrass in an established bluegrass-fescue lawn. Excellent retardation of crabgrass is obtained without noticeable damage to the desirable turf grasses.

EXAMPLE 16

carbanilic acid, 3-methylcyclohexyl ester	80%
calcium lignin sulfonate	2%
alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms	2%
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1%
tricalcium phosphate	7%
attapulgitic clay	8%

The ingredients are mixed and micropulverized to a particle size essentially below 50 microns and then reblended.

The above formulation is applied at a rate of four to six pounds of active ingredient in 60 gallons of water for the post-

emergence control of crabgrass along a roadside. This application gives outstanding retardation of crabgrass.

This wettable powder formulation in the amount of six pounds of active ingredient is added to 80 gallons of water. Three pounds of a surfactant is added to this dispersion. The resultant tank spray mixture is applied as a directed post-emergence spray to crabgrass and the grassy weed seedlings in the one to two leaf stage infesting one acre of young tomato plants. An effort is made to direct the spray to the weeds without wetting the stems and foliage of the tomato plants. The further growth of the grasses is arrested and they eventually die; the tomatoes continue normal growth and produce a good crop.

EXAMPLE 17

The following wettable powder formulation is prepared:

carbanilic acid, 2-methylcyclohexyl ester	52.6%
Pikes Peak clay	44.4%
sodium dioctyl sulfosuccinate	1.5%
sodium lignin sulfonate	1.5%

The above components are blended and micropulverized until homogeneous and then reblended.

This formulation is used for the post-emergence control of foxtail and barnyard grass seedlings in flax. For this purpose, the formulation is mixed at the rate of six pounds of active ingredient with 60 gallons of water, and the resulting suspension is applied to the weed infested middles of one acre of 5-inch tall flax. The weedy grass seedlings eventually die; the chemical treatment does not interfere with the normal growth of the crop.

This formulation has utility for the post-emergence control of crabgrass, foxtail, and barnyard grass (emergence to 3-leaf stage) in corn. A directed application to corn which is seven inches high at the rate of four pounds active per acre gives excellent growth retardation of the annual grasses.

This type of treatment is found effective for grass control in cotton, soybeans, peanut, sugar beet, tomato, carrot and peas.

EXAMPLES 18—124

The following compounds are substituted one at a time for the carbanilic acid, 2-methylcyclohexyl ester of Example 17 in like amount by weight and are formulated in like manner. These compounds when applied at the rate of 15 pounds per acre in 60 gallons of water give excellent growth retardation of crabgrass from emergence to 2-leaf stage growing along a walkway.

dimethylcyclohexyl



Ex.	18.	carbanilic acid, trans,cis - 2 - methylcyclopentyl ester	Ex.	50.	o - fluorocarbanilic acid, 2 - chlorocyclohexyl ester	
5	19.	carbanilic acid, trans,cis - 3 - methylcyclopentyl ester	51.	o - fluorocarbanilic acid, 2 - bromocyclohexyl ester		70
	20.	carbanilic acid, trans,cis - 1,2 - dimethylcyclopentyl ester	52.	o - fluorocarbanilic acid, cyclohexylmethyl ester		
	21.	carbanilic acid, 2,2 - dimethylcyclopentyl ester	53.	o - fluorocarbanilic acid, norbornyl ester		
10	22.	carbanilic acid, 3,3 - dimethylcyclopentyl ester	54.	o - fluorocarbanilic acid, bicyclooctane ester		75
	23.	carbanilic acid, 3 - methylcyclopentylmethyl ester	55.	carbanilic acid, 2,2 - dimethylcyclohexyl ester		
15	24.	carbanilic acid, 2 - methylcyclopentylmethyl ester	56.	carbanilic acid, 1,2 - dimethylcyclohexyl ester		
	25.	carbanilic acid, (cis - 2,3 - dimethylcyclopentylmethyl) - ester	57.	carbanilic acid, 4 - ethylcyclohexyl ester		80
	26.	carbanilic acid, 1 - methylcyclohexyl ester	58.	carbanilic acid, 3,3 - dimethylcyclohexyl ester		
20	27.	carbanilic acid, 2 - methylcyclohexyl ester	59.	carbanilic acid, cis - 2 - ethylcyclohexyl ester		
	28.	carbanilic acid, 3 - methylcyclohexyl ester	60.	carbanilic acid, 3 - ethylcyclohexyl ester		85
	29.	carbanilic acid, 4 - methylcyclohexyl ester	61.	3 - methylcarbanilic acid, cycloheptyl ester		
25	30.	carbanilic acid, 1 - ethylcyclohexyl ester	62.	3 - methylcarbanilic acid, cyclooctyl ester		
	31.	carbanilic acid, 3,4 - dimethylcyclohexyl ester	63.	carbanilic acid, 2,2 - dimethylcyclohexyl ester		90
30	32.	carbanilic acid, 1,3 - dimethylcyclohexyl ester	64.	carbanilic acid, 3,3 - dimethylcyclohexyl ester		
	33.	carbanilic acid, 2,4 - dimethylcyclohexyl ester	65.	carbanilic acid, 4,4 - dimethylcyclohexyl ester		95
35	34.	carbanilic acid, 3,5 - dimethylcyclohexyl ester	66.	carbanilic acid, 1,2 - diethylcyclohexyl ester		
	35.	carbanilic acid, 1,4 - dimethylcyclohexyl ester	67.	carbanilic acid, (2,3 - dimethylcyclohexylmethyl)ester		
	36.	carbanilic acid, 2,5 - dimethylcyclohexyl ester	68.	carbanilic acid, (2,6 - dimethylcyclohexylmethyl)ester		100
40	37.	carbanilic acid, (dl - cis - 2 - methylcyclohexyl)ester	69.	carbanilic acid, (3,3 - dimethylcyclohexylmethyl)ester		
	38.	carbanilic acid, (dl - trans - 2 - methylcyclohexyl)ester	70.	carbanilic acid, (2 - methylcyclohexylmethyl)ester		105
45	39.	carbanilic acid, (1 - cis - 3 - methylcyclohexyl)ester	71.	carbanilic acid, (cis - 2 - methylcyclohexylmethyl)ester		
	40.	carbanilic acid, (dl - cis - 3 - methylcyclohexyl)ester	72.	carbanilic acid, (trans - 2 - methylcyclohexylmethyl)ester		
	41.	carbanilic acid, (1 - trans - 3 - methylcyclohexyl)ester	73.	carbanilic acid, (cis - 3 - methylcyclohexylmethyl)ester		110
50	42.	carbanilic acid, cis - 2 - ethylcyclohexyl ester	74.	carbanilic acid, (trans - 3 - methylcyclohexylmethyl)ester		
	43.	carbanilic acid, trans - 2 - ethylcyclohexyl ester	75.	carbanilic acid, (trans - 4 - methylcyclohexylmethyl)ester		115
55	44.	carbanilic acid, 2,6 - dimethylcyclohexyl ester	76.	carbanilic acid, (1 - methylcyclohexylmethyl) ester		
	45.	carbanilic acid, 2,4 - dimethylcyclohexyl ester	77.	carbanilic acid, (1 - ethylcyclohexylmethyl) ester		
	46.	carbanilic acid, (3,5 - dimethylcyclohexyl) ester	78.	carbanilic acid, cycloheptyl ester		120
60	47.	carbanilic acid, (3,5 - dimethylcyclohexyl) ester	79.	carbanilic acid, 2,2 - dimethylcycloheptyl ester		
	48.	o - fluorocarbanilic acid, 2 - methylcyclohexyl ester	80.	carbanilic acid, 2 - methylcycloheptyl ester		
65	49.	o - fluorocarbanilic acid, 3 - methylcyclohexyl ester	81.	carbanilic acid, trans - 2,2 - dimethylcycloheptyl ester		125
			82.	carbanilic acid, cis - 2,2 - dimethylcycloheptyl ester		
			83.	carbanilic acid, 4 - methylcycloheptyl ester		130

- Ex.
 84. carbanilic acid, trans - 3 - methylcycloheptyl ester
 5 85. carbanilic acid, 4,4 - dimethylcycloheptyl ester
 86. carbanilic acid, 1 - methylcycloheptyl ester
 87. carbanilic acid, cyclooctyl ester
 10 88. carbanilic acid, cis - 2 - methylcyclooctyl ester
 89. carbanilic acid, trans - 2 - methylcyclooctyl ester
 90. carbanilic acid, 2,2 - dimethylcyclooctyl ester
 15 91. carbanilic acid, 1 - methylcyclooctyl ester
 92. carbanilic acid, 2 - norbornyl ester
 93. carbanilic acid, (2 - norbornylmethyl)-ester
 20 94. carbanilic acid, α - norpinyl ester
 95. carbanilic acid, β - norpinyl ester
 96. carbanilic acid, trans,cis - 1 - methylcyclopentyl ester
 25 97. 2 - methylcarbanilic acid, 2 - methylcyclohexyl ester
 98. 4 - methylcarbanilic acid, 2 - methylcyclohexyl ester
 99. 2 - methylcarbanilic acid, 3 - methylcyclohexyl ester
 30 100. 4 - methylcarbanilic acid, 3 - methylcyclohexyl ester
 101. 2 - methylcarbanilic acid, 3,4 - dimethylcyclohexyl ester
 102. 4 - methylcarbanilic acid, 3,4 - dimethylcyclohexyl ester
 35 103. 3 - methylcarbanilic acid, 2 - methylcyclohexyl ester
 104. 3 - methylcarbanilic acid, 2 - methylcyclohexyl ester
 40 105. 3 - methylcarbanilic acid, 1 - methylcyclopentyl ester
 106. 3 - methylcarbanilic acid, 2,2 - dimethylcyclohexyl ester
 45 107. 3 - methylcarbanilic acid, norbornyl ester
 108. 3 - methylcarbanilic acid, methyl-norbornyl ester
 109. 3 - methylcarbanilic acid, methyl(2 - methylnorbornyl) ester

EXAMPLE 110

- 50 A solution of 19.6 parts by weight of aniline in 200 parts of ether is treated with 19.7 parts by weight of 2 - chlorocyclohexyl chloroformate. The temperature is maintained
 55 below -30° with external cooling. The precipitate of aniline hydrochloride is filtered and the filtrate is evaporated in vacuo on a steam bath. The residual oil crystallizes on pouring into an excess of n-pentane. The product is filtered, washed with pentane and
 60 dried to yield 23 parts by weight of the 2 - chlorocyclohexyl ester of carbanilic acid, m.p. $97-99^{\circ}\text{C}$.

EXAMPLE 111

The following granular formulation can be used. A wettable powder is first prepared by micropulverizing the following ingredients

2 - chlorocyclohexyl ester of carbanilic acid	50%	
attapulgit clay	48%	70
dioctyl sodium sulfosuccinate	1%	
sodium lignin sulfonate	1%	

The wettable powder is distributed over the surface of #4 vermiculite by tumbling together. To make the combination more adherent the mix is sprayed with a mixture of ethylene glycol and water. The final ratio of ingredients is as follows

50% active wettable powder	4%	
#4 vermiculite	86%	80
ethylene glycol	5%	
water	5%	

In a modification of the above formulation the ethylene glycol can be replaced by a mixture of the sodium sulfates of mixed long chain alcohol fatty acid esters and diethylene glycol acetate in a ratio between 1:10 and 10:1 by weight.

The granular formulation described above has utility as a pre-emergence treatment for retarding the growth of crabgrass in an established Kentucky bluegrass-creeping red fescue lawn. The material is applied with a granule spreader at the rate of six pounds of active ingredient per acre prior to the germination of crabgrass. Such excellent retardation of crabgrass is obtained that it presents no competition to the established lawn.

Immediately after a field has been prepared for transplanting flue-cured tobacco seedlings, a fertilizer spreader is used to spread evenly 100 pounds per acre of the 4% active granular formulation over the entire area. After application, the tobacco is transplanted from the seed bed to the field. The application of granules in this manner results in outstanding control of crabgrass throughout the season with no injury to the tobacco crop.

EXAMPLES 112-114

The following compounds are substituted one at a time for the 2 - chlorocyclohexyl ester of carbanilic acid in Example 111 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

- Ex.
 112. 2 - chlorocyclohexyl ester of 3 - methylcarbanilic acid
 113. 2 - bromocyclohexyl ester of carbanilic acid
 114. 2 - bromocyclopentyl ester of carbanilic acid

EXAMPLE 115

The following wettable powder is suitable for any of the compounds described which melt above 90°C.

5	2-chlorocyclohexyl ester of carb-anilic acid	50%
	diatomaceous silica	48%
	coconut acid ester of sodium isethionate	1%
10	sodium lauryl sulfate	1%



1-1

The ingredients are blended and micro-pulverized to pass a 60-mesh screen.

This wettable powder formulation in the amount of four pounds of active ingredient is added to 80 gallons of water in a spray tank. A surfactant such as trimethyl nonyl polyethylene glycol ether is added to this mixture at the rate of six pounds. This tank spray mixture is applied to one acre of Kentucky 31 fescue lawn which is infested with crabgrass in the one to two leaf stage. Excellent retardation of crabgrass is obtained. It turns dark green, shows very slow growth, and the root system fails to develop normally. The crabgrass offers poor competition and is crowded out by the Kentucky 31 fescue. The fescue shows a reduced rate of growth without injury.

This formulation also has utility for the pre-emergence control of crabgrass, foxtail and barnyard or watergrass in new seedlings of peanuts, flax, carrots, corn, cotton, soybeans, oats, wheat, sugar beets, red clover, alfalfa, lespedeza, peas and tomato. To this end eight pounds of the 50% wettable powder is added to 80 gallons of water in a tractor-mounted spray tank. The growth and normal development of said grass weeds is suppressed; the crops emerge and continue to grow normally.

This formulation is used also for the post-emergence control of crabgrass, foxtail and barnyard grass seedlings from the time of their emergence to two weeks thereafter. A directed spray of three to four pounds of active ingredient in 40 gallons of water gives excellent growth retardation of these annual grasses in sugar beets, peas, tomato, soybeans, cotton and corn. The spray is directed to the base of the stem of the established economic crops.

EXAMPLES 116-117

The following compounds are substituted one at a time for the 2-chlorocyclohexyl ester of carbanilic acid of Example 115 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

- Ex.
116. 2-bromocyclohexyl ester of carbanilic acid
117. 2,2-dichlorocyclohexyl ester of carbanilic acid

EXAMPLE 118

A formulation example for 5-chloronorbonyl ester of carbanilic acid follows

5-chloronorbonyl ester of carb-anilic acid	25.00%
hydrated attapulgite	1.75%
Na ₂ HPO ₄	0.80%
sodium pentachlorophenate	0.60%
sodium lignin sulfonate	15.00%
water	56.85%

The above composition is mixed with an equal volume of Ottawa sand of 20-30 mesh and sandmilled for 45 minutes to yield a stable aqueous suspension which may be diluted with water for spray application.

This liquid dispersion is applied at the rate of eight pounds of active ingredient per acre in forty gallons of water for the regulation of crabgrass growth in a planting of arbor-vitae and privet. Crabgrass treated in the one to three leaf stage is retarded markedly. Crabgrass seeds in the soil germinate but fail to grow.

This formulation has utility for the regulation of crabgrass growth in an established Kentucky 31 fescue lawn. A rate of three to four pounds of active ingredient per acre gives excellent retardation of crabgrass when treated in the two leaf stage.

A further use for this formulation consists of the selective directed post-emergence control of crabgrass and barnyard grass seedlings in young stands of peanuts and soybeans. Application is made by mixing the dispersions at the rate of six pounds of active ingredient in sixty gallons of water and spraying at a volume of sixty gallons per acre. The grass weeds substantially cease further growth and eventually are overshadowed by the normally growing crops.

EXAMPLE 119

The 2-chlorocyclohexyl ester of carbanilic acid is formulated and applied in the manner of the 5-chloronorbonyl ester of carbanilic acid of Example 118. Like results are obtained.

Additionally, this suspension is extended with water in such a manner that three pounds per acre of active ingredient is applied on a 24 inch band with a specially designed tractor mounted sprayer arrangement which will apply the material to the sides and top of a row to be transplanted with burley tobacco. After application, the row is transplanted with tobacco within a period of ten days after treatment. The chemical application provides excellent control of crabgrass in the treated area for the entire growing season, thus facilitating the control of crabgrass and other grass weeds by accepted cultural practices between the rows.

EXAMPLES 120—125

The following compounds are substituted one at a time for the 5-chloronorbornyl ester of carbanilic acid in Example 118 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

5

Ex.

- 10 120. 3,4 - dichlorocyclohexyl ester of carbanilic acid
 121. 2,4 - dichlorocyclohexyl ester of carbanilic acid
 122. 4 - chlorocyclooctyl ester of carbanilic acid
 15 123. 2 - chlorocyclopentyl ester of carbanilic acid
 124. 2 - (5,6 - dibromonorbornyl)methyl ester of carbanilic acid
 20 125. 2 - (2 - chloro - 3 - methylnorbornyl)-methyl ester of carbanilic acid

EXAMPLE 126

- 25 The following wettable powder can be diluted with water and applied as a post-emergence spray or it may be made up as a tank mix in conjunction with 0.2—5 parts of trimethyl nonyl polyethylene glycol ether per part of active ingredient

- 30 2 - chlorocycloheptyl ester of 3 - methylcarbanilic acid 84%
 montmorillonite clay 13%
 dioctyl sodium sulfosuccinate 2%
 partially desulfonated sodium lignin sulfonate 1%

- 35 This wettable powder formulation is applied at the rate of four pounds of active ingredient in conjunction with four pounds of surfactant in 40 gallons of water as a directed post-emergence spray to crabgrass, foxtail and barnyard grass seedlings in a field of cotton when the cotton is six inches high.
 40 Excellent retardation of growth of the weedy grasses is obtained. Late germinating seedlings are retarded severely. Upon examination of the weeds, a severe retardation of the root system is noted. The cotton shows normal growth.
 45

- Another use for this wettable powder formulation is for the pre-emergence control of foxtail in new seedlings of wheat and
 50 oats. Application is made at the rate of four pounds of active ingredient in 30 gallons of water, sprayed by means of a boom-type spreader within a day after seeding the crops. The *Setaria* species emerge but soon cease to make further growth; the grain crops develop normally.
 55

A similar formulation of the 2-chlorocyclohexyl ester of carbanilic acid applied in like manner at the rate of four pounds

of active ingredient per acre, provides excellent control of *Setaria* species, barnyard grass and crabgrass in corn, soybeans, peanuts, wheat and oats. 60

EXAMPLE 127

The following emulsifiable oil can be extended with either oil or water 65

- 2 - chlorocyclooctyl ester of carbanilic acid 20%
 a blend of polyoxyethylene ethers and oil soluble sulfonates 5% 70
 alkylated naphthalene (principally α - methyl naphthalene) 75%

The above components are blended and agitated until a homogeneous mixture is obtained. 75

This emulsifiable formulation is extended with 40 gallons of diesel oil and applied at the rate of eight pounds of active ingredient per acre along the edge of a brick walk infested with young crabgrass. Excellent growth regulation of crabgrass is obtained. Weed seeds germinating after treatment show severe retardation. 80

A pre-emergence application of the above formulation at the rate of four pounds of active ingredient per acre in 40 gallons of water gives excellent retardation of crabgrass and foxtail in newly planted fields of soybeans or flax. The crops soon outgrow the severely stunted grass seedlings. 85 90

EXAMPLE 128

The following wettable powder is applicable to the low melting solids described in the examples as well as all the high melting solid compounds of this invention. 95

- 2 - bromocyclohexyl ester of carbanilic acid 25.00%
 alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms 1.00% 100
 low viscosity methyl cellulose 0.25%
 attapulgit clay 73.75%

The above components are blended and micropulverized until homogeneous and then reblended. 105

The formulation described above is applied pre-emergence at the rate of four pounds active ingredient per acre in 100 gallons of water for the control of growth of crabgrass in an established bluegrass-fescue lawn. Excellent retardation of crabgrass is obtained without noticeable damage to the desirable turf grasses. 110

EXAMPLE 129

	3,5 - dichlorocyclohexyl ester of carbanilic acid	80%
	calcium lignin sulfonate	2%
5	alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms	2%
	CaSO ₄ · 2H ₂ O	1%
10	tricalcium phosphate	7%
	attapulgite clay	8%

The ingredients are mixed and micro-pulverized to a particle size essentially below 50 microns and then reblended.

- 15 The above formulation is applied at a rate of six pounds of active ingredient in sixty gallons of water for the pre-emergence control of crabgrass along a roadside. This application gives outstanding retardation of
- 20 crabgrass. Germinating seedlings are retarded markedly.

- This wettable powder formulation in the amount of six pounds of active ingredient is added to 80 gallons of water. Three pounds of a surfactant is added to this dispersion.
- 25 The resultant tank spray mixture is applied as a directed post-emergence spray to crabgrass and seedlings in the one to two leaf stage infesting one acre of young tomato plants. An effort is made to direct the spray to the weeds without wetting the stems and foliage of the tomato plants. The further growth of the grasses is arrested and they eventually die; the tomatoes continue normal
- 30 growth and produce a good crop.
- 35

EXAMPLE 130

Granular formulation

- 40 The following granular formulation has general application to the cis(2 - chlorocyclohexyl)ester of carbanilic acid used in this invention.

	cis(2 - chlorocyclohexyl)ester of carbanilic acid	2%
	15—30 mesh attaclay granules	98%

- 45 The active material can be applied to the attaclay granules in several ways. (1) The active material can be dissolved in a volatile solvent such as acetone and sprayed on the tumbling granules, or (2) wettable powder containing the active material can be distributed on the surface of the granules. By moistening with water or a mixture of water and ethylene glycol dusting off is prevented.
- 50 In other granular formulation, if the melting point of the active ingredient is below 99°C., the active ingredient can be melted and sprayed over a tumbling mass of pre-formed clay, vermiculite or similar granules.

- 55 This granular formulation is applied pre-emergence with a granule spreader at the
- 60

rate of six pounds of active ingredient per acre for the control of growth of crabgrass in an established bluegrass-meadow, fescue lawn. The crabgrass emerges from the soil but fails to grow. The established lawn grasses show slight retardation with no objectionable injury.

65

EXAMPLES 131—182

The following compounds are substituted one at a time for the cis(2 - chlorocyclohexyl)-ester of carbanilic acid in Example 130 in like amount by weight and are formulated in like manner. These compounds are applied pre-emergence at the rate of ten pounds per acre for the control of crabgrass and foxtail in parking lots. Excellent control is obtained.

70

compounds

75

Ex.

131. trans,cis - 2 - chloro - 1 - methylcyclopentyl ester of carbanilic acid
132. trans,cis - 2 - chloro - 2 - methylcyclopentyl ester of carbanilic acid 80
133. trans,cis - 2 - chloro - 5 - methylcyclopentyl ester of carbanilic acid
134. 2 - chlorocyclopentyl ester of 3 - methylcarbanilic acid 85
135. 1 - chloro - 2 - methylcyclopentylmethyl ester of carbanilic acid
136. 1 - bromocyclopentylmethyl ester of 3 - methylcarbanilic acid
137. 1 - chlorocyclopentylmethyl ester of carbanilic acid 90
138. trans - 2 - chlorocyclohexyl ester of carbanilic acid
139. 4 - chlorocyclohexyl ester of 3 - methylcarbanilic acid 95
140. 2 - bromocyclohexyl ester of carbanilic acid
141. 2 - chlorocyclohexylmethyl ester of carbanilic acid
142. 2 - chlorocyclohexyl ester of 3 - methylcarbanilic acid 100
143. 2 - chloro - 5 - methylcyclohexyl ester of carbanilic acid
144. 4 - bromocyclohexyl ester of carbanilic acid 105
145. 2 - iodo - 1 - methylcyclohexyl ester of 3 - methylcarbanilic acid
146. 2 - chloro - 1 - methylcyclohexyl ester of carbanilic acid
147. 2 - bromo - 1 - methylcyclohexyl ester of 3 - methylcarbanilic acid 110
148. 2 - chloro - 5 - methylcyclohexyl ester of carbanilic acid
149. trans - 2 - iodocyclohexyl ester of 3 - methylcarbanilic acid 115
150. trans - 2 - bromocyclohexyl ester of 3 - methylcarbanilic acid
151. cis - 2 - chloro - 2 - methylcyclohexyl ester of carbanilic acid
152. 2 - bromocyclohexyl ester of 3 - methylcarbanilic acid 120
153. 2 - chlorocycloheptyl ester of carbanilic acid

154. 2-bromocyclooctyl ester of 3-methylcarbanilic acid
- 5 155. 2-chloro-6-methylcyclohexyl ester of carbanilic acid
156. 2-chloro-4-methylcyclohexyl ester of 3-methylcarbanilic acid
157. 2-chloro-3-methylcyclohexyl ester of carbanilic acid
- 10 158. 2,3-dibromocyclohexyl ester of 3-methylcarbanilic acid
159. (dl-2-chloro-2-methylcyclohexylmethyl) ester of carbanilic acid
- 15 160. 2-chlorocyclohexylmethyl ester of carbanilic acid
161. 1,2-dibromocyclohexylmethyl ester of 3-methylcarbanilic acid
162. 1-chlorocyclohexylmethyl ester of carbanilic acid
- 20 163. 1-bromocyclohexylmethyl ester of 3-methylcarbanilic acid
164. 2-chlorocycloheptyl ester of carbanilic acid
- 25 165. cis-2-chloro-5-methylcycloheptyl ester of 3-methylcarbanilic acid
166. cis-1-chloro-2-methylcycloheptyl ester of carbanilic acid
167. cis-2-chloro-1-methylcycloheptyl ester of 3-methylcarbanilic acid
- 30 168. trans-2-bromocycloheptyl ester of carbanilic acid
169. trans-2-iodocycloheptyl ester of 3-methylcarbanilic acid
- 35 170. 2-chlorocyclooctyl ester of carbanilic acid
171. cis-2-bromocyclooctyl ester of carbanilic acid
172. trans-2-bromocyclooctyl ester of carbanilic acid
- 40 173. trans-4-bromocyclooctyl ester of 3-methylcarbanilic acid
174. 5-chloro-2-norbornyl ester of carbanilic acid
- 45 175. 5-bromo-2-norbornyl ester of carbanilic acid
176. 5,6-difluoro-2-norbornyl ester of carbanilic acid
177. 5,6-dibromo-2-norbornyl ester of carbanilic acid
- 50 178. 6-chloro-2-norbornyl ester of carbanilic acid
179. 2(5-chloro-2-norbornylmethyl) ester of carbanilic acid
- 55 180. 2(5-bromo-2-norbornylmethyl) ester of carbanilic acid
181. 2(5,6-dichloro-2-norbornylmethyl) ester of carbanilic acid
182. 2-chlorocyclopentyl ester of carbanilic acid

EXAMPLE 183

Pellet formulation

The following pellet formulation is applicable to any halo-substituted cycloalkyl or bicycloalkyl carbanilic acid used in this invention.

5-chloro-2-norbornyl ester of 3-methylcarbanilic acid	11%
anhydrous sodium sulfate	10%
Mississippi sub-bentonite	33%
kaolin	33%
lignin sodium sulfonate	13%

70

These ingredients are mixed and blended by micropulverizing. Approximately 18% water as calculated on a wet basis is added to the formulation and thoroughly mixed. The resulting product is extruded into pellets through a screw type extruder fitted with a die containing orifices of 3/32 inch. The extruded strands are conveniently cut into small pellets as they come out of the extruder die. The pellets are air dried. After drying the pellets can be easily handled and applied as such. However, they readily soften and disintegrate when mildly agitated in water and can also be applied in water rather than as the pellets.

75

80

85

EXAMPLE 184

The following wettable powder formulation is prepared

2-chlorocyclohexyl ester of carbanilic acid	52.6%
Pikes Peak clay	44.4%
sodium dioctyl sulfosuccinate	1.5%
sodium lignin sulfonate	1.5%

90

The above components are blended and micropulverized until homogeneous and then rebled.

95

The formulation described above is applied pre-emergence at the rate of four pounds of active ingredient per acre in 100 gallons of water for the control of crabgrass growth in an established bluegrass-fescue lawn. Excellent retardation of crabgrass is obtained, without noticeable damage to the desirable turf grasses.

100

105

This formulation is also used pre-emergence at six pounds of active ingredient in 80 gallons of water for growth retardation of crabgrass without injury to a new seedling of Kentucky bluegrass. The crabgrass barely emerges and fails to make further growth, whereas the bluegrass grows vigorously and develops into a healthy stand of turf.

110

A further use for this formulation is the post-emergence control of foxtail and barnyard grass seedlings in flax. For this purpose the formulation is mixed at the rate of six pounds of active ingredient with 60 gallons of water, and the resulting suspension is applied to the weed infested middles of one acre of 5-inch tall flax. The grass weed seedlings eventually die; the chemical treatment in no way interferes with the normal growth of the crops.

115

120

A sufficient quantity of the above com-

125

- position is extended with water so that two pounds per acre of active ingredient is applied in 40 gallons of water per acre before flue-cured tobacco is transplanted. A tractor mounted sprayer designed to spray a blanket application to the prepared soil surface is used for application. After application is made, the tobacco plants are transplanted in the normal manner. This pre- and post-treatment results in the control of crabgrass throughout the growing season with no injury to the crop.

EXAMPLES 185—197

- The following compounds are substituted one at a time for the 2-chlorocyclohexyl ester of carbanilic acid in Example 184 in like amount by weight and are formulated and applied in like manner. Like results are obtained.

- 20 Ex.
185. 2-chlorocyclohexyl ester of 2-methyl-carbanilic acid
186. 3-chlorocyclohexyl ester of 2-methyl-carbanilic acid
25 187. 2-chlorocyclohexyl ester of 4-methyl-carbanilic acid
188. 3-chlorocyclohexyl ester of 4-methyl-carbanilic acid
189. 2-bromocyclohexyl ester of 2-methyl-carbanilic acid
30 190. 2-methylcyclohexyl ester of o-fluoro-carbanilic acid
191. 3-methylcyclohexyl ester of o-fluoro-carbanilic acid
35 192. 2-chlorocyclohexyl ester of o-fluoro-carbanilic acid
193. 2-bromocyclohexyl ester of o-fluoro-carbanilic acid
40 194. cycloheptyl ester of o-fluorocarbanilic acid
195. cyclooctyl ester of o-fluorocarbanilic acid
196. cyclohexylmethyl ester of o-fluorocarbanilic acid
45 197. norbornyl ester of o-fluorocarbanilic acid

EXAMPLE 198

- The following granular formulation can be used. A wettable powder is first prepared by micropulverizing the following ingredients

- 50 2-methylcyclohexanol ester of carbanilic acid (technical grade) 52.6%
attapulgitic clay 32.4%
55 sodium alkyl naphthalene sulfonate in which the alkyl group contains less than five carbon atoms 3.0%
fine silica 10.0%
sodium lignosulfonate 2.0%

- 60 The wettable powder is distributed over the surface of #4 vermiculite by tumbling

together. To make the combination more adherent the mix is sprayed with a mixture of propylene glycol and water. The final ratio of ingredients is as follows

50% active wettable powder (as described above)	10.0%	
propylene glycol	5.0%	
vermiculite/zenolite #4 agri-cultural grade	80.0%	70
water	5.0%	

In a modification of the above formulation the propylene glycol can be replaced by a mixture of the sodium sulfates of mixed long chain alcohol fatty acid esters and diethylene glycol acetate in a ratio between 1:10 and 10:1 by weight.

The granular formulation described above has utility as a pre-emergence treatment for retarding the growth of crabgrass in an established Kentucky bluegrass-creeping red fescue lawn. The material is applied with a granule spreader at the rate of eight pounds of active ingredient per acre prior to the germination of crabgrass. Such excellent retardation of crabgrass is obtained that it presents no competition to the established lawn.

EXAMPLE 199

The following granular formulation can be used. A wettable powder is first prepared by micropulverizing the following ingredients

2-chlorocyclohexanol ester of carbanilic acid (technical grade)	52.6%	
attapulgitic	32.4%	95
sodium alkyl naphthalene sulfonate in which the alkyl group contains less than five carbon atoms	3.0%	
fine silica	10.0%	100
sodium lignosulfonate	2.0%	

The wettable powder is distributed over the surface of #4 vermiculite by tumbling together. To make the combination more adherent the mix is sprayed with a mixture of propylene glycol and water. The final ratio of ingredients is as follows

50% active wettable powder (as described above)	10.0%	
propylene glycol	5.0%	110
vermiculite/zenolite #4 agri-cultural grade	80.0%	
water	5.0%	

In a modification of the above formulation the propylene glycol can be replaced by a mixture of the sodium sulfates of mixed long chain alcohol fatty acid esters and diethylene glycol acetate in a ratio between 1:10 and 10:1 by weight.

The granular formulation described above has utility as a pre-emergence treatment for retarding the growth of crabgrass in an established Kentucky bluegrass-creeping red fescue lawn. The material is applied with a granule spreader at the rate of eight pounds of active ingredient per acre prior to the germination of crabgrass. Such excellent retardation of crabgrass is obtained that it presents no competition to the established lawn.

EXAMPLE 200

2-methylcyclohexyl ester of carbanilic acid	25.00%
alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms	1.00%
low viscosity methyl cellulose	0.25%
attapulgit clay	73.75%

The above components are blended and micropulverized until homogeneous and then rebled.

The above formulation is applied at the rate of 3 to 6 pounds per acre pre-emergence to newly-seeded fall wheat. Excellent retardation and control of the growth of cheatgrass is obtained. The wheat grows normally and competes successfully with the cheatgrass.

EXAMPLE 201

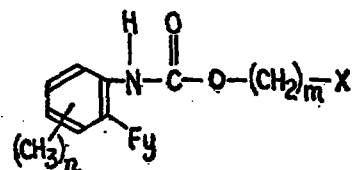
The following granular formulation is prepared and applied in the manner of the formulation of Example 1.

50% active wettable powder (as described in Example 4)	10.0%
propylene glycol	5.0%
vermiculite/zonolite #4 agri-cultural grade	80.0%
water	5.0%

Our divisional Application No. 35240/66, Serial No. 1,058,382, claims compositions containing the cyclohexanol ester of carbanilic acid and the use of that compound for inhibiting the growth of annual grasses. No claim is made in the present specification to compositions containing the cyclohexanol ester of carbanilic acid or to the use of that compound for inhibiting the growth of annual grasses.

Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

1. A composition for inhibiting the growth of annual grasses comprising at least one compound of the formula:



wherein X is saturated cycloalkyl of 5 to 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, or monohalomonomethyl-saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, saturated bicycloalkyl of 7 or 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, and monohalomonomethyl-saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms, monoethyl- or diethyl-saturated cyclohexyl, with the limitation that when X is cycloalkyl of 5, 7 and 8 carbon atoms and bicycloalkyl of 7 or 8 carbon atoms, $(CH_2)_n$ must be in the *meta* position; and each of m, n and y are 0 or 1; in association with an inert carrier which is at least in part an oil.

2. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with an inert carrier which is at least in part a solid.

3. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with an inert carrier and at least one other compound known for use as a plant nutrient, fertiliser, insecticide, fungicide, herbicide or nematocide.

4. A composition according to Claim 1, 2 or 3 containing a surface-active agent.

5. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with a surface-active agent and an inert carrier which is at least in part a liquid other than an oil.

6. A composition according to Claim 4 or 5 containing up to 10% by weight of the surface-active agent.

7. A composition according to Claim 6 containing 20 to 90% by weight of the said compound and $\frac{1}{4}$ to 10% by weight of the surface active agent.

8. A composition according to Claim 7 containing 35—85% by weight of the said compound.

9. A composition according to Claim 6 or 7 in the form of granules or pellets.

10. A composition according to Claim 9 containing 65—99% by weight of the inert solid diluent and 1—35% by weight of the active ingredient.

11. A composition according to Claim 10 containing 1—6% by weight active ingredient.

12. A composition according to Claim 6 or 7 in the form of densified pellets.



The granular formulation described above has utility as a pre-emergence treatment for retarding the growth of crabgrass in an established Kentucky bluegrass-creeping red fescue lawn. The material is applied with a granule spreader at the rate of eight pounds of active ingredient per acre prior to the germination of crabgrass. Such excellent retardation of crabgrass is obtained that it presents no competition to the established lawn.

EXAMPLE 200

2-methylcyclohexyl ester of carbanilic acid	25.00%
alkyl naphthalene sulfonic acid, Na salt, in which the alkyl group contains less than five carbon atoms	1.00%
low viscosity methyl cellulose	0.25%
attapulgite clay	73.75%

The above components are blended and micropulverized until homogeneous and then rebled.

The above formulation is applied at the rate of 3 to 6 pounds per acre pre-emergence to newly-seeded fall wheat. Excellent retardation and control of the growth of cheatgrass is obtained. The wheat grows normally and competes successfully with the cheatgrass.

EXAMPLE 201

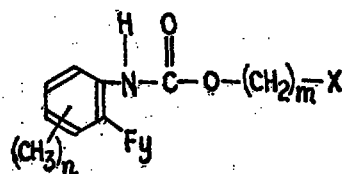
The following granular formulation is prepared and applied in the manner of the formulation of Example 1.

50% active wettable powder (as described in Example 4)	10.0%
propylene glycol	5.0%
vermiculite/zonolite #4 agricultural grade	80.0%
water	5.0%

Our divisional Application No. 35240/66, Serial No. 1,058,382, claims compositions containing the cyclohexanol ester of carbanilic acid and the use of that compound for inhibiting the growth of annual grasses. No claim is made in the present specification to compositions containing the cyclohexanol ester of carbanilic acid or to the use of that compound for inhibiting the growth of annual grasses.

Subject to the foregoing disclaimer,
WHAT WE CLAIM IS:—

1. A composition for inhibiting the growth of annual grasses comprising at least one compound of the formula:



wherein X is saturated cycloalkyl of 5 to 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, or monohalomonomethyl-saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, saturated bicycloalkyl of 7 or 8 carbon atoms, methyl-, dimethyl-, monohalo-, dihalo-, and monohalomonomethyl-saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms, monoethyl- or diethyl-saturated cyclohexyl, with the limitation that when X is cycloalkyl of 5, 7 and 8 carbon atoms and bicycloalkyl of 7 or 8 carbon atoms, $(CH_2)_n$ must be in the meta position; and each of m, n and y are 0 or 1; in association with an inert carrier which is at least in part an oil.

2. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with an inert carrier which is at least in part a solid.

3. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with an inert carrier and at least one other compound known for use as a plant nutrient, fertiliser, insecticide, fungicide, herbicide or nematocide.

4. A composition according to Claim 1, 2 or 3 containing a surface-active agent.

5. A composition for inhibiting the growth of annual grasses comprising a compound as defined in Claim 1 in association with a surface-active agent and an inert carrier which is at least in part a liquid other than an oil.

6. A composition according to Claim 4 or 5 containing up to 10% by weight of the surface-active agent.

7. A composition according to Claim 6 containing 20 to 90% by weight of the said compound and $\frac{1}{4}$ to 10% by weight of the surface active agent.

8. A composition according to Claim 7 containing 35—85% by weight of the said compound.

9. A composition according to Claim 6 or 7 in the form of granules or pellets.

10. A composition according to Claim 9 containing 65—99% by weight of the inert solid diluent and 1—35% by weight of the active ingredient.

11. A composition according to Claim 10 containing 1—6% by weight active ingredient.

12. A composition according to Claim 6 or 7 in the form of densified pellets.

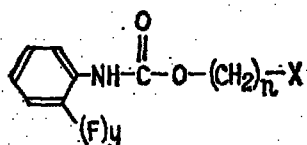


13. A composition according to Claim 12 containing 5—75% by weight active ingredient.

5 14. A composition according to Claim 6 or 7 in the form of an emulsifiable oil solution.

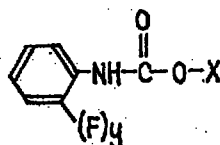
15. A composition according to Claim 14 containing 10—35% by weight of active ingredient.

10 16. A composition according to any one of the preceding claims which contains a compound of the formula:



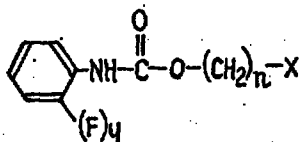
15 wherein n is 0 or 1; y is 0 or 1; and X is methyl or dimethyl saturated cycloalkyl in which each cycloalkyl has 6 to 8 carbon atoms, saturated bicycloalkyl or cycloalkyl of 7 or 8 carbon atoms or methyl norbornyl.

20 17. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:



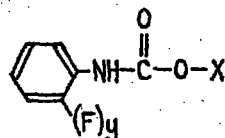
25 wherein y is 0 or 1; and X is saturated cycloalkyl of 7 to 8 carbon atoms, saturated bicycloalkyl of 7 or 8 carbon atoms, 2-methylcycloalkyl or 3-methylcycloalkyl in which the cycloalkyl has 5 to 8 carbon atoms.

30 18. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:



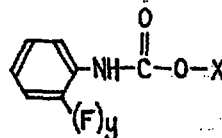
35 wherein n is 0 or 1; y is 0 or 1; and X is monohalo- or dihalo- saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, or monohalo-, or dihalo- saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms.

40 19. A composition according to any one of claims 1 to 15 which contains a compound of the formula:



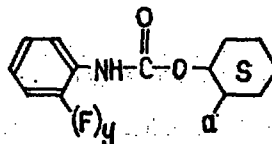
wherein y is 0 or 1; and X is monohalo- or dihalo- saturated cycloalkyl in which each cycloalkyl has 5 to 8 carbon atoms, or monohalo- or dihalo- saturated bicycloalkyl in which each bicycloalkyl has 7 or 8 carbon atoms.

20. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:



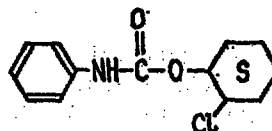
wherein y is 0 or 1; and X is 2-(monohalo)-saturated cycloalkyl of 6 to 8 carbon atoms, 5-halonorbornyl or 6-halonorbornyl.

21. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:

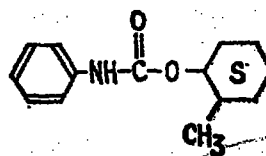


wherein y is 0 or 1; and a is CH₃, Cl or Br.

22. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:



23. A composition according to any one of Claims 1 to 15 which contains a compound of the formula:



24. A composition according to any one of Claims 1 to 15 containing a compound of the said formula specifically hereinbefore named.

25. A composition for selectively controlling the growth of annual grasses substantially as hereinbefore described.

26. A composition for selectively controlling the growth of annual grasses substantially as described in any of the Examples.

27. Method of selectively inhibiting the growth of annual grasses comprising applying to a locus infested or liable to be infested with said grasses a compound as defined in any one of the preceding claims

- in an amount sufficient to retard the growth
said grasses.
28. Method according to Claim 27
wherein the compound is applied to the locus
5 of said grasses in an amount of $\frac{1}{2}$ to 20 lb.
per acre.
29. A method for selectively controlling
the growth of annual grasses according to
Claim 27 substantially as hereinbefore
10 described.

30. A method for selectively controlling
the growth of annual grasses according to
Claim 27 substantially as described in any
of the Examples.

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