United States Patent Office

3,244,503

Patented Apr. 5, 1966

3,244,503

METHODS FOR THE CONTROL OF PLANTS

John C. Watts, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Dec. 14, 1964, Ser. No. 418,276
9 Claims. (Cl. 71—2.5)

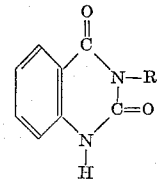
This application is a continuation-in-part of my application Serial No. 184,524, filed April 2, 1962, now abandoned.

This invention relates to the use of quinazolinediones and compositions containing them.

More specifically, this invention refers to the use of 2,4-,1H,3H)-quinazolinediones, their metal and quaternary ammonium salts, amine addition compounds, phenolic complexes and acid addition compounds as herbicides.

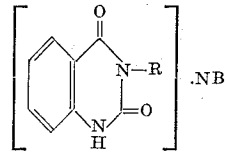
The compounds used in this invention are represented by the following formulas:

1

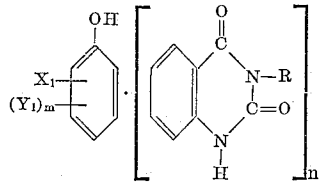


and the alkali, alkaline earth and quaternary ammonium salts thereof having 4 to 12 carbon atoms

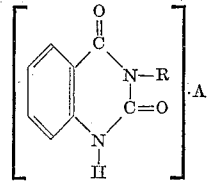
2



3



4



wherein

R is the radical



cycloalkyl having 3 through 10 carbon atoms in the alkyl group or cycloalkenyl having 4 through 10 carbon atoms in the alkenyl group;

X is hydrogen or methyl;

Y is an alkyl group of 1 through 4 carbon atoms;

Z is an alkyl group of 1 through 4 carbon atoms; and with the limitation that the total carbon atoms in Y and Z equal less than 6;

NB is a nitrogenous base having 1 through 12 carbon atoms and an ionization constant K_b of $\geq 10^{-5}$ in water;

X_1 is hydrogen, chlorine, nitro, alkyl of 1 through 3 carbon atoms, bromine or OR_1;

R_1 is alkyl of 1 through 3 carbon atoms;

Y_1 is hydrogen, chlorine or alkyl of 1 through 3 carbon atoms;

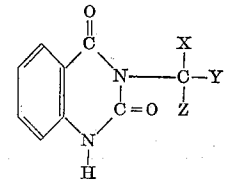
m is a whole positive integer less than 5;

n is 1 or 2; and

A is an acid having a dissociation constant in water of more than 2×10^{-5}.

A preferred group of compounds because of their high degree of herbicidal activity and low cost of manufacture is represented by the following formula

5



and their alkali metal salts

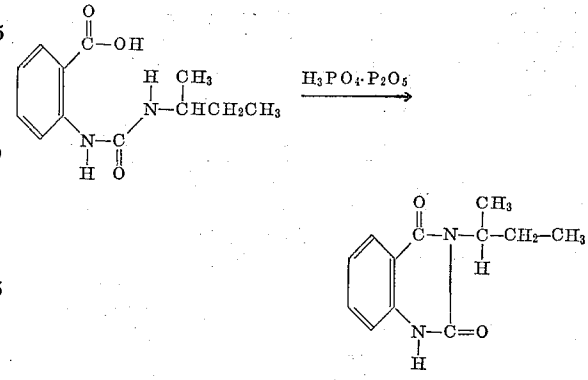
wherein

X, Y and Z have the same meaning as above.

It should be understood that the exact formulas of these salts, addition compounds and complexes are unknown. However, it is intended that this invention embrace these salts, addition compounds and complexes whatever their structure.

The free quinazolinedione compounds in this invention are made in the manner described in J. Org. Chem., 18, 1427 (1953), and J. Org. Chem., 26, 5238 (1961).

Where these methods fail to give the desired heterocyclic compound, cyclization can be accomplished using polyphosphoric acid as is illustrated below.



The metal and quaternary ammonium salts are prepared by the reaction of a quinazolinedione with the desired hydroxide.

The nitrogenous base addition compounds are prepared by the addition of the desired nitrogenous base to a solution of the desired quinazolinedione in a suitable inert organic solvent. The addition compound is isolated by standard procedures.

Suitable nitrogenous bases are substituted, unsubstituted, cyclic and acyclic amines, amidines and guanidines. The amines can be primary, secondary or tertiary amines, polyamines, arylamines, or heterocyclic amines. Illustrative of such amines are:

sec-butylamine
trimethylenediamine
ethanolamine
dodecylamine
ethylenediamine
hexamethylenediamine
hexamethyleneimine
cyclohexylamine
methylamine
dimethylamine

trimethylamine
ammonia
ethylamine
propylamine
cyclohexylamine
pyridine
piperidine
tetramethylguanidine
acetamidine
benzylamine
2-aminobutanol-1

The phenolic complexes are formed readily by comelting the quinazolinedione and phenol in a 1:1 to 2:1, quinazolinedione:phenol ratio. They can also be formed by codissolving the reactants, in the same ratio, in a non-polar solvent such as nitromethane or a mixture of nitromethane and cyclohexane.

Among the phenols that are particularly suited for the formation of complexes with the quinazolinediones used in this invention are:

m-methylphenol
p-nitrophenol
p-methoxyphenol
p-chlorophenol
p-methylphenol
phenol
2,4-dichlorophenol
2,4,6-trichlorophenol
pentachlorophenol
2,4-dichloro-o-cresol
2,4-dinitro-o-cresol
2,3,5,6-tetrachloro-4-methoxyphenol
4-bromo-o-cresol
4-nitro-o-cresol

To prepare the acid addition compounds of this invention, a substituted quinazolinedione reactant is mixed with an appropriate acid, at room temperature, in a liquid aromatic hydrocarbon. The reaction is immediate. Generally, any aromatic hydrocarbon can be used, but it is preferred that it be liquid between 20° C. and 30° C. and that it dissolve the reactants. Benzene, toluene, xylene and chlorobenzene are satisfactory. The ratio of reactants is preferably one to one.

The acid addition compounds either separate from the solution by precipitation or are precipitated with an excess of non-solvent liquid paraffin such as pentane, hexane, heptane or petroleum ether. In either case the product precipitates as a solid or a viscous oil which can be separated by filtration or vacuum evaporation. Alternatively, the product can be separated by vacuum evaporation of the reaction medium at low temperatures, preferably below 50° C. Precipitation with a non-solvent is the usual method.

Any acid having an ionization constant greater than 2×10^{-5} will form a quinazolinedione addition compound. Preferred acids are halogenated aliphatic acids containing from 2 to 5 carbon atoms, halogenated benzoic acid, halogenated phenylacetic acids, halogenated phenoxy acetic acids, organic sulfonic acids, organic phosphonic acids and inorganic phosphoric acids. These acids are preferred because of the quinazolinedione addition compounds formed from them are highly phytotoxic and show good oil solubility. Illustrative of these acids are:

2,3,5-trichlorobenzoic acid
2,3,6-trichlorobenzoic acid
2,3,5,6-tetrachlorobenzoic acid
2,3,5-triiodobenzoic acid
2-methoxy-3,6-dichlorobenzoic acid
2-methoxy-3,5,6-trichlorobenzoic acid
2-methyl-3,6-dichlorobenzoic acid
2,5-dichloro-3-aminobenzoic acid
2,5-dichloro-3-nitrobenzoic acid
2,3,6-trichlorophenylacetic acid

2,3,5,6-tetrachlorophenylacetic acid
2-methoxy-3,6-dichlorophenylacetic acid
2,4-dichlorophenoxyacetic acid
2,4,5-trichlorophenoxyacetic acid
phosphoric acid
methanephosphonic acid
phenylphosphoric acid
trichloroacetic acid
tribromoacetic acid
trifluoroacetic acid
alpha,alpha-dichloropropionic acid
alpha,alpha-dibromopropionic acid
alpha,alpha,beta-trichloropropionic acid
alpha,alpha,beta-trifluoropropionic acid
alpha,alpha-dichlorobutyric acid
alpha,beta-dichloroisobutyric acid
alpha,beta,beta-trichloroisobutyric acid
alpha,alpha-dichlorovaleric acid
methanesulfonic acid
ethanesulfonic acid
dodecylsulfonic acid
benzenesulfonic acid
p-tolylsulfonic acid
dodecylbenzenesulfonic acid
2,4,6-trichlorobenzenesulfonic acid
naphthalene-beta-sulfonic acid

USE

The compounds used in this invention, e.g., 3-isopropyl-2,4-(1H,3H)-quinazolinedione, its metal and quaternary ammonium salts, nitrogenous base and acid addition compounds and phenolic complexes are excellent broad spectrum herbicides at rates of 10 to 40 pounds of active per acre. Additionally, compounds used in this invention are selective weed control agents when used at low rates such as ¼ to 5 pounds per acre.

The quinazolinediones and their metallic and quaternary ammonium salts have utility for both pre-emergence and early directed post-emergence control of seedling annual and perennial weeds in such crops as corn, sugar cane, sorghum, alfalfa, peanuts, beans, soybeans, annual and perennial ornamental plants, such as marigold and arbor vitae and in established turf grasses such as bluegrass and Bermudagrass.

The amine addition compounds have some herbicidal formulation advantages over the free quinazolinediones. For example, the amine addition compounds are soluble in an excess of the amine used to form the addition compound and it is possible to prepare concentrated solutions of the amine addition compound in the amine, when a liquid amine is used. These concentrates can then be diluted with water or an oil. The particular diluent used will, of course, depend on the solubility properties of the addition compound.

The phenolic complexes have some advantages over the quinazolinediones per se, viz., higher solubility in oils and solvents. They are formulated into herbicidal compositions in the same way as are the quinazolinediones themselves.

The acid addition compounds of this invention are active as general-purpose weed killers, as soil sterilants, in soil-foliage applications, and as selective weed killers for either pre- or post-emergence weed control. The compounds control both annual and perennial broadleaf weeds and grasses.

COMPOSITIONS

Herbicidal compositions of this invention are formulated by mixing a compound of this invention together with one or more surface-active agents, or with inert solid diluents.

The surface-active agent used in this invention can be a wetting, dispersing or emulsifying agent which will assist dispersion of the composition. The surface-active agent or surfactant can include such anionic, cationic and non-ionic agents as have heretofore been generally em-

ployed in pest control compositions of similar types. Suitable surface-active agents are set out, for example in Searle, U.S. Patent 2,426,417; Todd, U.S. Patent 2,655,447; Jones, U.S. Patent 2,412,510; or Lenher, U.S. Patent 2,139,276. A detailed list of such agents is set forth in "Detergents and Emulsifiers—Up to Date" (1964) by John W. McCutcheon, Inc.

Suitable surface-active agents for use in compositions of the present invention are: polyethylene glycol fatty esters and fatty alkylol amide condensates, alkyl aryl sulfonates, fatty alcohol sulfates, dialkyl esters of sodium sulfosuccinates, fatty acid esters of sodium isethionate, polyoxyethylene ethers and thioethers, and long chain quaternary ammonium chloride.

Surface-active dispersing agents such as sodium ligno sulfonates, low viscosity methyl cellulose, polymerized sodium salts of alkylnaphthalene sulfonic acids are also suitable in the herbicidal compositions of this invention.

Among the more preferred surfactants are the anionic and non-ionic type. Among anionic surface-active agents, preferred ones are alkali metal or amine salts of alkylbenzene sulfonic acids such as dodecylbenzene sulfonic acid, sodium lauryl sulfate, alkylnaphthalene sulfonates, sodium N-methyl-N-oleoyltaurate, oleic acid ester of sodium isethionate, dioctyl sodium sulfosuccinate, sodium dodecyldiphenoloxide disulfonate. Among non-ionic compounds, preferred members are alkyl phenoxy poly(ethyleneoxy) ethanols such as nonylphenol adducts with ethylene oxide, trimethylnonylpolyethylene glycol ethers, polyethylene oxide adducts of fatty and rosin acids, long chain alkyl mercaptan adducts with ethylene oxide, and polyethylene oxide adducts with sorbitan fatty acid esters.

In general, less than 10% by weight of the wetting agent will be used in compositions of this invention and ordinarily the amount of wetting agent will be less than 1% by weight.

Surfactant levels as high as 0.5 to 6 parts for each part of quinazolinedione, however, give unusual and unexpected beneficial results. Such compositions have a greater herbicidal effectiveness than can be expected from a consideration of the activity of the components used separately.

The herbicidal compositions of this invention can also contain finely divided inert diluents such as talcs, natural clays such as kaolinites, and including attapulgite clay, pyrophyllite, diatomaceous earths, synthetic fine silicas, calcium silicates, carbonates, calcium phosphates, sulfur, lime, and such flours as walnut shell, wheat, redwood, soybean and cottonseed.

The amount of finely divided inert solid diluent can vary widely but will generally range from 10 to 99% by weight of the herbicidal composition.

When the compositions of the herbicidal quinazolinediones contain the finely divided inert diluents, these compositions can have a wide range of particle sizes. For example, compositions of active ingredient, inert diluent and a surface-active agent can be blended and ground to prepare wettable powders in which ordinarily the particle size is predominately under 50 microns.

Compositions of herbicidal quinazolinedione and inert solid diluent can also be formulated into granules and pellets. In such compositions, the diluent will generally range from 65 to 99% and the active ingredient can range from 1 to 35%. To prepare granules the herbicides can be dissolved in a solvent, and this solution can be sprayed over pre-formed clay granules to distribute the active ingredient over and throughout the granular mass. Such granules can range in particle size of from +60 mesh to −4 mesh, and 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 herbicide, for instance by grinding together, and then forming granules by adding water, tumbling, and drying the resulting spheres. Pellets can be prepared by extruding a mixture that comprises the quinazolinedione herbicides, pelleting clay diluent and water into strands, cutting these, and drying the product. Pellet size can range from 10 mesh to larger shapes such as ⅜ inch cubes. Pellets preferably contain from 5 to 35% of the herbicidal quinazolinedione. In addition to the diluents, pelletized and granular compositions can contain additives such as binders, surfactants and the like.

Compounds used in this invention can also be prepared in emulsifiable oil solutions. In these, the quinazolinedione, the surface-active agent and an oil form a liquid which can conveniently be poured and measured. Such solutions can be mixed with water at the point of application to form an emulsion containing the herbicide 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 amounts of surfactants to form objectionable foam. It is also possible to include in such formulations oils which have herbicidal action of their own.

The oil, such as isophorone, should preferably be water immiscible and be of a type in which the active agent will be soluble in the amounts used in particular formulations. Emulsifiable liquid compositions can be made with an aliphatic or aromatic hydrocarbon oil having a boiling point of 100° C. to 400° C. Typical of the hydrocarbon oils that can be used are commercial oils such as "Lion Herbicidal Oil No. 6," diesel oils, kerosene, paraffin oils and fuel oils.

In the herbicidal compositions containing oils the quinazolinedione 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.

Addtionally, it is possible to prepare aqueous suspensions of the water-insoluble quinazolinediones. By water insoluble is meant those compounds with a water solubility of less than 0.1%. To prepare these suspensions, a slurry is first prepared containing the active ingredient, a dispersing agent and a suspending agent. The slurry is wet ground until all particles have a particle size of less than 5 microns. This suspension can be further diluted with water prior to application.

Any of the above-described compositions can be formulated with other materials optionally, such as fertilizers, pest control agents including insecticides and fungicides and other herbicides. Highly effective herbicidal compositions can be prepared comprising at least one compound of this invention in admixture with another herbicidally effective ingredient.

Among the other herbicides that can be combined with the quinazolinediones of this invention are substituted ureas such as

3-(3,4-dichlorophenyl)-1,1-dimethylurea;
3-(3,4-dichlorophenyl)-3-methoxy-1,1-dimethylurea;
3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea;
3-(p-chlorophenyl)-1,1-dimethylurea;
3-phenyl-1,1-dimethylurea;

substituted triazines such as

2-chloro-4,6-bis(ethylamino)-s-triazine;
2-methylmercapto-4,6-bis(ethylamino)-s-triazine;
2-chloro-4,6-bis(methoxypropylamino)-s-triazine;
2-chloro-4-ethylamino-6-isopropylamino-s-triazine;
2-ethylamino-4-isopropylamino-6-methylmercapto-s-triazine;
2,4-bis(isopropylamino)-6-methylmercapto-s-triazine;
phenols such as pentachlorophenol;

carboxylic acids such as

2,4-dichlorophenoxyacetic acid, its salts and esters;
2,3,6-tri- or 2,3,5,6-tetrachlorobenzoic acid and its salts;
trichloroacetic acid and its salts, and
2,2-dichloropropionic acid and its salts;

carbamic acid esters such as

N-ethyl-N-butylthiocarbamic acid;
n-propylester;
maleic hydrazide;
dimethylarsinic acid;
disodium methylarsonate;
hydrated granulated sodium tetraborate;
sodium chlorate;
ammonium sulfamate;
N,N-dimethyl-alpha,alpha-diphenylacetamide;
N,N-di-n-propyl-2,6-dinitro-4-methylaniline;
N,N-di-n-propyl-2,6-dinitro-α,α,α-trifluoro-p-toluidine;
2,3,5,6-tetrachloroterephthalic acid, dimethyl ester;

substituted uracils such as

5-bromo-6-methyl-3-isopropyluracil;
5-bromo-3-tert-butyl-6-methyluracil;
5-bromo-3-cyclohexyl-6-methyluracil;
5-bromo-6-methyl-3-phenyluracil;
3-cyclohexyl-5,6-trimethyleneuracil;
3-n-butyl-5-methyluracil;
5-chloro-6-chloromethyl-3-cyclohexyluracil;
3-isopropyl-1-trichloromethylthio-5-bromo-6-methyluracil;
3-isopropyl-5,5-dichloro-6-methyl-6-ethoxyuracil.

Among the insecticides that can be combined with the quinazolinediones used in this invention are the following:

1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane;
2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane;
hexachloroepoxyoctohydro-endo,exo-dimethanonaphthalene;
1,2,3,4,10,10-hexachloro-1,4,4*a*,5,8,8*a*-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene.

Among the fungicides that can be mixed with the compounds used in this invention are:

p-dimethylaminobenzene diazosodium sulfonate;
quinone oxyaminobenzooxyhydrazine;
tetraalkylthiuram disulfide such as tetramethylthiuram disulfide and tetraethylthiuram disulfide;
metal salts of ethylene bisdithiocarbamic acid, e.g., sodium, manganese, zinc, and iron salts;
N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide;
N-trichloromethylthiophthalimide;
2,3-dichloro-1,4-naphthaquinone;
2,3,5,6-tetrachloro-1,4-benzoquinone;
2,4-dichloro-6-(p-chloroanilino)-s-triazine;
copper A;
metal salts of alkyl and dialkyl dithiocarbamic acid, e.g., Zn, Na, K, Fe, Mn, Ni;
zinc pyridinethione; and
S-(1-oxido-2-pyridyl)-isothiuronium chloride.

The method of applying compositions of this invention comprises applying a quinazolinedione, salt, addition compound or complex ordinarily in a herbicidal composition of one of the aforementioned types, to a locus to be protected from undesirable plant growth. The active compound, of course, is applied in amounts sufficient to exert the desired herbicidal action. The amount of the quinazolinedione compound to be used in clearing lands of weeds will naturally depend on the condition of the vegetation, the degree of herbicidal activity desired, the formulation used, the mode of application, the climate, the season of the year, and other variables. In general, however, applications at rates of ¼ to 5 pounds of the active ingredient per acre as a pre-emergence or directed post-emergence application as a liquid spray, in granules or dust, gives excellent control of broadleaf weeds and grasses, such as mustard, lambsquarters, chickweed, velvetleaf, crabgrass, millet, foxtail, barnyardgrass, cheat and seedling Johnsongrass.

Complete kill of vegetation is obtained with an extended residual period when the compounds are applied at a rate of about 10 to 40 pounds of active ingredient per acre on industrial areas and non-crop sites on farms. These rates of application give excellent control of wild oats, ryegrass, ragweed, purslane, cockelburr, quackgrass, plantain, wild carrot, sheep sorrel and broomsedge.

The following illustrative examples are provided to more clearly describe the invention. It should be understood that the percents used are all by weight unless otherwise specified.

Example 1

An improved yield of 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione is obtained by using the following procedures.

A mixture containing 3 parts by weight of o-(3-methyl-3-ureidopropyl)benzoic acid and 10 parts by weight of polyphosphoric acid is heated to 150–200° C. for two hours and then poured into 60 parts by weight of water. Essentially pure product precipitates and is filtered off. This product can be used without further purification. However, recrystalization from common solvents such as alcohol renders the product pure.

The following wettable powder formulation is then prepared.

	Percent
3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione	80
Partially desulfonated sodium lignin sulfonate	2
Dioctyl sodium sulfosuccinate	1
Attapulgite clay	17

The above components are blended and micropulverized until no more than 1% of the composition will fail to pass through a 325 mesh screen. For use where application equipment has little or no agitation to maintain suspension, the product can be further reduced in particle size by the use of a "fluid energy" mill such as a micronizer or air reductionizer until the particle size is substantially all below 10 microns.

The formulation prepared in the above-described manner is mixed with 60 gallons of water and applied as a foliar soil spray at the rate of 30 pounds (active) per acre to a non-cropland site for general weed control. Control of crabgrass, ryegrass, foxtail, quackgrass, ragweed, purslane, sheep sorrel and wild carrot is obtained.

Examples 2–7

By substituting like amount by weight of the appropriate starting materials the following additional compounds are made in the same manner as the 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione of Example 1. These compounds are formulated one at a time in like manner in like amount by weight and when applied to the same plants provide herbicidal activity similar to that obtained in Example 1.

Example:

2. 3-isopropyl-2,4-(1H,3H)-quinazolinedione
3. 3-(1-ethylpropyl)-2,4-(1H,3H)-quinazolinedione
4. 3-(2-norbornyl)-2,4-(1H,3H)-quinazolinedione
5. 3-(1,1-dimethylethyl)-2,4-(1H,3H)-quinazolinedione
6. 3-(1-methylbutyl)-2,4-(1H,3H)-quinazolinedione
7. 3-(1,1-dimethylpropyl)-2,4-(1H,3H)-quinazoline

Examples 8–10

By substituting like amount by weight of the appropriate starting materials the following additional compounds are made in the same manner as the 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione of Example 1. These compunods are formulated one at a time in like manner in like amount by weight.

When applied at the rate of 2 pounds of active per acre in 30 gallons of water, pre-emergence control of mustard and crabgrass is obtained in a field of seedling alfalfa.

A similar rate of application when applied before the plants emerge controls mustard, and crabgrass in a planting of marigolds.

Example:

8. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione
9. 3-(hexahydro-4,7 - methano - 5 - indanyl)2,4-(1H,3H)-quinazolinedione
10. 3 - (1,2,3,4 - tetrahydronaphthyl) - 2,4-(1H,3H)-quinazolinedione

Example 11

The following wettable powder composition is prepared:

	Percent
3-(1-methylpropyl)-2,4 - (1H,3H) - quinazolinedione	80.00
Alkyl naphthalene sulfonate, Na salt	1.75
Low viscosity methylcellulose	.30
Precipitated sodium silico aluminate	17.95

The above described composition is formulated in like manner to the wettable powder of Example 1 and then mixed with 60 gallons of water and applied to a locus at the rate of 20 pounds of active ingredient per acre. This application controls crabgrass, foxtail, wild mustard, chickweed and pigweed growing in storage areas.

Example 12

The following pellet composition is prepared:

	Percent
3-(1-methylbutyl)-2,4-(1H,3H)-quinazolinedione	25
Anhydrous sodium sulfate	10
Calcium, magnesium bentonite	65

The above components are mixed and micropulverized then pug milled with 15–20% water and extruded through ⅛ inch die holes while cutting the extrusions to a length of approximately ⅛ inch. The resulting ⅛" x ⅛" pellets are dried.

The formulation described above is applied by hand as a spot application for the control of weeds growing along pipeline rights-of-way. An application of 160 pounds of the formulation per acre gives control of plantain, sheep sorrel, wild carrot, crabgrass, cockleburr, quackgrass and ragweed.

Examples 13–59

The compounds listed below are substituted one at a time in like amount by weight for the 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione of Example 12. These compounds are formulated in like manner and when applied in like manner give substantially the same results obtained in Example 12.

Example:

13. 3-isopropyl-2,4-(1H,3H)-quinazolinedione
14. 3-(1-methylpropyl)-2,4-(1H,3H) - quinazolinedione
15. 3-(1-ethylpropyl)-2,4 - (1H,3H) - quinazolinedione
16. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione
17. 3-cyclopentyl-2,4-(1H,3H)-quinazolindione
18. 3-(1,1-dimethylpropyl)-2,4-(1H,3H) - quinazolinedione
19. 3-(2-norbornyl)-2,4-(1H,3H)-quinazolinedione
20. 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione
21. 3-cyclobutyl-2,4-(1H,3H)-quinazolinedione
22. 3-cyclopropyl-2,4-(1H,3H)-quinazolinedione
23. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione
24. 3-bornyl-2,4-(1H,3H)-quinazolinedione
25. 3-cyclodecyl-2,4-(1H,3H)-quinazolinedione
26. 3-(cyclobut-2-enyl)-2,4-(1H,3H) - quinazolinedione
27. 3-(cyclopent-2-enyl)-2,4 - (1H,3H) - quinazolinedione
28. 3-(cyclohex-3-enyl)-2,4-(1H,3H) - quinazolinedione
29. 3-(1,1-dimethylethyl)-2,4-(1H,3H) - quinazolinedione, methylamine salt
30. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione, dimethylamine salt
31. 3-isopropyl - 2,4 - (1H,3H) - quinazolinedione, N-methylethyldiamine salt
32. 3-(norbornyl) - 2,4 - (1H,3H) - quinazolinedione, diethylenediamine salt
33. 3 - (1,1 - dimethylbutyl) - 2,4 - (1H,3H)-quinazolinedione, ethanolamine salt
34. 3 - (1 - propylpropyl) - 2,4 - (1H,3H) - quinazolinedione, ethylenediamine salt
35. 3 - (cyclohept - 3 - enyl) - 2,4 - (1H,3H)-quinazolinedione
36. 3-(cyclooct-4-enyl)-2,4-(1H,3H) - quinazolinedione
37. 3 - (cyclodec - 5 - enyl) - 2,4-(1H,3H) - quinazolinedione
38. 3-(1,2-dimethylpropyl)-2,4-(1H,3H) - quinazolinedione
39. 3-tert.-amyl-2,4-(1H,3H)-quinazolinedione
40. 3-(1-methylpentyl)-2,4-(1H,3H) - quinazolinedione
41. 3-(1-ethylbutyl)-2,4-(1H,3H)-quinazolinedione
42. 3-(1,1-dimethylbuyl)-2,4 - (1H,3H) - quinazolinedione
43. 3-(1-ethyl-2-methylpropyl)-2,4-(1H,3H) - quinazolinedione
44. 3-(1,3-dimethylbutyl)-2,4-(1H,3H) - quinazolinedione
45. 3-(1-ethyl-1-methylpropyl)-2,4-(1H,3H) - quinazolinedione
46. 3-(1,1,-trimethylpropyl) - 2,4-(1H,3H) - quinazolinedione
47. 3-(1,2,2 - trimethylpropyl)-2,4-(1H,3H) - quinazolinedione
48. 3-(1-ethyl-1-methylbutyl)-2,4-(1H,3H) - quinazolinedione
49. 3-(1,1-dimethylpentyl)-2,4-(1H,3H) - quinazolinedione
50. 3 - cyclobutylmethanoindanyl - 2,4 - (1H,3H)-quinazolinedione
51. 3-isopropyl-2,4-(1H,3H)-quinazolinedione, sodium salt
52. 3-isopropyl-2,4-(1H,3H)-quinazolinedione, potassium salt
53. 3- isopropyl-2,4-(1H,3H)-quinazolinedione, calcium salt
54. 3-cyclobutyl-2,4-(1H,3H)-quinazolinedione, sodium salt
55. 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione, potassium salt
56. 3-(1 - methylpropyl)-2,4-(1H,3H) - quinazolinedione, tetramethylammonium salt
57. 3-(1,1-dimethylethyl) - 2,4 - (1H,3H) - quinazolinedione, tetrabutylammonium salt
58. 3-(1-methylpropyl)-2,4-(1H,3H) - quinazolinedione, zinc salt
59. 3-(1-methylbutyl)2,4-(1H,3H) - quinazolinedione, copper salt

Example 60

The following wettable powder composition is prepared:

	Percent
3-cyclopentyl-2,4-(1H,3H)-quinazolinedione	75
Dodecylbenzenesulfonic acid, dimethylamine salt	2
Alkyl aryl polyether alcohol	2
Diatomaceous silica	21

The above composition is blended and micropulverized. The resulting wettable powder is dispersible in either water or oil. It is also compatible with oil emulsions.

This formulation is dispersed in 30 gallons of "Lion Herbicidal Oil No. 6" and applied at the rate of 2 pounds of active per acre for the control of cheat and chickweed growing in a planting of established privet in a nursery. Special care is taken to avoid contact with the privet plants during spraying. Excellent weed control is obtained.

Example 61

The following granular composition is prepared:

	Percent
3-cyclooctyl-2,4-(1H,3H)-quinazolinedione	2
Attapulgite clay	98

The above composition is blended and micropulverized, then moistened with water and granulated. The moist granules are dried and screened to obtain a particle range of 15–30 mesh. These granules are applied by hand or with a commercial granule applicator.

The above formulation is applied with lawn spreaders adapted for granular application at the rate of 4 pounds of active per acre for the pre-emergence control of crabgrass in established Bermudagrass turf. Excellent control of crabgrass is obtained.

Examples 62–108

The active compounds in Examples 13 to 59 are each substituted one at a time for the 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione of Example 61 in like amount by weight and are formulated and applied in like manner. Control of a wide variety of weeds is obtained.

Example 109

PREPARATION OF QUATERNARY AMMONIUM SALT OF 3-ISOPROPYL-2,4-(1H,3H)-QUINAZOLINEDIONE

Twenty and four-tenths parts of 3-isopropyl-2,4-(1H,3H)-quinazolinedione are added to a single, necked round bottom flask. With stirring, 100 parts of a 1M methanolic solution of tetra-butyl ammonium hydroxide are added. Stirring is continued at room temperature for ½ hour. The solvent is removed in vacuo to give solid 3-isopropyl-2,4-(1H,3H)-quinazolinedione, tetrabutyl ammonium salt which is satisfactory for herbicidal use.

Examples 101–111

The following two compounds can be made in the manner of the quaternary ammonium salt of 3-isopropyl-2,4-(1H,3H)-quinazolinedione of Example 109 by substituting the analogous starting materials for those in Example 109.

Example:

110. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione, tetramethylammonium salt
111. 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione, tetraethylammonium salt

Example 112

PREPARATION OF ETHYLENEDIAMINE SALT OF 3-CYCLOHEXYL-2,4-(1H,3H)-QUINAZOLINEDIONE

A saturated solution of 12.2 parts of 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione in acetonitrile is prepared. With stirring, 3 parts of ethylenediamine are added at room temperature. The precipitate which forms is removed by filtration and used without further purification.

Examples 113–118

The following compounds are synthesized by using the procedures of Example 112 by using equivalent amounts of the obvious starting materials for ethylenediamine and 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione respectively.

Example:

113. 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione, dodecylamine salt
114. 3-isopropyl-2,4-(1H,3H)-quinazolinedione, t-butylamine salt
115. 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione, cyclohexylamine salt
116. 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione, ethylamine salt
117. 3-(1-methylbutyl)-2,4-(1H,3H)-quinazolinedione, trimethylamine salt
118. 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione, octylamine salt

Example 119

PREPARATION OF CONCENTRATED AMINE SOLUTION OF THE ETHANOLAMINE SALT OF 3-(1-METHYLPROPYL)-2,4-(1H,3H)-QUINAZOLINEDIONE

Four parts by weight of ethanolamine and one part of 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione are mixed at room temperature in a closed container for 24 hours. The clear solution which forms can be formulated and then diluted with water for herbicidal applications.

Example 120

PREPARATION OF SODIUM SALT OF 3-ISOPROPYL-2,4-(1H,3H)-QUINAZOLINEDIONE

A solution is prepared by mixing 40.8 parts of 3-isopropyl-2,4-(1H,3H)-quinazolinedione in a flask containing 42 parts of 5M aqueous sodium hydroxide solution. The solution which forms is suitable for further formulation and use as an herbicide.

Example 121

3-cyclohexyl-2,4-(1H,3H)-quinazolinedione, lithium salt is made in the manner of Example 120 by substituting the obvious starting materials in equivalent amounts for the 3-isopropyl-2,4-(1H,3H)-quinazolinedione and sodium hydroxide.

Example 122

An aqueous solution is prepared by adding 2 parts of sodium lauryl sulfate to an aqueous solution containing 5 parts of 3-cyclopropyl-2,4-(1H,3H)-quinazolinedione, tetrabutylammonium salt and 1 part of tetrabutylammonium hydroxide in 92 parts of water. The mixture is stirred until all of the sodium lauryl sulfate is dissolved. The resulting solution can be rapidly diluted with water to any use level at any time prior to application, if desired. At the time of dilution 3 parts of trimethylnonylpolyethylene glycol ether are added per part of active ingredient.

The above formulation is applied at the rate of 4 pounds of active per acre as a post-emergence directed spray in 40 gallons of water to seedling weed growing in sugar cane. Excellent control of crabgrass, foxtail, seedling Johnsongrass, pigweed, annual morning glory and chickweed is obtained.

Example 123

PREPARATION OF 1:1 COMPLEX OF 3-ISOPROPYL-2,4-(1H,3H)-QUINAZOLINEDIONE AND PENTACHLOROPHENOL

A mixture of 20.4 parts by weight of 3-isopropyl-2,4-(1H,3H)-quinazolinedione, 26.6 parts of pentachlorophenol and 125 parts of cyclohexane is stirred at reflux as 5 parts of nitromethane are slowly added. When no further change in the physical appearance of the reaction mixture is observed, it is chilled. The solid complex is filtered. It is suitable for use without further purification, but it can be recrystallized from solvents such as nitromethane, if desired.

Example 124

PREPARATION OF 2:1 COMPLEX OF 3-CYCLOHEXYL-2,4-(1H,3H)-QUINAZOLINEDIONE AND P-METHOXYPHENOL

A dry mixture of 24.4 parts by weight of 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione and 6.2 parts of p-methoxyphenol is gradually heated until a clear melt is formed. This melt is stirred to insure completion of the reaction. After 10–30 minutes stirring the melt is

cooled. The solid cake which forms is suitable for use in herbicidal compositions.

Example 125

The following formulation is prepared by blending the indicated ingredients and then micropulverizing until the particles of the phenol complex are all below 50 microns in diameter. The mixture is then reblended.

	Percent
3-isopropyl-2,4-(1H,3H)-quinazolinedione 1/1 complex with pentachloro phenol	50.0
Sodium lauryl sulfate	0.6
Sodium lignin sulfonate	2.0
Attaclay	47.4

The above formulation is used for a combination of contact and residual weed control on industrial areas. When an application of 30 pounds of the complex is sprayed per acre in 80 gallons of water, excellent control of existing vegetation is obtained around oil tanks on a tank farm. Control of crabgrass, foxtail, cheat, wild barley, luornegrass, ryegrass, ragweed, pigweed, cockleburr and lambsquarters is obtained.

Example 126

PREPARATION OF COMPLEX WITH 3-(2-NORBORNYL)-2,4-(1H,3H)-QUINAZOLINEDIONE AND TRICHLOROACETIC ACID

To 250 parts by weight of reagent grade xylene are added 64 parts by weight of 2-(2-norbornyl)-2,4-(1H,3H)-quinazolinedione and, with stirring, 41 parts of trichloroacetic acid. Stirring is continued at room temperature overnight.

Addition of 1900 parts of n-pentane causes precipitation of the pure 1:1 complex. Stirring is continued for an additional ½–3 hours to ensure complete precipitation. The pure product is removed by filtration.

Example 127

PREPARATION OF COMPLEX WITH 3-(HEXAHYDRO-4,7-METHANO-5-INDANYL)-2,4-(1H,3H)-QUINAZOLINEDIONE AND DODECYLBENZENE-SULFONIC ACID

Dodecylbenzenesulfonic acid (107 parts by weight) is dissolved in 200 parts of reagent grade xylene. To this solution is added, with stirring, 99 parts of 3-(hexahydro-4,7-methano-5-indanyl)-2,4-(1H,3H)-quinazolinedione. Next, 2700 parts of n-hexane are added. Stirring is continued for 2–3 days. The unreacted quinazolinedione is then filtered. The filtrate is diluted with 700 parts of n-pentane and cooled in an ice-salt bath. The pure 1:1 complex of 3-(hexahydro-4,7-methano-5-indanyl)-2,4-(1H,3H)-quinazolinedione and dodecylbenzenesulfonic acid which precipitates, is filtered and formulated directly in the following manner:

	Percent
3-(1,1-dimethylethyl)-2,4-(1H,3H)-quinazolinedione addition compound with dodecylbenzenesulfonic acid	40
Xylene	53
Dodecylbenzenesulfonic acid	7

The above formulation is mixed with 80 gallons of "Lion Herbicidal Oil No. 6" and applied at the rate of 20 pounds of active per acre for the control of cheat, volunteer wheat, ryegrass, crabgrass, quackgrass, foxtail, dandelion and plantain growing along railroad rights-of-way. Excellent weed control is obtained.

Example 128

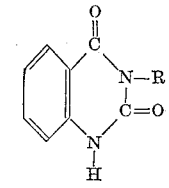
A tank mix is prepared by mixing three pounds of 3-(1-methylpropyl)-2,4-(1H,3H)-quinazolinedione and 12 pounds of Tergitol ® NPX (nonylphenylpolyethyleneglycol ether) in 35 gallons of water.

This tank mixture is applied at the rate of 35 gallons per acre as a directed post-emergence spray to a seedling stand of weeds growing in on established arbor vitae nursery. Excellent control of foxtail, crabgrass, chickweed, seedling Johnsongrass, pigweed and lambsquarters is obtained.

The invention claimed is:

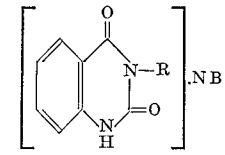
1. Method for the control of plants comprising applying to the locus to be protected, in amount sufficient to exert herbicidal action a compound selected from the group consisting of those of the formula:

I

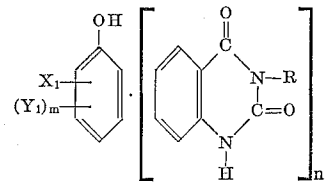


and the alkali, alkaline earth and quaternary ammonium salts thereof having 4 to 12 carbon atoms

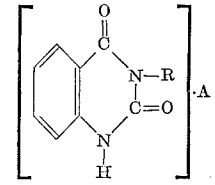
II



III



IV



wherein

R is selected from the group consisting of

the radical



cycloalkyl having 3 through 10 carbon atoms in the alkyl group and cycloalkenyl having 4 through 10 carbon atoms in the alkenyl group;

X is selected from the group consisting of hydrogen and methyl;

Y is alkyl of 1 through 4 carbon atoms;

Z is alkyl of 1 through 4 carbon atoms; with the limitation that the total carbons in Y and Z equal less than 6;

NB is a nitrogenous base having 1 through 12 carbon atoms and an ionization constant K_b of $\geq 10^{-5}$ in water;

X_1 is selected from the group consisting of hydrogen, chlorine, bromine, nitro, alkyl of 1 through 3 carbon atoms and OR_1;

Y_1 is selected from the group consisting of hydrogen, chlorine and alkyl of 1 through 3 carbon atoms;

R_1 is alkyl of 1 through 3 carbon atoms;

m is a whole positive integer less than 5;

n is a whole positive integer less than 3; and

A is an acid having a dissociation constant in water of more than 2×10^{-5}.

2. The method according to claim **1** wherein the active herbicidal ingredient is 3-isopropyl-2,4-(1H,3H)-quinazolinedione.

3. The method according to claim **1** wherein the active herbicidal ingredient is 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione.

4. The method according to claim 1 wherein the active herbicidal ingredient is 3-(methylpropyl)-2,4-(1H,3H)-quinazolinedione.

5. The method according to claim 1 wherein the active herbicidal ingredient is 3-(methylbutyl)-2,4-(1H,3H)-quinazolinedione.

6. The method according to claim 1 wherein the active herbicidal ingredient is 3-cyclopentyl-2,4-(1H,3H)-quinazolinedione.

7. The method according to claim 1 wherein the active herbicidal ingredient is 3-cyclooctyl-2,4-(1H,3H)-quinazolinedione.

8. The method according to claim 1 wherein the active herbicidal ingredient is 3-cyclohexyl-2,4-(1H,3H)-quinazolinedione, tetramethylammonium salt.

9. The method according to claim 1 wherein the active herbicidal ingredient is 3-(methylpropyl)-2,4-(1H,3H)-quinazolinedione, tetramethylammonium salt.

References Cited by the Examiner

UNITED STATES PATENTS

2,680,741	6/1954	Gilbert	260—260
2,940,844	6/1960	Gysin et al.	71—2.5

OTHER REFERENCES

Sandburg: Chemical Abstracts, vol. 52, column 1180(c), 1958.

LEWIS GOTTS, *Primary Examiner.*