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Baker et al.

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[45] **Apr. 29, 1975**

[54] **BIS-ANILIDE COMPOSITIONS AS ALGICIDAL AGENTS**

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[22] Filed: **Apr. 9, 1973**

[21] Appl. No.: **349,342**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 198,450, Nov. 12, 1971, abandoned.

[52] **U.S. Cl.**..... **71/67**; 260/558 R; 260/562 R; 71/118

[51] **Int. Cl.**..... **A01n 9/20**

[58] **Field of Search**..... 71/67, 118

[56] **References Cited**

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3,661,552 5/1972 Rumanowski..... 71/118

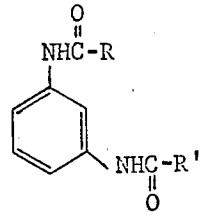
FOREIGN PATENTS OR APPLICATIONS

719,324 10/1969 Belgium

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[57] **ABSTRACT**

This invention relates to the utility of certain bis-anilide compositions of the general formula:



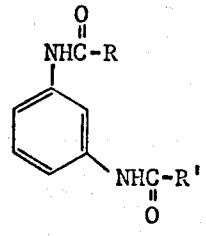
wherein R is alkyl having from 2 to 7 carbon atoms, inclusive, and R′ is selected from the group consisting of benzyl, 3,4-dichlorophenyl, 2,4-dichlorophenyl, 2,4-dichlorophenoxymethyl, 1-isobutenyl, alkyl having from 2 to 7 carbon atoms, inclusive, and haloalkyl having 1 to 2 carbon atoms, inclusive, as algicidal agents.

29 Claims, No Drawings

BIS-ANILIDE COMPOSITIONS AS ALGICIDAL AGENTS

This application is a continuation-in-part of copending application Ser. No. 198,450, filed Nov. 12, 1971 now abandoned.

This invention relates to the utility as algicidal agents for the control of algae when used in an algicidally effective amount of certain substituted bis-anilides of the general formula:



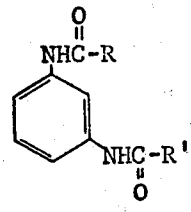
wherein R is alkyl having from 2 to 7 carbon atoms, inclusive, and R' is selected from the group consisting of benzyl, 3,4-dichlorophenyl, 2,4-dichlorophenyl, 2,4-dichlorophenoxymethyl, 1-isobutenyl, alkyl having from 2 to 7 carbon atoms, inclusive, and haloalkyl having 1 to 2 carbon atoms, inclusive. It was found that these compounds have an algicidal property and provide beneficial results in controlling the growth of algae.

Controlling the growth of algae by employing the compounds described herein can be accomplished by applying an aligicidally effective amount to the environment in which algae growth is normally encouraged. The compounds may be applied to any environmental area which is a host to algae or susceptible to algae attack and growth. By controlling, it is meant the inhibition, eradication or elimination, and prevention of the growth of the organism to be controlled.

The term alkyl as used herein, i.e., both in the specification and claims, contemplates linear and branched chain alkyl radicals containing from 2 to 7 carbon atoms, inclusive, such as ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, sec.-butyl, tert.-butyl, n-amyl, isoamyl, n-hexyl, 1,1-dimethylbutyl, and the like. The term haloalkyl as used herein contemplates halogen substituted alkyl radicals containing from 1 to 2 carbon atoms, inclusive, such as monochloromethyl, dichloromethyl, trichloromethyl, monochloroethyl, dichloroethyl, trichloroethyl, pentachloroethyl, bromomethyl, bromoethyl, iodomethyl, iodoethyl, trifluoromethyl, pentafluoroethyl, chlorofluoromethyl, chlorofluoroethyl, monofluorotetrachloroethyl, and the like.

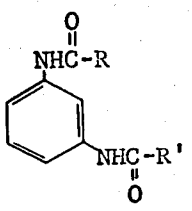
The following compounds in Table I can be used, for example, according to the invention hereindescribed. Compound numbers have been assigned and are used throughout the balance of this application.

TABLE I



COMPOUND NUMBER	R	R'	PHYSICAL CONSTANT m.p. °C.
1	C_2H_5	CCl_3	159-161
2	C_2H_5	CF_3	196-197
3	i-C_3H_7	CCl_3	160-162
4	$C(CH_3)_2C_3H_7$	$CH_2C(CH_3)_3$	105-110
5	$CH_2CH_2CH(CH_3)_2$	$C(CH_3)_2C_3H_7$	114-116
6	$CH(CH_3)C_3H_7$	benzyl	149.5-151
7	$C(CH_3)_2C_3H_7$	benzyl	142-143.5
8	$CH(CH_3)C_3H_7$	$CH(CH_3)C_3H_7$	111-115
9	$C(CH_3)_3$	3,4-di-Cl-phenyl	187-191
10	$C(CH_3)_2C_3H_7$	2,4-di-Cl-phenyl	153-157
11	$C(CH_3)_2C_3H_7$	CH_2O-2,4-di-Cl-phenyl	126-129
12	C_2H_5	$CH_2C(CH_3)_3$	177-179

TABLE I—Continued



COMPOUND NUMBER	R	R'	PHYSICAL CONSTANT m.p. °C.
13	C_2H_5	3,4-di-Cl-phenyl	175-177
14	C_2H_5	CCl_2CH_3	163-165
15	$C(CH_3)_2C_3H_7$	CF_3	117-120
16	$C(CH_3)_3$	$CH=C(CH_3)_2$	112-117
17	$CH(CH_3)C_3H_7$	$C(CH_3)_3$	145-148
18	C_2H_5	$CH(C_2H_5)C_4H_9$	126-129
19	$C(CH_3)_3$	C_2F_5	187-190

The compounds mentioned thus far, and those contemplated, can be prepared, for example, according to the following methods.

The compounds herein disclosed are prepared by one of several general methods. One such general method is the condensation between the appropriate m-phenylene diamine and an appropriate acid anhydride or acid chloride to prepare the desired meta-bis-symmetrically substituted anilide. Another general method is the condensation between the appropriate m-monosubstituted amino anilide and an appropriate acid anhydride or acid chloride to prepare the desired meta-bis-assymetrically substituted anilide. The reactions proceed readily in the liquid phase. The employment of a solvent is also useful, facilitating processing, as well as agitation of the reactants. When using a starting material containing an acid chloride, it is preferred to carry out the reaction in the presence of a hydrogen halide acceptor such as triethylamine, pyridine, picoline, sodium carbonate and the like. The reactions are preferably carried out at temperatures that permit operation in the liquid phase. Upon completion of the reaction, normal work-up procedures are applicable to recover the purified compound, such as, solvent extraction, crystallization, distillation and the like.

The following illustrated examples describe in detail, without restriction thereto, the preparation of several representative compounds.

EXAMPLE I

Preparation of 3'-trichloroacetamido propionanilide.

Meta-amino propionanilide, 9.8 g., was dissolved in acetone and triethylamine, 7.0 g., added. To this solution was added 11.0 g. of trichloroacetylchloride. The reaction flask was cooled in a water bath during the addition. After stirring the solution for one-half hour, it was poured into water. The solid product was recovered by filtration and washed consecutively with dilute hydrochloric acid and water. The product was dried in a vacuum oven. There was obtained 15.3 g. of the title product, m.p. 159°–161°C.

EXAMPLE II

Preparation of 3'-(2,2-dimethylvaleramido)-t-butyl-acetanilide.

In a similar procedure as Example I, 12.4 g. of 3-amino t-butylacetanilide was reacted with 9.0 g. of 2,2-dimethylvaleryl chloride in 100 ml. of acetone in the presence of 6.5 g. of triethylamine. There was obtained 16.9 g. of the title compound, m.p. 105°–110°C.

Additional examples of compounds prepared in this manner are 3'-(2,4-dichlorophenylamido)-2,2-dimethylvaleranilide, 3'-(2,4-dichlorophenoxyacetamido)-2,2-dimethylvaleranilide, and 3'-(3,3-dimethylacrylamido)pivalanilide.

The following examples are given for the purpose of illustrating the effects according to the instant invention:

ALGICIDAL TEST PROCEDURE

Sufficient candidate toxicant is diluted in acetone to give an 0.5 percent mixture which is then diluted into 20 milliliters of warm modified Jack Meyers Agar Medium ("Algae Culture from Laboratory to Pilot Plant", 1953, Page 94). The dilutions of the test compounds are selected concentrations of from 0.5 to 50 μg/ml. including 1.0, 5.0 and 10.0 μg/ml. The selected concentrations are tested in 20 × 100 mm. Petri dishes. After the agar solidifies, separate Petri dishes are inoculated with the desired organism, such as *Scenedesmus obliquus* or *Chlorella pyrenoidosa*. The innoculated samples are then allowed to grow at room temperature under fluorescent lamps using a 14 hour light period each day. After one to two weeks, depending upon

the growth of the untreated controls, the results are recorded as to the level necessary to control the specific organism. The results obtained with representative compounds and their concentrations are given in Table II.

TABLE II

COMPOUND NUMBER	ALGICIDE TEST *Chlorella pyrenoidosa* (concentration, μg/ml.)	*Scenedesmus obliquus* (concentration, μg/ml.)
1	>1.0*	0.5
2	>1.0*	(0.5)
3	>1.0*	0.5
4	>1.0*	1.0
5	>1.0*	(1.0)
6	>1.0*	0.5
7	>1.0*	0.5
8	>1.0*	1.0
9	>1.0*	0.5
10	>1.0*	1.0
11	>1.0*	0.5
12	>5.0	(5.0)
13	>5.0	1.0
14	(5.0)	(1.0)
15	>5.0	(1.0)
16	>5.0	(5.0)
17	>50.0	50.0
18	>5.0	1.0
19	50.0	(1.0)
20	>50.0	(50.0)
21	>50.0	(5.0)
22	50.0	5.0
23	(50.0)	(5.0)
24	(50.0)	50.0
25	50.0	5.0
26	50.0	5.0
27	(50.0)	1.0
28	50.0	1.0
29	(5.0)	1.0
30	(5.0)	1.0

( ) denotes partial control at the indicated concentration
— denotes not tested
*denotes highest concentration tested

The manner in which the water area may be treated for the control of algae will vary with the specific problems encountered. An acute problem in the storage and utilization of industrial process water is the fouling of such water and systems in which the water is used by the growth of algae. Entire areas such as a pond or lake may be treated. Drainage ditches and other water-flowing sites may be treated.

In addition to use in ponds and lakes, this invention is applicable to the control of algae in industrial cooling towers and other water recirculating systems as used in paper manufacturing processes, for example.

The substances to be employed according to the present invention can be used as such or in the form of formulations with carrier vehicles. Examples and emulsifiable concentrates, spray powders, pastes, soluble powders, and the like. Suitable carrier vehicles or assistants are mainly: Solvents, such as, optionally chlorinated, aromatic hydrocarbons (e.g., xylene, benzene, chlorobenzenes), paraffins (e.g., petroleum fractions), alcohols (e.g., methanol, ethanol, butanol), amines (e.g., ethanolamine, dimethyl formamide), as well as water; finely divided solid carriers, for example, natural and synthetic stone meals or powders (kaolin, alumina, chalk, i.e., calcium carbonate, talc, highly disperse silicic acid, silicates, e.g., alkali silicates); emulsifiers, such as non-ionic and anionic emulsifiers (e.g., polyoxyethylene fatty acid esters and polyoxyethylene fatty alcohol ethers, alkyl sulfonates and aryl sulfonates) especially magnesium stearate, sodium oleate, etc., and dispersing agents such as lignin, sulfite waste liquors and methyl cellulose.

As already mentioned above, the active compounds or agents to be employed according to the instant invention can be present in the aforesaid formulations in mixture with one another and with other known active substances.

The algicidal compositions of the invention also comprise aqueous emulsions. The aqueous emulsions can be prepared by dissolving a surfactant of the type noted hereinabove and pouring the emulsifiable concentrate so obtained into water with vigorous agitation. The aqueous emulsions of the invention can also be prepared by dissolving the active ingredient in a water-miscible solvent such as Carbitol (diethylene glycol monoethyl ether), acetone, a lower alkanol, Cellosolve (ethylene glycol monoethyl ether), dioxan, and the like, if desired, in association with a surfactant such as noted above, to obtain an emulsifiable concentrate which is poured into water with vigorous agitation. The aqueous emulsions of the invention can also be prepared by dissolving the active ingredient and a surfactant such as noted above in an organic solvent which is immiscible with water. The resulting emulsifiable concentrate is then admixed with water with vigorous agitation to form an emulsion. The water-immiscible organic solvents which are suitable for use include cyclohexanone, summer oils, aromatic hydrocarbons such as benzene, toluene, xylene, and high-boiling petroleum hydrocarbons such as kerosene, diesel oil, and the like.

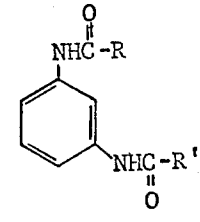
The aqueous emulsions of the invention can be supplied to the user in the form of the emulsifiable concentrates described above which require dilution with water before use. Both the concentrated compositions and the diluted compositions are included within the scope of the present invention.

Formulations contain, in accordance with the present invention, in general from 0.1 to 95, preferably 0.5 to 90, per cent by weight of active compound or agent. The agents according to the present invention or their preparations are applied in the usual way, e.g., by spraying, dusting, sprinkling or atomizing. The active substances can be applied, according to the purpose in view, in a concentration of 5 to 0.0005 percent. In special cases it is, however, possible or even necessary to go below or above these concentrations. The remainder of active algicidal composition being an adjuvant which can be a liquid extending agent or surfact active agent, but preferably is an admixture thereof.

Various changes and modifications are possible without departing from the spirit and scope of the invention described herein and will be apparent to those skilled in the art to which it pertains.

What is claimed is:

1. The method for inhibiting and preventing algae growth in water, which comprises adding to the algae environment an algicidally effective amount of a compound of the formula



wherein R is alkyl having from 2 to 7 carbon atoms, inclusive and R′ is selected from the group consisting of benzyl, 3,4-dichlorophenyl, 2,4-dichlorophenyl, 2,4-dichlorophenoxymethyl, 1-isobutenyl, alkyl having from 2 to 7 carbon atoms, inclusive, and haloalkyl having 1 to 2 carbon atoms, inclusive.

2. The method according to claim **1** in which R is alkyl and R′ is alkyl.

3. The method according to claim **2** in which R is 1,1-dimethylbutyl and R′ is neopentyl.

4. The method according to claim **2** in which R is 3-methylbutyl and R′ is 1,1-dimethylbutyl.

5. The method according to claim **2** in which R is ethyl and R′ is neopentyl.

6. The method according to claim **2** in which R is 1-methylbutyl and R′ is tertiary-butyl.

7. The method according to claim **2** in which R is ethyl and R′ is 1-ethylpentyl.

8. The method according to claim **2** in which R is 1-methylbutyl and R′ is 1-methylbutyl.

9. The method according to claim **1** in which R is alkyl and R′ is haloalkyl.

10. The method according to claim **9** in which R is ethyl and R′ is trichloromethyl.

11. The method according to claim **9** in which R is ethyl and R′ is trifluoromethyl.

12. The method acccording to claim **9** in which R is isopropyl and R′ is trichloromethyl.

13. The method according to claim **9** in which R is ethyl and R′ is 1,1-dichloroethyl.

14. The method according to claim **9** in which R is 1,1-dimethylbutyl and R′ is trifluoromethyl.

15. The method according to claim **9** in which R is tertiary-butyl and R′ is pentafluoroethyl.

16. The method according to claim **9** in which R is ethyl and R′ is 1,1-dichloro-2,2,2-trifluoroethyl.

17. The method according to claim **9** in which R is 1,1-dimethylbutyl and R′ is pentafluoroethyl.

18. The method according to claim **1** in which R is alkyl and R′ is benzyl.

19. The method according to claim **18** in which R is 1-methylbutyl.

20. The method according to claim **18** in which R is 1,1-dimethylbutyl.

21. The method according to claim **1** in which R is alkyl and R′ is 3,4-dichlorophenyl.

22. The method according to claim **21** in which R is tertiary-butyl.

23. The method according to claim **21** in which R is ethyl.

24. The method according to claim **1** in which R is alkyl and R′ is 2,4-dichlorophenyl.

25. The method according to claim **24** in which R is 1,1-dimethylbutyl.

26. The method according to claim **1** in which R is alkyl and R′ is 2,4-dichlorophenoxymethyl.

27. The method according to claim **26** in which R is 1,1-dimethylbutyl.

28. The method according to claim **1** in which R is alkyl and R′ is 1-isobutenyl.

29. The method according to claim **28** in which R is tertiary-butyl.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,642

DATED : April 29, 1975

INVENTOR(S) : Don R. Baker et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In printing the patent, the following portion of Table I was omitted:

COMPOUND NUMBER	R	R'	PHYSICAL CONSTANT m.p. °C.
20	$C(CH_3)_3$	$CH_2C(CH_3)_3$	184-185
21	$CH(CH_3)_2$	$C(CH_3)_2C_3H_7$	115-120
22	$CH(CH_3)C_3H_7$	$C(CH_3)_2C_3H_7$	glass
23	$CH_2CH(CH_3)C_2H_5$	C_2H_5	123-126
24	$CH_2CH(CH_3)C_2H_5$	$C(CH_3)_3$	134-136
25	$CH_2CH(CH_3)C_2H_5$	$CH(CH_3)C_3H_7$	107-108
26	$CH_2CH(CH_3)C_2H_5$	$CH_2CH(CH_3)C_2H_5$	132-134
27	C_2H_5	C_2F_5	172-175
28	$CH(CH_3)C_3H_7$	C_2F_5	126-128
29	$C(CH_3)_2C_3H_7$	C_2F_5	112-114
30	C_2H_5	CCl_2CF_3	141-143

Signed and Sealed this

Twenty-eighth Day of December 1976

[SEAL]

Attest:

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