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4esticidal compositions containing ethoxylated fatty amines for increasing the effectiveness of endothall and salts thereof

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ABSTRACT

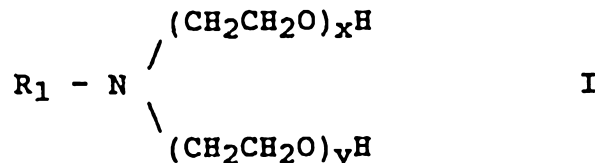
Pesticidal compositions for application to chlorophyll-containing algae or plants containing endothall or a salt thereof and at least one ethoxylated amine of formula (I) in which R_1 is an alkyl group having 8 to 22 carbon atoms, and is saturated or unsaturated; and the poly(oxyethylene) content ($x + y$) is greater than 3 but less than or equal to 15. Also disclosed are methods of increasing the effectiveness of endothall or a salt thereof which comprises adding to the endothall or salt thereof an amount of an ethoxylated amine of formula (I) effective to increase the pesticidal activity of the endothall or salt thereof.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~The claimed invention is:~~xxx

1. A pesticidal composition for application to chlorophyll-containing algae or plants comprising endothall or a salt thereof and at least one ethoxylated amine of formula I



in which R_1 is an alkyl group having 8 to 22 carbon atoms and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15; wherein the ethoxylated amine of formula I is present in an amount effective to increase the pesticidal activity of the endothall or salt thereof.

2. The pesticidal composition of claim 1, wherein $(x+y)$ is between 3 and 10; R_1 is an alkyl group having 10 to 20 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 5.0 to 12.

3. The pesticidal composition of claim 1, wherein $(x+y)$ is greater than 3 but less than or equal to 8; R_1 is an alkyl group having 12 to 18 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 6.0 to 11.

4. The pesticidal composition of claim 1, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

5. The pesticidal composition of claim 2, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

6. The pesticidal composition of claim 3, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

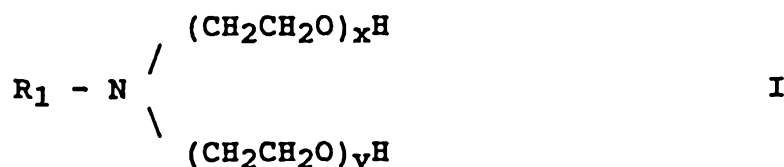
7. The pesticidal composition of claim 1, wherein the composition further comprises water.

8. The pesticidal composition of claim 1, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

9. The pesticidal composition of claim 2, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

10. The pesticidal composition of claim 3, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

11. A method of increasing the pesticidal effectiveness of endothall or a salt thereof which comprises applying to chlorophyll-containing algae or plants endothall or a salt thereof and an amount of an ethoxylated amine of formula I effective to increase the pesticidal activity of the endothall or salt thereof, wherein the ethoxylated amine of formula I has the following structure:



in which R_1 is an alkyl group having 8 to 22 carbon atoms, and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15.

12. The method of claim 11, wherein $(x+y)$ is between 3 and 10; R_1 is an alkyl group having 10 to 20 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 5.0 to 12.

13. The method of claim 11, wherein $(x+y)$ is greater than 3 but less than or equal to 8; R_1 is an alkyl group having 12 to 18 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 6.0 to 11.

14. The method of claim 7, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine)

salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

15. The method of claim 8, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

16. The method of claim 9, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

17. The method of claim 7, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

18. The method of claim 8, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

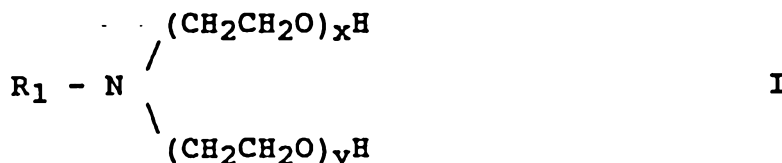
19. The method of claim 9, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

20. The method of claim 11, wherein said ethoxylated amine of formula I and endothall or a salt thereof are simultaneously applied to said algae or plants.

21. The method of claim 11, wherein said ethoxylated amine of formula I and endothall or a salt thereof are applied in the form of an aqueous composition which contains both the ethoxylated amine and the endothall or salt thereof.

22. A concentrated pesticidal formulation comprising:

- (a) endothall or a salt thereof;
- (b) a solvent; and
- (c) at least one ethoxylated amine of formula I:



in which R_1 is an alkyl group having 8 to 22 carbon atoms, and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15; component (a) is present in an amount to be pesticidally effective upon dilution; component (b) is present in an amount effective to increase the solubility of component (c)

in the concentrated formulation; and component (c) is present in an amount effective to increase the pesticidal activity of component (a) upon dilution.

23. The concentrated pesticidal formulation of claim 22, wherein the amount of component (b) present also increases the solubility of component (c) in a diluted formulation upon dilution of the concentrated pesticidal formulation with water.

24. The concentrated pesticidal formulation of claim 22, wherein the formulation further comprises up to about 14.1% water.

25. The concentrated pesticidal formulation of claim 15, wherein the solvent is a substituted or unsubstituted C₁-C₆ alcohol or a substituted or unsubstituted C₂-C₆ glycol.

26. The concentrated pesticidal formulation of claim 25, wherein the solvent is ethanol, propanol, butylene glycol, propylene glycol, dipropylene glycol, or hexylene glycol.

27. The concentrated pesticidal formulation of claim 26, wherein the solvent is propylene glycol.

DATED this 23rd day of July 1999.

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AUSTRALIA

Patents Act 1990

**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title:

PESTICIDAL COMPOSITIONS CONTAINING ETHOXYLATED FATTY
AMINES FOR INCREASING THE EFFECTIVENESS OF ENDOTHALL AND
SALTS THEREOF

The following statement is a full description of this invention, including the
best method of performing it known to us :-

Pesticidal Compositions Containing Ethoxylated
Fatty Amines For Increasing The
Effectiveness of Endothall And Salts Thereof

The present invention utilizes at least one ethoxylated amine of formula I, defined below, to increase the effectiveness of endothall and salts thereof, which are known pesticides. The invention thus relates to pesticidal compositions and concentrated pesticidal formulations containing endothall or a salt thereof and at least one ethoxylated amine of formula I, defined below. The present invention also relates to a method for increasing the effectiveness of endothall or a salt thereof by applying, for instance, to a plant at least one ethoxylated amine of formula I in conjunction with endothall or a salt thereof.

In spite of the international concern about pesticides, the amount of pesticides being used continues to grow. Organic chemicals registered and applied as pesticides have achieved widespread use throughout the world in the production of agronomic and horticultural crops. Common examples of pesticides are herbicides. A herbicide may be used for the prevention or eradication of at least one specific weed. Other types of herbicides, such as harvest aids or those used for vegetation management, provide an action different from killing a specific weed. Other common examples for use of selected pesticidal products are for the prevention or eradication of an insect or fungus. A general discussion of pesticides is provided in Crowley, "A Pesticide Primer," Hazleton Wisconsin Agricultural Newsletter, 1:1-6 (1990).

A pesticide is thus any substance or mixture of substances that is useful for preventing, destroying, repelling, or mitigating any pest, or used as a plant growth regulator, seed protectant, defoliant, or desiccant. Examples of pesticides are herbicides, desiccants, plant growth regulators, defoliants, and algicides.

Endothall is a phytotoxicant used to kill chlorophyll-containing vegetation or chlorophyll-containing algae in numerous industrial and non-industrial applications. Endothall is the common name for the active ingredient (7-oxabicyclo[2,2,1]heptane-2,3-dicarboxylic acid) contained in the agricultural products Des-i-cate® and Accelerate®, currently manufactured, formulated, and marketed by Atochem North America (Philadelphia, PA). An alternate formulation containing endothall is Hydrothol® 191 which is marketed as Bulab® 6050 by Buckman Laboratories, Inc., Memphis, TN. Bulab® 6050 is an aquatic algicide and herbicide for use in irrigation and drainage canals, lakes, and ponds to control weeds and algae. Bulab® 6050 contains 53.0% mono(N,N-dimethylalkyl-amine) salt of endothall and 47.0% inert ingredients. One gallon of Bulab® 6050 contains approximately two pounds of endothall.

Accelerate® is registered with the Environmental Protection Agency as a harvest aid for cotton production. As such the product is applied by spraying on cotton plants 1-2 weeks prior to harvest. This kills the leaves and facilitates the mechanical harvesting of the cotton bolls. Des-i-cate® is registered with the Environmental Protection Agency for use as a potato vine killer and as a harvest aid for alfalfa and clover. In much of the potato acreage throughout the world, the vines are chemically killed ("desiccated") to allow easier passage of the harvesting equipment through the fields. Also, vine desiccation enhances "skin set" on the potato tuber.

Insufficient plant desiccation, however, can be a problem, especially in fields with dense growth, by allowing stem regrowth which complicates harvesting. Sequential applications 7-10 days apart are an option, provided that the grower can afford the additional cost.

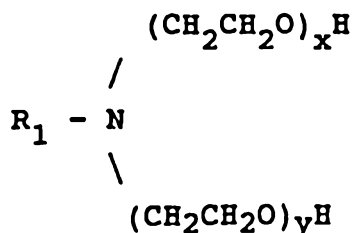
Pesticides are usually part of a formulation which contains not only the active ingredient, but also other materials, agents, or adjuvants. The formulation is typically a liquid or a powder which is designed to be mixed

with water so that the active ingredient will remain suspended uniformly throughout the water during application.

Pesticide formulations may contain agents (adjuvants) which improve the water/pesticide suspension and facilitate the coverage of the application over the target plants. An adjuvant is "an ingredient in a (pesticide or other agrichemical) prescription, which aids or modifies the action of the principal ingredient". Chow, "Adjuvants and Agrochemicals", Vol. 1, CRC Press (1989). An adjuvant may be an oil, surface tension reducing agent, solvent, activator, stabilizer, sticker, and a foaming or anti-foaming agent. The choice of adjuvant depends on the physical or chemical property to be modified. Chemically, surfactants are the most important and widely used adjuvants. Surfactants may affect many properties of the formulation such as solubility, volatility, specific gravity, corrosiveness, efficacy, and freezing and flash points.

The effectiveness of a pesticide is dependent on the quantity applied, the method of application, and the environmental conditions during the application. The objective of the grower or pesticide applicator is to achieve a desired result with the least amount of chemical and at the lowest cost. Therefore, a need exists for an effective and EPA approved pesticide formulation which uses less active ingredients to lessen or avoid adverse environmental effects and to reduce the cost of application.

Accordingly, the present invention is directed to a pesticidal composition for application to chlorophyll-containing algae or plants comprising endothall or a salt thereof and at least one ethoxylated amine of formula I



In formula I, R_1 is an alkyl group having 8 to 22 carbon atoms and may be saturated or unsaturated. The poly(oxyethylene) content ($x+y$) is greater than 3 but less than or equal to 15. In the pesticidal composition, the compound of formula I is present in an amount effective to increase the pesticidal activity of the endothall or salt thereof.

The present invention also provides a method of increasing the effectiveness of endothall or a salt thereof which comprises applying to chlorophyll-containing algae or plants endothall or a salt thereof and an amount of at least one ethoxylated amine of formula I, defined above, effective to increase the pesticidal activity of the endothall or a salt thereof.

The invention, in a further embodiment, provides a concentrated pesticidal formulation comprising:

- (a) endothall or a salt thereof;
- (b) a solvent; and
- (c) at least one ethoxylated amine of formula I, defined above.

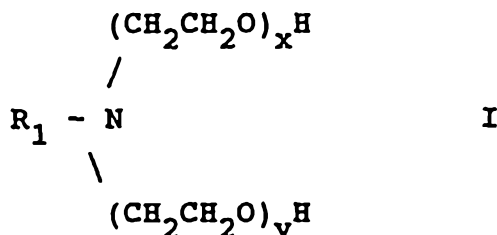
In the concentrated pesticidal formulation, component (a) is present in an amount to be pesticidally effective upon dilution. Component (b) is present in an amount effective to increase the solubility of component (c) in the concentrated formulation. Component (c) is present in an amount effective to increase the pesticidal activity of component (a) upon dilution. Advantageously, the ethoxylated amine of formula I not only increases the effectiveness of endothall or a salt thereof, but in a preferred embodiment may act as an emulsifier. Thus, in that preferred embodiment, additional emulsifiers need not be added to the composition upon dilution.

The invention thus provides improved performance of endothall or a salt thereof which can result, desirably, in the use of less endothall or a salt thereof providing both economic and environmental benefits.

Additional advantages of this invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by the practice of this invention.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the present invention as claimed.

As a first embodiment, the invention provides a pesticidal composition for application to chlorophyll-containing algae or plants comprising endothall or a salt thereof, and at least one ethoxylated amine compound of formula I



In formula (I), R_1 is an alkyl group having 8 to 22 carbon atoms, preferably 10 to 20 carbon atoms, and most preferably 12 to 18, carbon atoms. The alkyl group can be either saturated or unsaturated, and can be derived from, but not limited to, tallow, or from soybean, coconut, or cottonseed oil. The poly(oxyethylene) content ($x+y$) of the ethoxylated amine is greater than 3 but less than or equal to 15. It is preferred that ($x+y$) is between 3 and 13, more preferably between 3 and 10 and most preferably greater than 3 but less than or equal to 8. Ethoxylated amines sold commercially under the tradename ETHOMEEN by Akzo Chemicals Inc., Chicago, IL. Other ethoxylated amines are discussed in "Surfactant Specialties: Product Guide" from Chemax, Inc., Greenville, S.C.

The endothall or a salt thereof may be obtained from any commercial source discussed above. Accelerate® and Des-i-cate® products contain mixed mono and di(N,N-dimethylalkylamine) salts of endothall, which have an average molecular formula of $\text{C}_{14}\text{H}_{31}\text{N}$. Accelerate® and Des-i-cate®

products contain 5.5 weight percent of endothall. Bulab® 6050 and Hydrothol® 191 products are solutions of 53 weight percent mono(N,N-dimethylalkylamine) salts of endothall and 47 weight percent inert ingredients. The mono(N,N-dimethylalkylamine) salts are derived from coconut oil. Bulab® 6050 and Hydrothol® 191 products contain 23 weight percent of endothall.

In a preferred embodiment of the concentrated pesticidal composition, the endothall or a salt thereof is the mono(N,N-dimethylalkylamine) salt of endothall. The mono(N,N-dimethylalkylamine) salt may be derived from coconut oil.

In the pesticidal composition, the ethoxylated amine is present in an amount effective to increase the pesticidal activity of endothall or its salt. The weight ratio of endothall:ethoxylated amine of formula I preferably range from 1:1 to 1:99, more preferably 1:1 to 1:12, and most preferably, 1:9 to 1:12. The phrase "an amount effective to increase the activity of endothall or its salt" means that the combination of a given amount of endothall or its salt and an adjuvant has a greater activity than of the given amount of endothall and no adjuvant. Therefore, reduced amounts of endothall along with an adjuvant can give the same or better activity than larger amounts of endothall alone.

When selecting an ethoxylated amine, the hydrophilic-hydrophobic-balance (HLB) value can be used as a guide for particular applications. The following HLB ranges and applications provide a guidelines for applications and water solubility or dispersibility.

HLB VALUE

APPLICATION

3-6	water-in-oil emulsification
7-9	wetting agents
8-15	oil-in-water emulsification
13-15	detergents
15-18	solubilizers

<u>HLB VALUE</u>	<u>SOLUBILITY IN WATER</u>
1-4	not water dispersible
3-6	disperse poorly in water
6-8	appear milky after vigorous agitation
8-10	milky but stable dispersions
10-13	translucent to clear dispersions
above 13	clear solutions

Endothall, for instance, is generally marketed as a water soluble formulation. The final formulation of endothall with adjuvant(s) is preferred to be a water-based solution or a stable dispersion in water at the application concentration. The adjuvant preferably has an HLB value of 4.8 to 13, more preferably 5.0 to 12, and most preferably 6.0 to 11.

The HLB values of ethoxylated amines are dependent on the alkyl group as well as on the number of ethoxy groups. The higher the number of carbon atoms in the alkyl group and the lower the number of ethoxy groups, the lower the HLB values. The presence of double bonds in the alkyl groups increases the HLB values. Some HLB values for preferred ethoxylated amines of formula I are:

<u>ETHOXYLATED AMINE</u>	<u>HLB VALUE</u>
Ethoxylated (5) cocoalkylamine	10.4
Ethoxylated (15) cocoalkylamine	15.0
Ethoxylated (5) tallowalkylamine	9.0
Ethoxylated (15) tallowalkylamine	14.3
Ethoxylated (20) tallowalkylamine	15.7

"Surfactant Specialties: Product Guide", Chemax, Inc., Greenville, S.C. The number in parenthesis is the number of ethoxy groups, (x+y).

HLB values provide an index to select among a series of ethoxylated amines to be used in preparing formulations for a particular application or use (i.e. based on numerically different HLB values). Routine biological testing, such as

described in the examples which follow, would then serve to identify the most effective formulation. The values may vary slightly due to methods of determination, chemical sources, temperature, and manufacturing. When an appropriate adjuvant is used, the addition of a coupling or emulsifying agent in the product is unnecessary except perhaps to provide a small percent as solvent.

A pesticidal composition according to the invention may further comprise water or organic solvents. Aqueous compositions, such as solutions or dispersions, are preferred. Other materials, salts, additives, and/or adjuvants such as oils, surface tension reducing agents, solvents, activators, stabilizers, stickers, foaming or anti-foaming agents, surfactants, emulsifiers, and dispersants known in the art, may be added to the composition.

Endothall and its salts are generally water soluble. As indicated above, solvents may also be added to the compositions of the invention. Water soluble solvents are preferred and include, but are not limited to, glycerine, diethylene glycol, dipropylene glycol, hexylene glycol, dipropylene glycol monomethyl ether, ethyl acetate, ethyl alcohol, glycerol mono-, di-, and triacetate methyl alcohol, propylene glycol, sorbitol, butanol, ethylene glycol monobutylether, ethylene glycol monomethylether, isobutyl alcohol, isopropyl alcohol, polyethylene glycol (as defined in 21 C.F.R. 172.260(a)) n-propanol, N-methyl pyrrolidone, tetrahydrofurfuryl alcohol, and propylene glycol monomethylether.

The invention also provides a method of increasing the effectiveness of endothall or a salt thereof which comprises applying to chlorophyll-containing algae or plants endothall or a salt thereof and an amount of an ethoxylated amine of formula I effective to increase the pesticidal activity of the endothall or a salt thereof. The definition and preferred embodiments of the ethoxylated amine of formula I as employed in this method are the same as above.

The endothall or a salt thereof is preferably applied, along with the ethoxylated amine of formula I, to an exposed portion of the algae or plant. The ethoxylated amine of formula I and endothall or a salt thereof may be applied simultaneously or separately and in any order. In a preferred embodiment, the ethoxylated amine of formula I and endothall or a salt thereof are applied simultaneously in the form of an aqueous composition which contains both the ethoxylated amine and the endothall or a salt thereof.

The plant may be any chlorophyll-containing vegetation and preferably is a commercial or garden crop. For example, the preferred crop may be selected from potato vines, cotton plants, hops, alfalfa, and clover. In a further preferred embodiment, the crop is selected from potato vines and cotton plants.

The invention also provides a concentrated pesticidal formulation comprising (a) endothall or a salt thereof; (b) a solvent; and (c) at least one ethoxylated amine of formula I, defined above. The preferred embodiments of the ethoxylated amine of formula I and other aspects of the composition are the same as above.

The concentrated pesticidal formulation comprises component (a) in an amount to be pesticidally effective upon dilution. Component (b) is present in an amount effective to increase the solubility of component (c) in the concentrated formulation. Component (c) is present in an amount effective to increase the pesticidal activity of component (a) upon dilution. The concentrated pesticidal formulation may preferably comprise component (b) in an amount effective to increase the solubility of component (c), but also to avoid or prevent gelling of the concentrated formulation.

Most often the concentrated formulations are diluted with water before application. The concentrated pesticidal formulation may itself also contain water, preferably up to about 14.1% water.

The solvent may be a substituted or unsubstituted C_1-C_6 alcohol or a substituted or unsubstituted C_2-C_6 glycol. The

solvent may be ethanol, propanol, butylene glycol, propylene glycol, dipropylene glycol, hexylene glycol, glycerine, diethylene glycol, dipropylene glycol monomethyl ether, ethyl acetate, ethyl alcohol, glycerol mono-, di-, and triacetate methyl alcohol, sorbitol, butanol, ethylene glycol monobutylether, ethylene glycol monomethylether, isobutyl alcohol, isopropyl alcohol, polyethylene glycol (as defined in 21 C.F.R. 172.260(a)) n-propanol, N-methyl pyrrolidone, tetrahydrofurfuryl alcohol, and propylene glycol monomethylether. Preferred solvents are propylene glycol and dipropylene glycol.

The pesticidal concentrated formulations may be diluted with water to form stable solutions. These stable solutions may be applied to chlorophyll-containing algae and plants using conventional agricultural or pesticidal spray equipment. The pesticidal concentrated formulations may contain other additives known in the art such as surfactants, emulsifiers, dispersants, etc.

The following examples describe a series of greenhouse and field trials in which two chemically distinct products (1) endothall or a salt thereof and (2) ethoxylated amines, were combined to provide a new and more phytotoxic combination. The examples given describe a series of greenhouse and field trials with cotton plants which demonstrate:

(a) the marked enhancement of the phytotoxicity of endothall (Bulab® 6050 product) by the ethoxylated fatty amines of formula I;

(b) the influence of the initial concentration of the ethoxylated fatty amine in the formulation on the resultant phytotoxicity.

The following examples are given to illustrate the invention. It should be understood, however, that the invention is not to be limited to the specific conditions or details set forth in these examples.

Example 1

Experimental formulations A through H and W were prepared with the components and amounts (% w/w) designated in Table I. Each formulation was 50% (w/w) of the endothall source (Bulab® 6050). These formulations were compared on a side-by-side basis relative to phytotoxicity to cotton plants.

To conduct this initial survey, cotton (*Gossypium hirsutum* L. var DPL 50) seeds were planted in four-inch square plastic pots containing a commercial planting medium (Premier Pro-Mix BX sold by most commercial greenhouse suppliers). Seedlings were grown under ambient greenhouse conditions. The seedlings were thinned to two plants per pot. At the time of chemical application the cotton seedlings had developed two fully expanded true leaves. The treatments were delivered across the tops of the cotton plants in a controlled and reproducible manner using a custom made spray booth (R&D Sprayers, Inc., Opelousas, LA). Pressure regulated (40 psi) applications were made through a standard agricultural nozzle tip (LE-1, 80). Each formulation from Table I was applied to three pots at each of three aqueous dilutions (1.0, 0.5, and 0.25% v/v).

Table I.
Components and formulae (% w/w) of
experimental desiccants.

<u>Component</u>	<u>Formulation</u>								
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>W</u>
Bulab® 6050	50	50	50	50	50	50	50	50	50
Propylene glycol	15	15	15	15	15	15	15	15	
A. Ethomeen C/12	35								
B. Ethomeen C/15		35							
C. Ethomeen S/15			35						
D. Ethomeen T/15				35					
E. Ethomeen O/12					35				
F. Ethomeen 18/20						35			
G. Ethomeen S/20							35		
H. Ethomeen 18/15								35	
W. Water									50

Ethomeen is a tradename for ethoxylated amine products from Akzo Chemicals Inc., Chicago, IL.

C = derived from coconut oil

S = derived from soybean oil

T = derived from tallow

O = oleic acid (a specific unsaturated acid found in the above oils)

18 = a saturated 18-carbon (octadecyl) function.

The last number in the component name is used to determine the number of ethoxy groups in that amine by subtracting 10. For instance, in "Ethomeen C/15", the number of ethoxy groups is 5 (=15-10), and in Formula I, (x+y) is equal to 5. Ethomeen C/15 is the reaction product of 5 moles ethylene oxide reacted with coconut amine.

The treated plants were incubated in a greenhouse for five days and then evaluated (Table II). The results in Table II were determined by subjectively scoring the treatments for gross phytotoxicity on a 0 - 10 scale. The primary symptom caused by endothall is a relatively rapid onset of necrosis (desiccation) of leaf and stem tissue. At the time of evaluation, if the treatment provided no visible

effect, then a score of 0 was given. If the plants were dead, then a score of 10 was given. Intermediate degrees of phytotoxicity were described by assigning an appropriate relative number on the 0-10 scale.

Table II.

Gross phytotoxicities of formulations
foliarly applied to cotton plants.

<u>Formulation</u>	<u>Ethoxy Groups</u>	<u>Concentration (% v/v)</u>			
		<u>0.0</u>	<u>0.25</u>	<u>0.5</u>	<u>1.0</u>
A	2	-	0	2	5
B	5	-	0	2	7
C	5	-	0	6	9
D	5	-	0	3	8
E	2	-	0	1	6
F	10	-	0	1	7
G	10	-	0	1	7
H	5	-	0	1	6
W	0	-	0	1	7

Control 0 - - -
0 = No effect, 10 = Dead
Observations made five days after application

The number of ethoxy groups in a particular amine is determined by subtracting 10. For instance, in formulation B, the number of ethoxy groups is 5 (=15-10) and in Formula I, (x+y) is equal to 5.

The data in Table II demonstrate that none of the formulations were phytotoxic at the lowest rate of application (0.25%). However, at 0.5%, formulation C was clearly the most phytotoxic, while formulation D was the second most phytotoxic. Formulations A and B were more phytotoxic than the formulation with endothall alone. Formulation W (an equivalent amount of

The four dot patterns are as follows:

- 0:** A 5x5 grid with the top row and the two side columns filled with dots.
- 1:** A 5x5 grid with the middle vertical column filled with dots.
- 2:** A 5x5 grid with the top row, the middle horizontal row, and the rightmost column filled with dots.
- 3:** A 5x5 grid with the top row, the middle horizontal row, and the two side columns filled with dots.

The four dot patterns are arranged vertically. The first pattern represents the digit '0', the second '1', the third '2', and the fourth '3'. Each pattern is a 5x5 grid of dots with some dots missing to form the digit shape.

The four dot patterns are arranged vertically. The first pattern represents the digit '0', the second '1', the third '2', and the fourth '3'. Each pattern is a 5x5 grid of dots with some dots missing to form the digit shape.

The four dot patterns are as follows:

- 0:** A 5x5 grid where the top row is all dots, the second row has dots at (1,1), (1,2), (1,4), (1,5), the third row has dots at (2,1), (2,2), (2,4), (2,5), the fourth row has dots at (3,1), (3,2), (3,4), (3,5), and the bottom row is all dots.
- 1:** A 5x5 grid where the top row has dots at (1,1), (1,2), (1,3), (1,4), the second row has dots at (2,1), (2,2), (2,3), (2,4), the third row has dots at (3,1), (3,2), (3,3), (3,4), the fourth row has dots at (4,1), (4,2), (4,3), (4,4), and the bottom row has dots at (5,1), (5,2), (5,3), (5,4).
- 2:** A 5x5 grid where the top row has dots at (1,1), (1,2), (1,3), (1,4), the second row has dots at (2,1), (2,2), (2,3), (2,4), the third row has dots at (3,1), (3,2), (3,3), (3,4), the fourth row has dots at (4,1), (4,2), (4,3), (4,4), and the bottom row has dots at (5,1), (5,2), (5,3), (5,4).
- 3:** A 5x5 grid where the top row has dots at (1,1), (1,2), (1,3), (1,4), the second row has dots at (2,1), (2,2), (2,3), (2,4), the third row has dots at (3,1), (3,2), (3,3), (3,4), the fourth row has dots at (4,1), (4,2), (4,3), (4,4), and the bottom row has dots at (5,1), (5,2), (5,3), (5,4).

The image shows four 5x5 dot patterns arranged horizontally. The first pattern represents the digit '0', the second '1', the third '2', and the fourth '3'. Each pattern is composed of black dots on a white background.

The four 5x5 dot patterns are as follows:

- 0:** A 5x5 grid with the top row and the two side columns filled with dots, forming a rectangular shape.
- 1:** A 5x5 grid with dots forming a vertical line in the center column, and a horizontal line at the bottom row.
- 2:** A 5x5 grid with dots forming a shape that resembles a '2', with a horizontal line at the top, a vertical line in the middle, and a horizontal line at the bottom.
- 3:** A 5x5 grid with dots forming a shape that resembles a '3', with a horizontal line at the top, a vertical line in the middle, and a horizontal line at the bottom.

The four 5x5 dot patterns are as follows:

- 0:** A 5x5 grid with the top row and the two side columns filled with dots, forming a rectangular shape.
- 1:** A 5x5 grid with dots forming a vertical line in the center column, and a horizontal line at the bottom row.
- 2:** A 5x5 grid with dots forming a shape that resembles a '2', with a horizontal line at the top, a vertical line in the middle, and a horizontal line at the bottom.
- 3:** A 5x5 grid with dots forming a shape that resembles a '3', with a horizontal line at the top, a vertical line in the middle, and a horizontal line at the bottom.

Ethomeen O/15 was not part of Example 1 but formulations containing Ethomeen O/15 were prepared since O/15 is in the same family as Ethomeen S/15 and T/15. However, Formulations I, J, and K were omitted from the greenhouse phase of the trial. Formulations I, J, and K were omitted in order to utilize the available plant material for a comparison of Ethomeen S/15 (Formulation C, Table I, and L, M, and N, Table III) with Ethomeen T/15 (Formulation D, Table I and O, P, and Q, Table III). These two ethoxylated fatty amines were the most effective from Table II.

All of the formulations in Table III contained 30% (w/w) of Bulab® 6050 to allow for a wider range of proportions of the other components. Formulations L, M, and N are variants of Formulation C from Example 1. Formulations O, P, and Q are variants of Formulation D from Example 1. Within each set of three formulations for a given ethoxylated fatty amine, the weight ratio of ethoxylated fatty amine to Bulab® 6050 ranges from 2:1 to 1:0.5.

In this trial, the growing of the cotton seedlings and the application of the treatments was conducted as described in Example 1. Each formulation was applied at four aqueous dilutions (4.0, 2.0, 1.0, and 0.5% v/v). The concentrations were increased to accommodate the reduced level of Bulab 6050 in the formulations.

Evaluations of the treatments were done three days after application and the gross phototoxicity determined as in Example 1. The results, shown in Table IV, demonstrate that at given concentrations less than 4.0%, the resultant phytotoxicity is increased with an increasing level of ethoxylated fatty amine in the original formulation (i.e., L > M > N and O > P > Q). Except for Formulations N and Q at the 0.5% application level, all formulations at a given concentration were somewhat to greatly more phytotoxic than Formulation X containing endothall alone. This clearly demonstrates (a) the enhancement by the ethoxylated fatty

amine of the phytotoxicity of endothall (Bulab 6050), and (b) the influence of the initial concentration of the ethoxylated fatty amine in the formulation on the resultant phytotoxicity.

Table IV.

Gross phytotoxicities
foliarly applied to cotton plants.

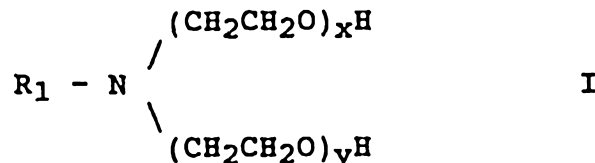
<u>Formulation</u>	<u>Concentration (% v/vi)</u>				
	<u>0.0</u>	<u>0.5</u>	<u>1.0</u>	<u>2.0</u>	<u>4.0</u>
L	-	3	5	7	9
M	-	1	3	8	9
N	-	0	1	4	9
O	-	2	6	8	9
P	-	1	2	7	9
Q	-	0	1	4	8
R	-	1	3	7	9
X		0	0	2	5
Control	0				

Observations made three days after application

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

~~The claimed invention is:~~xxx

1. A pesticidal composition for application to chlorophyll-containing algae or plants comprising endothall or a salt thereof and at least one ethoxylated amine of formula I



in which R_1 is an alkyl group having 8 to 22 carbon atoms and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15; wherein the ethoxylated amine of formula I is present in an amount effective to increase the pesticidal activity of the endothall or salt thereof.

2. The pesticidal composition of claim 1, wherein $(x+y)$ is between 3 and 10; R_1 is an alkyl group having 10 to 20 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 5.0 to 12.

3. The pesticidal composition of claim 1, wherein $(x+y)$ is greater than 3 but less than or equal to 8; R_1 is an alkyl group having 12 to 18 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 6.0 to 11.

4. The pesticidal composition of claim 1, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

5. The pesticidal composition of claim 2, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

6. The pesticidal composition of claim 3, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

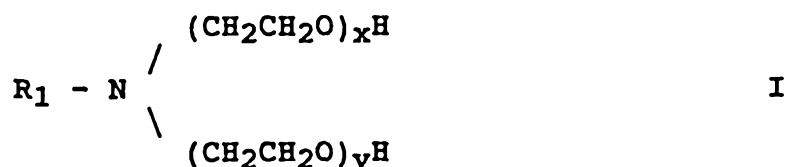
7. The pesticidal composition of claim 1, wherein the composition further comprises water.

8. The pesticidal composition of claim 1, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

9. The pesticidal composition of claim 2, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

10. The pesticidal composition of claim 3, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

11. A method of increasing the pesticidal effectiveness of endothall or a salt thereof which comprises applying to chlorophyll-containing algae or plants endothall or a salt thereof and an amount of an ethoxylated amine of formula I effective to increase the pesticidal activity of the endothall or salt thereof, wherein the ethoxylated amine of formula I has the following structure:



in which R_1 is an alkyl group having 8 to 22 carbon atoms, and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15.

12. The method of claim 11, wherein $(x+y)$ is between 3 and 10; R_1 is an alkyl group having 10 to 20 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 5.0 to 12.

13. The method of claim 11, wherein $(x+y)$ is greater than 3 but less than or equal to 8; R_1 is an alkyl group having 12 to 18 carbon atoms derived from tallow, or from soybean, coconut, or cottonseed oil; and the HLB value of the compound of formula I is 6.0 to 11.

14. The method of claim 7, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine)

salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

15. The method of claim 8, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

16. The method of claim 9, wherein the endothall or salt thereof is selected from mono(N,N-dimethylalkylamine) salts of endothall or mixed mono and di(N,N-dimethylalkylamine) salts of endothall.

17. The method of claim 7, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

18. The method of claim 8, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

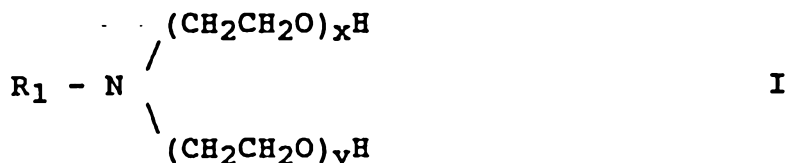
19. The method of claim 9, wherein the weight ratio of endothall:ethoxylated amine of formula I is 1:9 to 1:12.

20. The method of claim 11, wherein said ethoxylated amine of formula I and endothall or a salt thereof are simultaneously applied to said algae or plants.

21. The method of claim 11, wherein said ethoxylated amine of formula I and endothall or a salt thereof are applied in the form of an aqueous composition which contains both the ethoxylated amine and the endothall or salt thereof.

22. A concentrated pesticidal formulation comprising:

- (a) endothall or a salt thereof;
- (b) a solvent; and
- (c) at least one ethoxylated amine of formula I:



in which R_1 is an alkyl group having 8 to 22 carbon atoms, and is saturated or unsaturated; and the poly(oxyethylene) content $(x+y)$ is greater than 3 but less than or equal to 15; component (a) is present in an amount to be pesticidally effective upon dilution; component (b) is present in an amount effective to increase the solubility of component (c)

in the concentrated formulation; and component (c) is present in an amount effective to increase the pesticidal activity of component (a) upon dilution.

23. The concentrated pesticidal formulation of claim 22, wherein the amount of component (b) present also increases the solubility of component (c) in a diluted formulation upon dilution of the concentrated pesticidal formulation with water.

24. The concentrated pesticidal formulation of claim 22, wherein the formulation further comprises up to about 14.1% water.

25. The concentrated pesticidal formulation of claim 15, wherein the solvent is a substituted or unsubstituted C₁-C₆ alcohol or a substituted or unsubstituted C₂-C₆ glycol.

26. The concentrated pesticidal formulation of claim 25, wherein the solvent is ethanol, propanol, butylene glycol, propylene glycol, dipropylene glycol, or hexylene glycol.

27. The concentrated pesticidal formulation of claim 26, wherein the solvent is propylene glycol.

DATED this 23rd day of July 1999.

BUCKMAN LABORATORIES INTERNATIONAL, INC.

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