

PATENT SPECIFICATION

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(54) SELECTIVE HERBICIDES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns selective herbicides.

1 - Methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4 - (1H, 3H)-dione and its use as a broad spectrum herbicide are disclosed in our British Patent Specification No. 1,435,585.

The present invention results from the discovery that this compound exhibits a surprising selective herbicide activity. That is, although this compound is known to be a potent broad-spectrum industrial herbicide, it has unexpectedly been found that this compound, when applied under the proper conditions, will effectively control many broadleaved and grassy weeds in various crops including sugarcane, evergreen seedlings, coffee, tea, oil palm and rubber crops with safety to the crop.

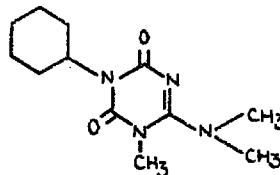
In addition, 3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea and its herbicidal use are disclosed and claimed in U.S. Patent No. 2,655,445, granted October 13, 1953 to Charles W. Todd.

Another aspect of the present invention results from the discovery that, especially for use in the selective control of broadleaved and grassy weeds in sugarcane, 1-methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione can be advantageously combined with other known herbicides, in particular with diuron [3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea].

It has been explained above that although 1 - methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione is known to be a potent broad-spectrum industrial herbicide, it was unexpectedly found that this compound, when applied under proper conditions, will effectively control many broadleaved and grassy weeds in sugarcane crops with safety to the crops.

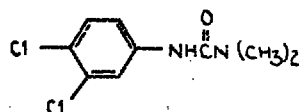
It has also been unexpectedly found that the sugarcane, rubber and oil palm crops will tolerate higher levels of 1 - methyl - 3 - cyclohexyl - 6 - dimethyl - s - triazine - 2,4(1H, 3H) - dione without significant injury when this compound is applied to the sugarcane plants in admixture with appropriate amounts of diuron, i.e., the diuron exerts a definite and significant safening effect on the 1 - methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione with respect to sugarcane crop injury.

This invention therefore relates to the use of 1 - methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione



(I)

alone or in combination with 3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea



(II)

as a selective herbicide, especially in sugarcane, evergreen seedlings, coffee, tea, oil palm and rubber crops, and compositions containing such a combination, including tank mixes and preblends, of active ingredients.

One aspect of our invention is a herbicidal composition comprising in admixture 1 - methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4 - (1H, 3H) - dione and 3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea, wherein the weight ratio of said triazinedione to said urea is from 1:1 to 1:8, and a surface active agent and/or a solid or liquid diluent.

Another aspect of our invention is a method for preventing or controlling undesired vegetation in crops without causing significant injury to said crop comprising applying to the locus of said crop an effective amount of the composition defined above.

Our invention also extends to a method of increasing the crop safety especially with respect to sugarcane plants, rubber plants, and oil palm plants of the herbicide 1 - methyl - 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione comprising admixing with said triazinedione herbicide an amount of 3 - (3,4 - dichlorophenyl) - 1,1 - dimethylurea such that the weight ratio of said triazinedione to said urea is from 1:1 to 1:8.

In yet another aspect our invention provides a method for preventing or controlling undesired vegetation in crops without causing significant injury to said crop comprising applying to the locus of said crop an amount of 1 - methyl 3 - cyclohexyl - 6 - dimethylamino - s - triazine - 2,4(1H, 3H) - dione effective to prevent or control said undesired vegetation without significantly injuring said crop.

The compound of formula I and said combination compositions can be applied either preemergence or post-emergence to effectively control a variety of broadleaved and grassy weeds especially in the above-mentioned crops with safety to the crop, e.g. application can be made preemergence to plant and stubble cane or as a directed post-emergence application after top growth is well started. In fact, most surprisingly the above-mentioned combination compositions can be applied to sugarcane crops with greater safety to the crops than can be achieved by application of compound I alone.

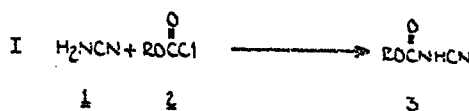
DESCRIPTION OF THE INVENTION.

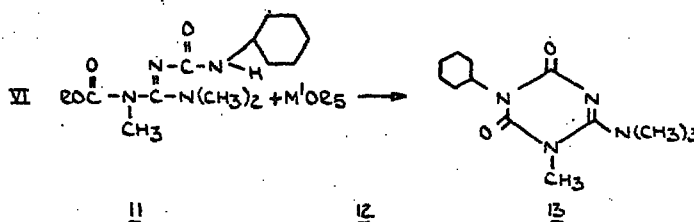
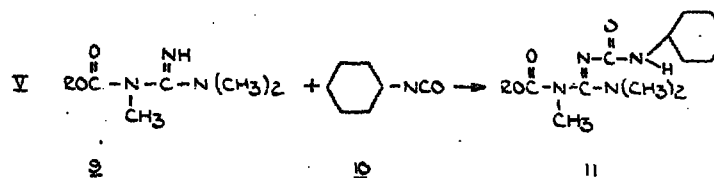
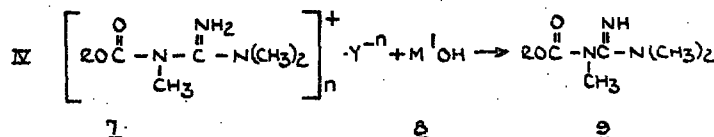
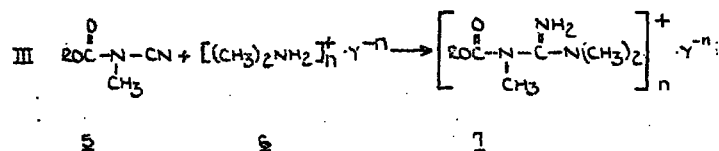
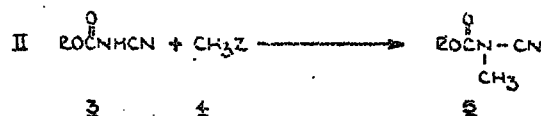
Synthesis of the compound.

The compound of formula I can be made by the process described and exemplified in our Specification No. 1,435,585 and in our U.S. Patent No. 3,983,116, and by the process described and exemplified in U.S. Patent No. 3,850,924.

In addition, the following preferred process can be used to prepare the compound of formula I:

Equation I represents preparation of the starting material as described in U.S. Patent No. 3,657,443.



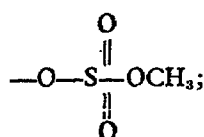


wherein

R is ethyl, *n*-propyl, or isopropyl;

Y is Cl⁻ or SO₄⁼; *n*=1 when Y is Cl⁻ and *n*=2 when Y is SO₄⁼;

Z is iodide, bromide or



M' is alkali metal; and

R₃ is hydrogen or alkyl of 1—4 carbon atoms.

Step I and II are performed sequentially in water. Compound 5 is isolated by separating it from the aqueous brine formed in these reactions.

After the reaction of step III is completed, compound 7 and any unreacted compound 6 must be converted to the free base forms with an alkali metal hydroxide. The untreated amine, (CH₃)₂NH, must be removed so that it will not be present in step V.

In the following detailed description, all temperatures are in degrees centigrade and all percentages are by weight unless otherwise stated.

An aqueous solution of the sodium salt of compound 3 containing from 15—35% of compound 3, preferably 20—30%, is reacted at 10—70°, preferably 40—45°, with 0.9—2.0, preferably 1.45—1.55 molecular equivalents of an alkylating agent 4 (for example, dimethyl sulfate) during a period of 1—16 hours, preferably 2—4 hours (equation II). Methyl iodide or bromide can be used instead of dimethyl sulfate; the sulfate is preferred for economic reasons.

As the reaction proceeds, a second phase of compound 5 forms. After the reaction has proceeded for the desired time, the upper layer is separated and the lower,

aqueous, layer can be discarded, or if economic conditions justify, this layer can be extracted with an organic solvent, preferably toluene, or distilled to recover the small amount of compound 5 contained therein.

The upper layer is added to an aqueous solution containing 15—75% of the amine hydrochloride or 15—45% of the amine sulfate, compound 6, preferably 25—50% of the hydrochloride (equation III). The mole ratio of amine salt to compound 5 can be from 0.8—3, preferably 1.0—1.35. The mixture is then agitated for 0.5—6 hours at 50—100°, preferably 85—95° (equation III). Higher temperatures require shorter reaction time and vice versa. It is important to control the pH between 5.8 and 8.0 during reaction III. If the pH is too low, the reaction will be very slow; if the pH is too high, the product 7 will decompose. This control is most conveniently maintained by using electrodes to monitor the pH and adding base, for example, sodium hydroxide, potassium hydroxide, or calcium hydroxide as needed. Sodium hydroxide is preferred.

It should be realized that in these highly concentrated solutions, pH readings may be only coincidentally related to the hydrogen ion concentration. However, when the meters and electrodes are calibrated against a standard buffer before use, the pH response of the electrodes in the reaction mass indicates the state of the reaction.

The resulting reaction mass contains compound 7 and by-product tri-substituted guanidine as well as unreacted compound 6, all present as salts. Before proceeding with step V it is necessary to convert compound 7 into its free base, compound 9. This also converts unreacted compound 6 into free amine, $(\text{CH}_3)_2\text{NH}$ which is removed to prevent the formation of by-product ureas. This operation can be effected by adding 10—50% aqueous sodium hydroxide until the pH is 11.0 to 12.5 as determined by a glass electrode meter combination and extracting with an organic solvent. Distillation of a portion of the organic solvent used for extraction removes the more volatile amine, $(\text{CH}_3)_2\text{NH}$. The amine can also be removed directly from the aqueous alkaline solution by distillation. The former procedure is preferred.

The extraction procedure can be performed by passing the aqueous alkaline solution through a continuous counter-current extractor where the organic phase is a solvent such as methylene chloride, benzene, chlorobenzene, toluene, or xylene; toluene is preferred. A batchwise extraction can also be performed. Temperature can vary between 9° C. and 65° C. The amount of solvent can vary from 0.5 to 10 parts per part aqueous phase, depending on economic factors. The exit organic solvent is sent to a still where amine, $(\text{CH}_3)_2\text{NH}$, and any entrained water are distilled overhead, leaving a residual solution of compound 9. The concentration of compound 9 will, of course, depend on the operating parameters of the extractor and still.

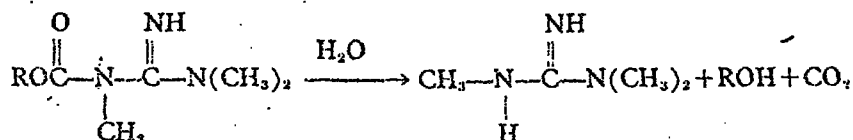
The residual solution of compound 9 is analyzed by gas chromatography for tri-substituted guanidine and for compound 9. If any guanidine is present, a stoichiometric amount of 5—10% aqueous sulfuric or hydrochloric acid, preferably sulfuric, is added to form the salt of the guanidine.

Isocyanate 10 is now added. The amount added can vary from 0.8 to 1.0 moles of compound 10 per mole of compound 9; 0.90—0.98 is preferred. The resulting reaction mass is stirred at 10—90° C., preferably 50—75° C., until the reaction is complete. Reaction time can be from 0.5 to 8 hours.

If less than a stoichiometric amount of compound 10 has been added, the pH is adjusted to 5.5 by adding 5—10% sulfuric or hydrochloric acid, sulfuric is preferred. If acid has been added, the mixture is allowed to settle, and the layers are separated. The lower, aqueous, layer is recycled to the extraction step, and the upper layer is dried by distilling until a constant head temperature is attained either under vacuum or at atmospheric pressure; absolute pressure of 100 to 400 mm Hg is preferred.

If acid is not used, the reaction mass does not have to be distilled. The product 11 can be isolated by concentration and/or cooling of the solution until crystallization occurs followed by filtration or centrifugation. However, it is usually more convenient to carry it forward as a solution to the next step (equation VI).

Compound 9 is subject to decomposition in aqueous solution, particularly under conditions of high temperature and pH. Under such conditions it tends to decompose into the corresponding tri-substituted guanidine as illustrated in the following equation:



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The rate of decomposition is directly proportional to the pH and temperature. Therefore, when removing amine, $(\text{CH}_3)_2\text{NH}$, by direct distillation from water, it is preferred to use a vacuum or inert gas to perform the operation as rapidly as possible.

The above-mentioned aqueous distillation procedure can be operated batch-wise or continuously. It is preferred to carry out the operation in a continuous manner so that the exposure of compound 9 to high temperature and high pH is reduced to a minimum. This is accomplished by adding aqueous alkali metal hydroxide to the product from step III in a pipeline reactor or by running the product and an alkali metal hydroxide into a small agitation vessel with a short hold-up time, no more than 10, preferably no more than 2 minutes. The separate flow rates are adjusted so that the resulting pH is between 11.0 and 13.0. If the concentration of amine salt used is such that alkali metal salt precipitates during this neutralization, additional water should be added to maintain this salt in solution. The overflow from this vessel is fed through a distillation column operated under vacuum. The column is heated by feeding steam into the bottom. Amine, $(\text{CH}_3)_2\text{NH}$, and water are taken off as distillate overhead and an aqueous solution of compound 9 and tri-substituted guanidine as bottoms.

The conditions under which the column can be operated are selected so that the temperature of the feed through the column is not over 50°C . This necessitates cooling the product from equation III to approximately 30°C before adding the caustic. The column is operated at an absolute pressure of 25—300 mm of mercury, preferably 50—150 mm, and the amount of steam fed to the bottom of the column is adjusted such that the amount of water taken overhead along with the amine is equivalent to 5—25% of the weight of the reaction mass from equation IV.

The bottoms from the above distillation are fed into a hold tank which is maintained at a pH of 5—7 by the continuous addition of either sulfuric or hydrochloric acid; hydrochloric is preferred. The concentration of compound 9 in the neutralized solution is maintained at 15—50%, preferably 20—40%. The concentration will depend upon the concentration of the aqueous solution of the amine, the concentration of the base and acid solutions employed in the previous steps, and the amount of concentration or dilution which occurred during the distillation. The temperature of this solution is maintained at 25 — 45° , preferably 25 — 35° , by either cooling the bottoms in a continuous-type cooler before neutralization or by cooling the neutralization vessel itself.

When the amine has been removed by direct distillation from water, step V is performed by preparing a mixture of the above solution and a solvent such as benzene, chlorobenzene, toluene, or xylene; toluene is preferred. The amount of solvent added should be sufficient to dissolve the amount of compound 11 which will be formed. Generally, the amount of solvent used is about 7—10 times the amount of compound 11 present in the aqueous solution.

An amount of compound 10 which is stoichiometrically equivalent to 85—100%, preferably 90—98%, of compound 9 present in the aqueous layer is now added in one portion or continuously for up to three hours, preferably 30 minutes to one hour and 50% aqueous caustic is added simultaneously with good agitation at a rate which will maintain the pH at 9—10, preferably 9.3—9.7. The caustic addition is continued until the pH is almost constant. The temperature is maintained at 10 — 90°C ., preferably 35 — 50°C ., during the addition by external heating and cooling as required. The caustic addition time is from 1—8 hours. The pH is then adjusted to 6.0 with acid. The agitation is stopped and the layers allowed to separate. The lower aqueous layer is removed and the upper organic layer is dried by distilling until a constant head temperature is attained either under vacuum or at atmospheric pressure; absolute pressure of 100—400 mm Hg is preferred.

The solution or slurry containing compound 11 is cooled if necessary to 25 — 55°C while anhydrous free dimethylamine is added. It is preferred to add the amine at 25 — 55°C , but higher or lower temperatures can be used depending on the solubility of the amine in the particular solvent. It is important to have at least 0.5, and preferably 1.0—8.0, moles of amine per mole of compound 11.

Next the ring closure catalyst (compound 12) is added (equation VI). The catalyst is an alkali metal alkoxide or hydroxide. Alkali metal alkoxides can be added either as dry solid or as a solution in the alcohol. Alkali metal hydroxides can be added as a solution in an alcohol. Dry sodium methoxide or a solution of sodium methoxide in methanol is a preferred catalyst. The amount of catalyst needed is from 0.1 to 5.0 mole percent of compound 11. Higher concentrations are not desirable because side reactions begin to intervene. A preferred concentration of compound 12 is from 2.0 to 4.0 mole percent of compound 11. The temperature is not critical

and the ring closure reaction can proceed at temperatures from 0° to 120° provided that the amine is kept within the reaction system. The reaction is normally exothermic and the solution may be cooled if a lower temperature is required to retain the amine. It is critical that the amine remain present until ring closure is about complete.

After the catalyst is added, the reaction mass is held for 15 seconds to 2 hours to insure completion of the ring closure. The reaction is rapid and normally is about complete in less than 15 minutes. The more completely anhydrous the reaction mass, the more rapid is the reaction. An amount of acid equivalent in moles to the amount of the catalyst is added to the reaction mass after ring-closure is complete. This acid neutralizes the catalyst and/or reaction by-products which catalyze product decomposition during the isolation step. Preferably, the acid is added as soon as possible after ring-closure is complete. The type of acid, either organic or inorganic, is not critical; but organic acids are preferred, particularly acetic acid. The added amine, by-product alkanols, and part of the solvent are then removed by distillation either at atmospheric or reduced pressure.

Alternatively, the ring-closure reaction can be performed in a continuous manner. In this embodiment the catalyst is mixed with the reaction mass containing compound 11 and the amine in a pipeline reactor. The acid is added downstream after the temperature rise is complete. The amine, by-product alcohols and part of the solvent are then removed by distillation.

The residue is washed at 30—100° C., preferably 50—70° C., with 5% aqueous alkali metal hydroxide, preferably sodium hydroxide, in an amount equal to or slightly greater than (up to 20% molar excess) the amount of catalyst. The layers are allowed to settle, the aqueous layer is removed, and the organic layer is washed with water in an amount approximately equivalent in volume to the caustic wash. Again the layers are allowed to settle, the aqueous layer is removed, and the pH of the wet organic layer is adjusted to 6—7 with acid. (The pH is measured using a glass-calomel combination electrode). Organic acids are preferred for this operation; acetic acid is especially preferred. This washing procedure removes by-products formed during the ring-closure reaction. If a less pure product is satisfactory, the washing steps can be eliminated.

The product can be isolated from the organic solvent either after the washing operation or without washing, through concentration of the organic phase by distillation. The concentrate is then diluted with a poor solvent for compound 13, e.g., hexane, which caused compound 13 to precipitate. The stable crystalline product is recovered by conventional methods.

In the following examples, all parts are by weight and all temperatures in degrees centigrade unless otherwise indicated.

Example 1.

A. Synthesis N-ethoxycarbonyl-N-methylcyanamide (Equations I and II)

657 Parts of ethyl chloroformate and 945 parts of a 50% aqueous sodium hydroxide solution were added simultaneously to a solution of 504 parts of a 50% aqueous cyanamide solution in 825 parts of water at 25° during a period of 90 minutes and at a pH of 6.9 to 7.1. As the addition of the reactants progressed, the temperature of the reaction mass was allowed to rise to 53—55° and was maintained within that range by cooling. When the addition was complete, the reaction mass was cooled to 40°. Dimethylsulfate (1,134 parts) was then added during one hour with stirring while maintaining the pH at 7 to 7.1 by the addition of 50% aqueous sodium hydroxide solution. After holding 3 hours at 40° the resulting two-phase solution was transferred to a separatory funnel. The upper phase of N-ethoxycarbonyl-N-methylcyanamide was separated and the lower aqueous phase was sent to secondary recovery, either distillation or extraction. The upper phase of 669 parts was 93% N-ethoxycarbonyl-N-methylcyanamide (81% yield). This upper phase is usually pure enough for subsequent steps. However, vacuum distillation was used to provide pure N-ethoxycarbonyl-N-methylcyanamide, b.p. 67° at 2.2 mm.Hg.

B. Synthesis of N-ethoxycarbonyl-N,N',N'-trimethylguanidine (Equations III and IV)

A solution of 339 parts of dimethylamine hydrochloride in 500 parts of water was heated to 50° and 458 parts of the upper phase from (A) was added to it. The resulting two-phase mixture was then heated for approximately 2.25 hours at 90° and pH of 6.5, after which time the starting N-ethoxycarbonyl-N-methylcyanamide had nearly completely disappeared. The pH was kept at 6.5 by adding 50% sodium hydroxide as required. The solution was then cooled to 40° and 25% aqueous sodium

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6	7	1,546,228	7
ded mic ne		hydroxide solution was added to reach pH 11.5. Repeated extraction of the reaction solution with toluene and partial evaporation of the toluene gave a solution containing 489 parts of crude N-ethoxycarbonyl-N,N',N'-trimethylguanidine from which the pure product was isolated by distillation at 70°/0.3 mm.Hg.	
to	5	C. Synthesis of Ethyl N-(N'-cyclohexylcarbamoyl-N,N-dimethylamidino)-N-methylcarbamate (Equation V)	5
out the of cid m- ter al; ect as-	10	11 Parts of cyclohexyl isocyanate was added to 16 parts of N-ethoxycarbonyl-N,N',N'-trimethylguanidine in 150 parts of toluene. The temperature was kept at 50 to 75° for 1.25 hours to complete reaction. The product, ethyl-N-(N-cyclohexylcarbamoyl-N,N'-dimethylamidino)-N-methylcarbamate was isolated by crystallization, filtration, and drying, m.p. 97—98°. Preferably, however it is kept as a toluene solution carried forward as such to the next step (Equation VI).	10
er. nd nt	15	D. Synthesis of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H) dione (Equations II, III, IV, VI)	
us ly ed in rs ic n- is he an	20	A 50% stoichiometric excess of dimethylsulfate (1234 parts) was added at 40° during one hour with agitation to 3141 parts of an aqueous solution containing 888 parts of the sodium salt of compound 3 (R=ethyl) which had been adjusted to pH 7 with 50% aqueous sodium hydroxide. The reaction was allowed to continue for three hours while the temperature was maintained at 40° by external heating or cooling and at pH 7 by the addition of 50% aqueous sodium hydroxide as required. During the reaction a separate phase of compound 5 (R=ethyl) was formed.	15
eg a- 3, ct	25	When the reaction was about complete, the agitation was stopped and the layers allowed to separate. The upper layer of 728 parts was 93% pure compound 5 (R=ethyl). It was separated and added to 1,200 parts of an aqueous solution containing 540 parts of dimethylammonium chloride. The resulting mixture was heated to 90° and stirred for 2.25 hours at pH 6.5. The pH was maintained at 6.5 by adding 50% sodium hydroxide as required. The solution was then fed into a mixing tee along with 25% aqueous sodium hydroxide. The separate feed rates were adjusted so that the effluent from the tee was kept at pH 11.0—11.5. The effluent from this vessel was fed into the top of a continuous counter-current extractor, which operates as a 5 theoretical plate column. Toluene was fed into the bottom of the column at a rate of 2.25 pounds of toluene per pound of aqueous feed. The toluene solution at the top of the column overflows into an amine stripper.	20
es	30	In the stripper, excess dimethylamine, entrained water, and some toluene solvent are distilled overhead through a packed column. The residual toluene solution of 7743 parts contained 777 parts of compound 9 (R=ethyl). Analysis showed by-product 1,1,3-trimethylguanidine to be present in this residue, and a small amount of sulfuric acid solution was added to exactly neutralized all the 1,1,3-trimethylguanidine but little or none of compound 9.	25
	35	507 Parts of cyclohexylisocyanate was added to this residue. The mixture was then stirred at 50—75° for 1.25 hours. It was cooled to 40° and sulfuric acid solution was added with good stirring until the pH of the aqueous phase was 5.5. The organic phase was separated and dried by brief azeotropic distillation at a pressure of 100 mm mercury. The organic phase of 8,200 parts contained 1,205 parts of compound 11 (R=ethyl).	30
	40	Dimethylamine (1,095 parts) was added to the solution of compound 11 while the temperature was maintained at 25—50° by external cooling. Then 35 parts of a 25% solution of sodium methoxide in methanol was added with good agitation. The reaction is slightly exothermic and the temperature increased 4° during 15—45 seconds. The reaction was allowed to continue for an additional two minutes; then 9.72 parts of acetic acid were added. The solution was then distilled until a constant 110° head temperature showed that dimethylamine and by-product alkanols have been completely removed. The still bottoms were cooled to 60° and washed with a small quantity of 5% sodium hydroxide followed by a small quantity of water. The amount of sodium hydroxide was calculated so that it was equivalent in moles to the acetic acid added earlier.	35
	45	The toluene phase was then concentrated by distillation until the concentration of compound 13 reached 50% by weight. The residue was cooled to 40° and stirred while n-hexane was added slowly.	40
	50	The weight of n-hexane used was 80% of the total weight of the 50% solution. During the n-hexane addition the solution was seeded with compound 13. The crystals were recovered by filtration and dried to give 920 parts of compound 13 m.p. 112—115° C.	45
	55		50
	60		55
			60

Formulation and use of the compound.

The compound of formula I and compositions comprising a combination of the compound of formula I and the compound of formula II are useful for control of undesired vegetation especially in sugarcane fields, in stands of evergreen seedlings, and in stands of certain woody perennial crops such as coffee, tea, oil palm and rubber; i.e. the compound of formula I and the above-mentioned combination of compositions can be used to control a variety of broadleaved and grassy weeds and even weed trees in the above-mentioned crops with safety to said crops.

The precise amount of compound to be used in any given situation will vary according to the time of treatment, the weed species and soil type involved, the formulation used, the mode of application, prevailing weather conditions, particularly rainfall, foliage density and like factors. In addition, the particular crop species and age of planting should be taken into consideration.

Certain varieties of sugarcane, such as the Queensland varieties and most other shallow rooted varieties, for example 48—103 (Louisiana), 50—28 (Texas), 53—263 (Hawaii) and P.R. 1048 (Puerto Rico), are known to be susceptible to weed killers and may be injured at relatively low rates. Tolerance of such susceptible varieties to the compound of formula I under the particular field conditions in use should be determined by routine experimentation before adoption as field practice to prevent possible crop injury. Similar considerations will apply to the other crops mentioned.

In any event, use rates necessary to provide effective control, even with respect to many weed species that are resistant to other herbicides, are quite low. Since so many variables play a role, it is not possible to state the rate of application suitable for all situation. However, broadly speaking, the compound of formula I is used at levels of e.g. 0.25 kg/ha to 4 kg/ha. The lower rate given here will provide only a brief effect on weeds under many use conditions. The higher rate, on the other hand, will be excessive and can cause crop injury except where soils have a high colloidal content, where the more resistant crop varieties are grown, or where the crop plants are well established (e.g. "stubble" or "ratoon" cane). The most preferred rate is in the range of 0.5 to 1 kg/ha. With respect to coffee, tea, oil palm and rubber crops, the preferred use rate is in the range of 0.5 to 2 kg/ha. With respect to evergreen seedlings the compound of formula I can be used at levels of e.g. 0.5 to 12 kg/ha, with a more preferred rate in the range of 1—10 kg/ha, and the most preferred rate in the range of 2 to 8 kg/ha.

With respect to the combination compositions mentioned above, the compound of formula I will be combined with the compound of formula II in ratios (by weight of active component) of from 1:1 to 1:8, preferably 1:1 to 1:4.

With respect to sugarcane, the application may be made preemergence to the plant and stubble cane or as a directed postemergence spray after top growth is well started. Applications may be broadcast (i.e., cover the entire surface of the field) or limited to only a portion such as a band over the row. In all instances, the treatment should be applied uniformly.

With respect to evergreen seedlings, the application may be made preemergence to post emergence to the weed plants to be controlled. Preemergence applications are most effective when made within a few weeks prior to expected germination of the weed species. Postemergence applications are preferably made during the period of active growth of the weed species. The applications may be made prior to the planting of the desirable tree species or to land on which they are already present. In the latter case, treatment is best applied either before or well after the period of most active growth of the crop trees. Successful applications may be made during the active growing season, however, if care is taken to avoid foliage. In all instances, the treatment should be applied uniformly.

With respect to coffee, tea, oil palm and rubber crops, the application may be made preemergence or postemergence, for example as a spray at a rate of from 500 to 2000 liters per hectare, to the weed plants to be controlled. Preemergence applications are most effective when made within a few weeks prior to expected germination of the weed species. Postemergence applications are preferably made during the period of active growth of the weed species. The applications may be made prior to the planting of the desirable crop species or to land on which they are already present. In the latter case, treatment is best applied either before or well after the period of most active growth of the crop trees. Successful applications may be made during the active growing season, however, if care is taken to avoid the foliage. In all instances, the treatment should be applied uniformly.

Proper application of this compound results in good control of many serious and troublesome weeds that may occur in sugarcane fields. Some of the many different

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weed species controlled are wild turnip (*Brassica campestris*), johnsongrass seedlings (*Sorghum halepense*), common ragweed (*Ambrosia artemisiifolia*), common crabgrass (*Digitaria sanguinalis*), foxtail (*Setaria sp.*), pigweed (*Amaranthus sp.*), Florida beggarweed (*Desmodium tortuosum*), cocklebur (*Xanthium pennsylvanicum*), morning-glory (*Ipomoea scp.*), carpetweed (*Mollugo verticillata*), smartweed (*Polygonum sp.*), goosegrass (*Eleusine indica*), curly dock (*Rumex crispus*), burning nettle (*Urtica urens*), common yarrow (*Achillea millefolium*), chicory (*Cichorium intybus*), guinea-grass (*Panicum maximum*), torpedograss (*Pancium repens*), purslane (*Portulaca oleracea*), barnyardgrass (*Echinochloa crusgalli*), dallisgrass (*Paspalum dilatatum*), vaseygrass (*Paspalum urvillei*), catsear (*Hypochaeris sp.*), chickweed (*Stellaria media*), goldenrod (*Solidago sp.*), darnel (*Lolium temulentum*), smooth crabgrass (*Digitaria ichaemum*), coffee senna (*Cassia occidentalis*), lambsquarters (*Chenopodium album*), henbit (*Lamium amplexicaule*), crowfoot (*Ranunculus sp.*), wild euphorbia (*Euphorbia sp.*), *Ageratum conyzoides*, *Digitaria ciliaris*, *Synedrella vialis*, *Richardia brasiliensis*, *Dactyloctenium aegyptium*, *Eragrostis tenella*, fescue (*Festuca spp.*), panic grass (*Panicum spp.*), orchard grass (*Dactylis glomerate*), vaseygrass (*Paspalum urvillei*), quackgrass (*Agropyron repens*), broomsedge (*Andropogon virginicus*), sweet vernal grass (*Anthoxanthum odoratum*), bluegrass (*Poa spp.*), Bermudagrass (*Cynodon dactylon*), brackfern (*Pteris aquilina*), wild carrot (*Daucus carota*), horseweed (*Erigeron canadensis*), campion (*Silene stellata*), Canada thistle (*Cirsium arvense*), ragwort (*Senecio spp.*), broom (*Cytisus spp.*), honeysuckle (*Lonicera japonica*), brambles (*Rubus spp.*), wild grape (*Vitis spp.*), groundsel tree (*Baccharis halimifolia*), toetoe (*Cortaderia spp.*), persimmon (*Diospyros virginiana*), red maple (*Acer rubrum*), red gum (*Liquidambar styraciflua*), eucalyptus (*Eucalyptus regnans*), post oak (*Quercus stellata*), blackjack oak (*Quercus marilandica*), hackberry (*Celtis occidentalis*), and sassafras (*Sassafras varifolium*), and nutsedge (*Cyperus sp.*). Of particular interest is the high activity of the compound of this invention on actively growing nutsedge.

Among the valuable tree species that benefit from the method of this invention are: oil palm (*Palms spp.*), rubber (*Castilla elastica*), coffee (*Coffea arabica*) and tea (*Thea sinensis*), loblolly pine (*Pinus taeda*), longleaf pine (*Pinus palustris*), slash pine (*Pinus caribaea*), shortleaf pine (*Pinus echinata*), ponderosa pine (*Pinus ponderosa*), Austrian pine (*Pinus nigra*), Monterey pine (*Pinus radiata*), Douglas fir (*Pseudotsuga taxifolia*) and western hemlock (*Tsuga heterophylla*).

The compound of formula I can be used for weed control in the above-mentioned crops, either alone or in combination with other selective herbicides. An important function of the added herbicide is to prolong the period of weed control obtained. Compounds particularly effective for this purpose are diuron [3-(3,4-dichlorophenyl)-1,1-dimethylurea], linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methyl-urea], bromacil [3-(*sec*-butyl)-5-bromo-6-methyluracil], terbacil [3-*tert*-butyl-5-chloro-6-methyluracil], and metribuzin [4-amino-6-*tert*-butyl-3-methylthio-1,2,4-triazine-5-one]. The optimum ratio between the compound of formula I and the additional herbicide can be readily determined by a person of ordinary skill in the art of weed control.

In addition, in the case of combinations of the compound of formula I with diuron, not only is the period of weed control extended, but also the diuron exerts a definite and significant safening effect on the compound of formula I with respect to its phytotoxicity on the crop plants, in particular on the sugarcane plants and the rubber plants, thereby enabling said plants to tolerate higher levels without significant injury. Naturally, higher levels of the compound of formula I permit better control of resistant weed species.

Combinations of diuron and the compound of formula I may be effectively used in ratios of from 1:1 to 8:1 (by weight), preferably 1:1 to 4:1 (by weight). The safening effect of diuron on the compound of formula I has been demonstrated in a number of field tests.

The compound of formula I and combinations of the compounds of formulas I and II can be formulated in the various ways which are conventional for herbicides of similar physical properties. Useful formulations include wettable and soluble powders, suspensions and solutions in solvents and oils, aqueous dispersions, dusts, granules pellets, and high-strength compositions. Broadly speaking, these formulations comprise e.g. about 1—99% by weight of herbicidally active material and at least one of

- (a) about 0.2—20% by weight of surface active agent, and
- (b) about 5—99% by weight of solid or liquid diluent.

More specifically, the various types of formulations will generally contain these ingredients in the following approximate proportions:

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PERCENT BY WEIGHT

		Herbicide	Diluent	Surfactant	
	Wettable				
	Powders	25—90	0—74	1—10	
5	Suspensions or				5
	Solutions	5—50	40—95	0—10	
	Aqueous				
	Dispersions	10—50	40—89	1—10	
	Dusts	1—25	70—99	0—5	
10	Granules and				10
	Pellets	1—35	65—99	0—15	
	High-Strength				
	Compositions	90—99	0—10	0—2	

15 The manner of making and using such herbicidal formulations is described in numerous patents. See, for example, USP 3,309,192; USP 3,235,357; USP 2,655,445; USP 2,863,752; USP 3,079,244, USP 2,891,855; and USP 2,642,354. 15

20 Compounds of formula I and II formulated in a 1:8 ratio (by weight) as wettable powders yield a good product within the range given above. If the ratio is increased to 1:4 or 1:2, deterioration in the physical properties of the mixture may occur at the highest concentration of active, and may make it desirable to reduce the total active content of the combination to less than the highest percentage given. This deterioration of physical properties is typical of the interaction between the compounds at the high ratios. By blending additional or different diluents and reducing the total active content, one skilled in the art will be able to formulate these combinations satisfactorily. The optimum percentage of each component in a specific formulation can be determined by testing the formulation using standard quality control procedures. 25

30 For example, compounds of formula I and II are formulated separately, mixed in a 1:8 ratio, blended and packaged. Similarly, compounds of formula I and II are formulated separately, mixed in a 1:4 or 1:2 ratio along with additional diluents, thoroughly blended and packaged. In the compositions described hereinafter percentages are by weight. 30

Example II.

Solution

35	1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione	25.5%	35
	ethylene glycol monobutylether	53.2%	
	ethanol	8.1%	
	water	13.2%	

40 The ingredients were combined, warmed and stirred to produce a solution which was subsequently extended with water for spraying. 40

Example III.

Wettable Powder

45	1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione	25%	45
	diatomaceous earth	71.5%	
	diocetyl sodium sulfosuccinate	1.5%	
	low viscosity methyl cellulose	2%	

The ingredients can then be thoroughly blended and passed through a hammer mill to produce particles mostly all below 100 microns.

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Example IV.

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1.5% Granule

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione	1.5%
Athapulgi clay granules	98.5%

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The active ingredient was dissolved in an ethanol-water mixture and sprayed onto a bed of the clay granules rotating in a mixer. The granules were removed and dried in a vacuum oven prior to packaging.

Example V.

5	Water soluble Powder		5
	1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione	94%	
	Zeolex 7A	3.8%	
	sugar	1.0%	
10	Methocel F-50	1.0%	10
	aerosol OT-B	.2%	

"Zeolex" is a registered Trade Mark for ultra fine precipitated hydrated sodium silica-aluminates (microlitic zeolites) available from J. M. Huber Corporation, New York, U.S.A. "Methocel" is a registered Trade Mark of Dow Chemical Co., Michigan, U.S.A. for cellulose esters. Aerosol OT-B is the diocetyl ester of sodium sulfosuccinic acid in powder form, available from American Cyanamid Co., New York, U.S.A.

The ingredients were thoroughly blended and passed through a hammer mill to produce particles mostly below 100 microns.

Example VI.

20	Diuron wettable powder	58.50% by weight	20
	1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione, water soluble powder	14.60% by weight	
	Borden Clay	13.45% by weight	
25	Hi Sil 233	13.45% by weight	25

"Hi Sil" is a registered Trade Mark for precipitated fine particle silica available from PPG Industries Inc., Pennsylvania, U.S.A. The materials are mixed, blended, and then packaged.

Example VII.

30	Diuron wettable powder	48% by weight	30
	1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione, water soluble powder	24% by weight	
	Borden Clay	14% by weight	
	Hi Sil 233	14% by weight	

The materials are mixed, blended, and then packaged.
The same consideration should be given in using other methods to formulate these combinations, for example:

Additional ingredients may be added to one of the components prior to combining the two compounds. The compound of formula I, formulated with sodium acetate and additional diluent to give an 80% (active) formulation, may be combined directly with an 80% (active) formulation of compound of formula II to give a useful combination.

One component may be specially treated prior to the combination. The compound of formula I may be treated as taught in U.S. Patent 3,920,442 and then mixed directly with an 80% (active) formulation of compound of formula II.

When technical materials of the two compounds are mixed within the ratio range cited in this case, the two crystalline materials form a soft semi-crystalline mass. This may be dissolved in a suitable solvent, such as dimethylformamide, to give a solution which may be used directly as a spray, or could be applied in known manner to a preformed granular carrier for preparation of granules.

The selective herbicidal activity of the compound of formula I and combination compositions in the above-mentioned has been tested many times under varied climate and soil conditions. The following tests are considered representative in demonstrating selective herbicidal activity of the compound of formula I and in demonstrating the safening effect of the compound of formula II when used under appropriate conditions.

Example VIII.

Sugarcane in Louisiana that had been planted in August was treated pre-emergence with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione

at rates, of 1, 2, and 4 kg/ha. The soil type was Commerce silt loam and the sugarcane variety was CP—61—37. The effect of treatment was observed 170 days later (after nearly 70 cm. of rainfall). At this time, a weed population made up primarily of henbit (*Lamium amplexicaule*), chickweed (*Stellaria sp.*) and annual grasses had been controlled at all rates without injury to the crop.

Example IX.

CI—54—378 variety of sugarcane was planted 7 inches deep in Willow-Elder muck soil in Florida on September 8. Six days later, pre-emergence applications of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione were made at rates of 0.5, 1 and 2 kg/ha. Weed control on February 1, the following year was 75, 83 and 99%, respectively, for the three rates. The weed population in untreated ureas adjacent was made up largely of goosegrass (*Eleusine indica*), wandering jew (*Zebrina pendula*) and purslane (*Portulaca oleracea*). This weed control was obtained without injury to the crop.

Example X.

In Taiwan, 61 and 79% weed control was provided by 0.5 kg/ha of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione in two separate tests. At a 1 kg/ha rate weed control in the two tests was 85 and 94%, respectively. The weeds controlled included torpedograss (*Panicum repens*) and two species of *Digitaria*. Only trace effects upon the cane were noted at the 1 kg rate.

Example XI.

Application of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione at rates of 0.5, 0.75, 1.0 and 2.0 kg/ha were made pre-emergence to recently planted sugarcane of the NCO—310 and CP—61—37 varieties at three separate locations in the Rio Grand Valley. In all cases, weed control was 90% or better 12 weeks after treatment. Rates up to and including 1 kg/ha has no adverse effect upon the sugarcane. The 2 kg rate was also safe on a loam soil but caused some chlorosis and stunting on sandy soil.

Similar applications made on the same cane varieties and in the same area but post-emergence to a ratoon crop also gave 90% weed control (for 3.5 months in this case) without crop injury. Sombinations of the compound of this invention with terbacil and with metribuzin were included in these tests with excellent results.

Example XII.

In South Africa, application of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione at rates of 1.5 and 3 kg/ha were made pre-emergence to cane on a clay soil with 1% organic matter. After 43 days, weed control was excellent at both rates with no adverse effect upon the cane.

Example XIII.

Plots in a sugarcane field in Hawaii were treated with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione at rates of 1, 2, 4 and 8 kg/ha. Weed control was excellent at even the 1 kilo. rate through a 90 day period during which about 80 cm of rainfall was received. There was no injury to the cane at the 1 and 2 kilo. rates but evident damage at 4 and 8 kilo. Weeds controlled included the genera *Ageratum*, *Setaria*, *Digitaria*, *Oxalis* and *Rhus*. Additions of 2 kg/ha or more of diuron prolonged the weed control without contributing to cane injury.

Example XIV.

In Louisiana, 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione was applied post-emergence to sugar cane variety CP 52—68 stubble cane, in heavy clay soil, in March at rates of 0.5, 1.0, 2.0 and 4.0 lbs/acre. Thirty (30) days after treatment, no phytotoxicity was observed at any rate. Raoul grass (*Rottboellia exaltata*) was controlled 50%, 78%, 93% and 99% respectively for each of the rates. A variety of of broadleaved weeds including mature Carolina Geranium and various unidentified broadleaved seedlings were controlled 73%, 91%, 92% and 95%, respectively. Seventy-five (75) days after treatment, no significant phytotoxicity was observed at the two lower rates, an acceptable level of phytotoxicity was observed at the 2.0 lb. rate, and an unacceptable level of phytotoxicity was observed at the 4.0 lb. rate with 63%, 79%, 95% and 94% control of Raoul grass, respectively.

Example XV.

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione (I) was applied pre-emergence both alone and in combination with 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (II) to sugarcane in Thailand. The soil was a loamy sand with 1.8% organic matter. The data below were taken 4 weeks after application and shows much less injury from a combination of I and II than from the same rate of I alone, as well as improved weed control for the combination. The ratings are given on a numerical scale from 0 to 100, where 0 indicates no crop injury or weed control, and 100 indicates crop kill or complete weed control.

TABLE 1.
RESPONSE 4 WEEKS AFTER TREATMENT

TREATMENT	RATE (KG/HA)	CROP PHYTOTOXICITY (%)	WEED CONTROL (%)
I	0.5	11	85
I	1.0	30	85
I and II	0.5 and 1.0	8	85
I and II	1.0 and 1.0	13	93

Example XVI.

In Australia, 1-methyl-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione (I) was applied alone and in combination with 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (II) preemergence to newly planted sugarcane. The soil was an alluvial, sandy loam with 1.2% organic matter. The data below were taken 5 weeks after treatment and shows that the combination was less phytotoxic to the crop and as effective in weed control. The ratings are given on a numerical scale from 0 to 100, where 0 indicates no crop injury or weed control, and 100 indicates crop kill or complete weed control.

TABLE 2
PLANT RESPONSE AFTER 5 WEEKS

TREATMENT	RATE (KG/HA)	CROP PHYTOTOXICITY (%)	WEED CONTROL (%)
I	0.75	20	99
I	1.0	30	100
I	1.5	40	100
I	2.0	42	100
II	3.5	0	93
I and II	0.5 and 1.0	3	97
I and II	0.5 and 2.0	10	99
I and II	1.0 and 1.0	18	99
I and II	1.0 and 2.0	29	100

Example XVII.

5 1-methyl-3-cyclohexyl-6-dimethylmethylamino-s-triazine-2,4-(1H,3H)-dione (I) was applied alone and in combination with 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (II) preemergence to sugarcane in Australia. The data below were taken 8 weeks after treatment and shows that the combination offered enhanced weed control with comparable safety to the crops as compared with an equivalent amount of compound I used alone. The ratings are given on a numerical scale from 0 to 100, where 0 indicates no crop injury or weed control and 100 indicates crop kill or complete weed control.

TABLE 3.
PLANT RESPONSE AFTER 8 WEEKS

TREATMENT	RATE (KG/HA)	CROP PHYTOTOXICITY (%)	WEED CONTROL (%)
I	0.75	13	63
I	1.0	18	73
I	1.5	30	94
I	2.0	33	93
II	4.0	0	87
I and II	0.5 and 2.0	3	84
I and II	0.5 and 3.0	10	91
I and II	0.75 and 2.0	15	87
I and II	0.75 and 3.0	13	88

Example XVIII.

10 A late post plant application of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione (I) alone and in combination with 3-(3,4-dichlorophenyl)-1,1-dimethyl urea (II) was made to sugarcane (C.V. Pinda) growing in a sandy loam soil. The major weeds present (which were also treated postemergence) were *Digitaria* spp. and *Echinochloa colonum*. The table below presents the results on this test. I, alone, at 0.67 kg/ha provided acceptable weed control with a slight reduction in phytotoxicity at 28 days after treatment.

TABLE 4

TREATMENT lb. a.i./acre	WEED CONTROL days after treatment (%)		CROP PHYTO. % days after treatment	
	Early 14	Final 28	Early 14	Final 28
I - 0.45	51.67	21.67	0	0
I - 0.67	90	80	13.3	6.6
I - 0.9	94	70	20	16.6
I - 1.35	98.34	29.34	20	2
I + II - 0.45 + 0.8	75	33.34	0	0
I + II - 0.45 + 1.2	85	51.67	0	0
I + II - 0.45 + 1.6	78.34	48.34	3.3	3.3
I + II - 0.67 + 0.8	91.67	52.5	0	0
I + II - 0.67 + 1.2	88.34	58.34	6.7	6.6
I + II - 0.67 + 1.6	96.34	76.67	13.3	13.3
Untreated control	26.67	5	0	0

Example XIX.

A ratoon sugarcane crop (C.V. Pinda) was treated with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione (I) alone and in combination with 3(3,4-dichlorophenyl)-1,1-dimethylurea (II) growing in a sandy loam soil. The major weed species were *Eragrostis tennella*, *Dactyloctenium aegyptium*, *Ipomoea* spp., and *Digitaria* spp. The results are contained in the following table. They demonstrate the efficacy of the triazinedione alone and the safening effect on the crop and longer duration control from combinations with the substituted urea.

TABLE 5

TREATMENT lb. a.i./acre	WEED CONTROL days after treatment (%)		CROP PHYTO. % days after treatment	
	Early 14	Final 28	Early 14	Final 28
I - 0.45	83.33	61.67	0	0
I - 0.67	95	99	1.67	1
I - 0.9	100	100	0.33	2
I - 1.35	100	100	3.67	2.67
I + II - 0.45 + 0.8	96.67	99	0	0
I + II - 0.45 + 1.2	98	100	1	1
I + II - 0.45 + 1.6	100	100	0	0
I + II - 0.67 + 0.8	100	100	0	0
I + II - 0.67 + 1.2	100	100	0	0.67
I + II - 0.67 + 1.6	100	100	0.33	0.67
Untreated control				

Example XX.

On April 11, 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione was applied in North Carolina to a series of field plots supporting a cover of oak and pine trees as well as mixed low-ground cover. Trees were still dormant at the time of treatment. Use rates included were 4, 8 and 16 kg/ha of the active compound. The soils in the test area were a light sand. By September 11, virtually all of the groundcover plants and all of the trees except for loblolly pine had been killed at the lowest treatment level. The oak trees killed were post oak and blackjack oak. The pine trees had survived and remained in a healthy condition even on the plots treated at the 8 kilogram rate.

Example XXI.

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione was applied at the rate 1 kg/ha to nursery flats of silt loam soil that had previously been seeded with Douglas fir and a selection of weeds including ryegrass, mustard, pigweed and chickweed. The chemical application was made prior to the emergence of any of the plants. This treatment killed all of the representative weeds but allowed the normal development of the Douglas fir.

Example XXII.

A test area in Texas covered with a stand of persimmon, pine and groundsel tree, as well as a variety of low-growing plants was selected. Random plots were treated with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione at rates of 4.8 and 16 kg/ha. The chemical was applied on May 24 with a solid-stream single nozzle directed in such a way as to reach the soil with a minimum of foliage contact. By September 27 (after 68 cm of rainfall), the 4 kilogram rate had provided effects noted below on the undesired plant species:

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	Plant Species	Percent kill by September 27	
5	Persimmon	92	
	Groundsel tree	100	
	Honeysuckle	90	5
	Blackberry	100	
	Vaseygrass	100	
	Bermudagrass	100	
	Sunflower	100	
10	Pine, on the other hand, was not killed even at the rate of 8 kg/ha. In September of the following year, weed control remained excellent and the pine continued to thrive.		10
	Example XXIII.		
15	In New Zealand, 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione was applied in February at rates of 8 and 12 kg/ha to field plots supporting toetoe and bracken fern. Control of both weed species was obtained at the lower use rate. In May, 1-year old seedlings of <i>Pinus radiata</i> were planted in the treated plots. The pine showed no phytotoxicity symptom.		15
	Example XXIV.		
20	In July, in New Zealand, newly planted seedlings of <i>Pinus radiata</i> and <i>Eucalyptus regnans</i> were treated with overall sprays of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione at rates of 1, 2 and 4 kg/ha. All eucalyptus plants died. Pine, on the other hand, showed no adverse effect at the 1 and 2 kilogram rates and only a slight yellowing at the 4 kilogram level.		20
	Example XXV.		
25	One-year old seedlings of <i>Pinus radiata</i> in New Zealand were treated in October, two months after planting, with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)dione at rates of 2, 4 and 8 kg/ha. Subsequent growth measurements indicated that all rates of treatment improved the growth of the pine seedlings due to control of the competing vegetation.		25
	Example XXVI.		
30	Broadcast treatments with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione at the rate of 3 kg/ha were made in April to field plots in Georgia. Five months after treatment, broomsedge had been killed whereas loblolly pine was uninjured. Rainfall during this exposure period was about 40 cm.		30
	Example XXVII.		
35	In April in North Carolina, directed sprays (sprays directed to the soil) of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione were applied to 4-year old loblolly pine trees. Rates used were 1,2,4 and 8 hg/ha. By June, weed plants including sumac and red gum had been seriously injured at the 2 kilogram rate. The pine, on the other hand, was thriving on the 4 kilogram plots and remained alive even in the 8 kilogram treatments.		35
	Example XXVIII.		
45	In another North Carolina field test, overall applications of the compound I were made to loblolly pine transplants three months after they had been set. Use rates were 1, 2 and 4 kg/ha. About two months after treatment, all use rates had provided 80% or more control of a mixed weed population with excellent survival of the pine. Additionally, the pines on the treated plots were thriving especially well due to release from competition.		45
	Example XXIX.		
50	Applications of the compound of formula I at rates of 1, 2, and 3 kg/ha were made to Austrian pine in April near Olympia, Washington. The treatments were applied directly over the pines which were about 30 cm tall. Although groundsel was controlled at all rates, the pine trees showed no adverse effects.		50

Example XXX.

In the Pacific Northwest, 2 kg/ha of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)dione provided commercially acceptable control (80—85%) of quackgrass, sedges, bramble and Canada thistle. Seedling Douglas fir planted about two weeks after these treatments tolerated as much as 6 kg/ha of the herbicide. Douglas fir trees 1 to 3 meters tall were treated over the top with similar margin of safety.

Example XXXI.

1-Methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione was applied pre- and post-emergence to weeds in three-year old rubber trees growing in Malaysia. Postemergence applications included in anionic wetting agent—Teepol (registered Trade Mark) surfactant (available from Shell Chemicals U.K. Ltd.). The soil was a sandy clay loam. Applications were made to plots at the rates shown in the table below. Weeds were removed by hand from the preemergence plots before treatment. The postemergence plots contained many annual weeds, some of which were flowering. The ratings for crop response are given in a numerical scale from 0 to 9, where 0 indicates no crop damage and 9 indicates complete kill. The ratings for weed control are given in percent.

TABLE 6.

Rate (kg/ha)	Time of Application	% Weed Control		Crop Response	
		1 Mo.	3 Mos.	1 Mo.	3 Mos.
1	pre-	93	81	0	0
2	pre-	96	95	0	0
4	pre-	98	96	0	1
1	post-	86	80	0	0
2	post-	88	67	0	0.7
4	post-	97	89	0	2
control	post-	1.3	2	—	—

Example XXXII.

A test with 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione (I) alone and in combination with 3-(3,4-dichlorophenyl)-1,1-dimethylurea (II) was conducted on rubber in Malaysia. The crop was 2—1/2 year old and field planted in a sandy loam. The treatments were applied to plots 2×14 m. The data that follows, taken three months after application, show the efficacy and the safening effect of the combinations.

TABLE 7.

Treatment	Rate, kg/ha	Response ^{1/3} Months after Treatment	
		Crop Phytotoxicity %	Weed Control %
I	0.5	8	11
	0.75	16	33
	1.0	28	45
I & II	0.5+1.0	2	43
	0.5+2.0	0	56
	0.75+1.0	4	69
	0.75+2.0	4	64
	1.0+1.0	6	66
	1.0+2.0	12	78

1/ 0=no response or weed control
100=crop killed or complete weed control

Example XXXIII.

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine 2,4(1H,3H)-dione (I) alone and in combination with 3(3,4-dichlorophenyl)-1,1-dimethyl urea (II) was applied as

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a directed postemergence treatment to weeds surrounding 2—1/2 year old rubber plants growing in a sandy loam soil. The major weeds present were *Paspalum conjugatum*, *Digitaria adscendens*, *Eleusine indica*, *Dactyloctenium aegyptium*, *Cassia mimosoides*, *Borreria laevi* and *Mimosa invisa*. The results of this experiment shown in the following table demonstrate the effectiveness of combinations of A and B for weed control and reduced crop injury.

Treatments	Rate	Weed Control		Crop Phytotoxicity	
		Days after Treatment (%)		Days after Treatment (%)	
		Early 13	Final 88	Early 13	Final 88
I	0.5	26.1	18.0	0	10
I	0.75	61.6	40.2	0	20
I	1	75.7	57.3	2	36
I+II	0.5+1	50.5	45.7	0	8
I+II	0.5+2	79.8	59.1	0	2
I+II	0.75+1	89.6	72.3	0	4
I+II	0.75+2	91.9	78.3	0	6
I+II	1+1	78.9	66.7	0	6

Example XXXIV.

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione (I) alone and in combination with 3(3,4-dichlorophenyl)-1,1-dimethyl urea (II) was applied postemergence as a directed spray to weeds surrounding one-year old field-planted oil palm growing in a sandy clay loam. The major weeds were *Paspalum conjugatum* and *Peuraria javanica*. The results, shown in the accompanying table, demonstrate the efficiency of combinations of I and II for weed control and the reduced crop toxicity from such combinations.

TABLE 8.

lb. product/acre	Weed Control		Crop Phytotoxicity	
	Days after Treatment (%)		Days after Treatment (%)	
	Early 30	Final 67	Early 30	Final 67
I 0.5	56.5	67.1	0	32.0
I 0.75	70.5	83.8	0	24.0
I 1.0	77.5	80.1	0	66.0
I 1.5	81.0	88.0	10.0	80.0
I 0.5+II 1.0	74.5	83.4	0	16.0
I 0.5+II 1.5	80.0	87.5	0	14.0
I 0.5+II 2.0	81.2	88.7	0	36.0
Untreated	0	0	0	0

Example XXXV.

Twelve-year old tea plants growing in a diluvium loam with 18% organic matter were treated with 3-cyclohexyl-1-methyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione. The treatments were applied as a directed spray in a 2 M² area underneath three tea bushes and preemergence to the weeds. The major weeds present were: crabgrass (*Digitaria adscendens*), flat-sedge (*Cyperus microiria*), smart weed (*Polygonum nodosum*) and tansy (*Polygonum nepalense*). The data below show the treatments to be effective and not damaging to the crop.

TABLE 9.

Rate, Kg prod./ha	% of Weed Control		Crop Phytotoxicity
	after 30 days	after 69 days	
1	95	69	none
2	100	84	none
4	100	97	none
Check —	0	0	none

Example XXXVI.

1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione was applied as a direct spray under mature coffee bushes. The data below show that the compound provided weed control with an adequate safety margin.

TABLE 10

Rate, kg/ha	% Control of Weeds - 38 Days						Crop Phytotoxicity %	
	Cyperus sp.	Digit- aria sp.	Rich- ardia sp.	Amaran- thus sp.	Galini- soga parviflora sp.	Com- melina spp.	38 Days	69 Days
0.5	60	90	95	95	95	93	0	0
1.0	65	97	98	98	98	98	20	0
2.0	70	100	100	100	100	98	40	60
4.0	75	100	100	100	100	98	60	80
Control —	0	0	0	0	0	0	0	0

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising in admixture 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4-(1H,3H)-dione and 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, wherein the weight ratio of said triazinedione to said urea is from 1:1 to 1:8, and a surface active agent and/or a solid or liquid diluent.

2. A composition according to claim 1 wherein said weight ratio is from 1:1 to 1:4.

3. A composition according to claim 1, substantially as hereinbefore described.

4. A composition according to claim 1, substantially as hereinbefore described with reference to Examples VI or VII.

5. A method for preventing or controlling undesired vegetation in crops without causing significant injury to said crop comprising applying to the locus of said crop an effective amount of a composition of claim 1, 3 or 4.

6. A method according to claim 5, comprising applying to the locus of said crop an effective amount of a composition of claim 2.

7. A method according to claim 5 or 6 wherein the crop is sugarcane, evergreen seedlings, coffee, tea, rubber or oil palm.

8. A method according to claim 7 wherein the crop is sugarcane.

9. A method according to claim 7 wherein the crop is rubber.

10. A method according to claim 7 wherein the crop is oil palm.

11. A method according to claim 5, substantially as hereinbefore described.

12. A method according to claim 5, substantially as hereinbefore described with reference to any of Examples XV—XIX or XXXII—XXXIV.

TABLE 9.

Rate, Kg prod./ha	% of Weed Control		Crop Phytotoxicity
	after 30 days	after 69 days	
1	95	69	none
2	100	84	none
4	100	97	none
Check —	0	0	none

Example XXXVI.

1-methyl-3-cyclohexyl-6-dimethylamino-*s*-triazine-2,4(1H,3H)-dione was applied as a direct spray under mature coffee bushes. The data below show that the compound provided weed control with an adequate safety margin.

TABLE 10

% Control of Weeds — 38 Days							Crop Phytotoxicity %	
Rate, kg/ha	Cyperus sp.	Digit- aria sp.	Rich- ardia sp.	Amaran- thus sp.	Galini- soga parviflora sp.	Com- melina spp.	38 Days	69 Days
0.5	60	90	95	95	95	93	0	0
1.0	65	97	98	98	98	98	20	0
2.0	70	100	100	100	100	98	40	60
4.0	75	100	100	100	100	98	60	80
Control —	0	0	0	0	0	0	0	0

WHAT WE CLAIM IS:—

1. A herbicidal composition comprising in admixture 1-methyl-3-cyclohexyl-6-dimethylamino-*s*-triazine-2,4-(1H,3H)-dione and 3-(3,4-dichlorophenyl)-1,1-dimethyl-urea, wherein the weight ratio of said triazinedione to said urea is from 1:1 to 1:8, and a surface active agent and/or a solid or liquid diluent.

2. A composition according to claim 1 wherein said weight ratio is from 1:1 to 1:4.

3. A composition according to claim 1, substantially as hereinbefore described.

4. A composition according to claim 1, substantially as hereinbefore described with reference to Examples VI or VII.

5. A method for preventing or controlling undesired vegetation in crops without causing significant injury to said crop comprising applying to the locus of said crop an effective amount of a composition of claim 1, 3 or 4.

6. A method according to claim 5, comprising applying to the locus of said crop an effective amount of a composition of claim 2.

7. A method according to claim 5 or 6 wherein the crop is sugarcane, evergreen seedlings, coffee, tea, rubber or oil palm.

8. A method according to claim 7 wherein the crop is sugarcane.

9. A method according to claim 7 wherein the crop is rubber.

10. A method according to claim 7 wherein the crop is oil palm.

11. A method according to claim 5, substantially as hereinbefore described.

12. A method according to claim 5, substantially as hereinbefore described with reference to any of Examples XV—XIX or XXXII—XXXIV.



13. A method of increasing the crop safety especially with respect to sugarcane plants, rubber plants, and oil palm plants of the herbicide 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione comprising admixing with said triazine-dione herbicide an amount of 3-(3,4-dichlorophenyl)-1,1-dimethylurea such that the weight ratio of said triazinedione to said urea is from 1:1 to 1:8.

14. A method according to claim 13 wherein said weight ratio is from 1:1 to 1:4.

15. A method for preventing or controlling undesired vegetation in crops without causing significant injury to said crop comprising applying to the locus of said crop an amount of 1-methyl-3-cyclohexyl-6-dimethylamino-s-triazine-2,4(1H,3H)-dione effective to prevent or control said undesired vegetation without significantly injuring said crop.

16. A method according to claim 15 wherein the crop is selected from sugarcane, evergreen seedlings, coffee, tea, rubber and oil palm.

17. A method according to claim 16 wherein the triazine is applied at a rate of 0.25 to 4.0 kilograms per hectare.

18. A method according to claim 17 wherein the triazine is applied at a rate of 0.5 to 1.0 kilogram per hectare.

19. A method according to any of claims 16—18 wherein the triazine is applied preemergence and the crop is plant or stubble cane.

20. A method according to any of claims 16—18 wherein the triazine is applied postemergence to sugarcane after top growth of the cane is well started.

21. A method according to claim 16 wherein the crop is evergreen seedlings.

22. A method according to claim 21 wherein the triazine is applied preemergence with respect to the undesired vegetation.

23. A method according to claim 21 wherein the triazine is applied postemergence at a time other than during the active growing season of the evergreen seedlings.

24. A method according to claim 21, 22 or 23 wherein the triazine is applied at a rate of 1—10 kilograms per hectare.

25. A method according to claim 24 wherein the triazine is applied at a rate of 2—8 kilograms per hectare.

26. A method according to any of claims 21—25 wherein the evergreen seedlings are pines, Douglas fir (*Pseudotsuga taxifolia*) or hemlock (*Tsuga heterophylla*).

27. A method according to any of claims 15—26 wherein the triazine is applied in combination with an effective amount of another selective herbicide.

28. A method according to claim 27 wherein said another selective herbicide is 3-(3,4-dichlorophenyl)-1,1-dimethylurea.

29. A method according to any of claims 15—18 wherein the crop is oil palm, rubber, coffee or tea.

30. A method according to claim 29 wherein the triazine is applied preemergence with respect to the undesired vegetation.

31. A method according to claim 29 wherein the triazine is applied postemergence at a time other than during the active growing season of the crops.

32. A method according to claim 29, 30 or 31 wherein the triazine is applied in combination with an effective amount of 3-(3,4-dichlorophenyl)-1,1-dimethylurea.

33. A method according to claim 29 wherein the crop is rubber.

34. A method according to claim 29 wherein the crop is tea.

35. A method according to claim 29 wherein the crop is coffee.

36. A method according to claim 29 wherein the crop is oil palm.

37. A method according to claim 15, substantially as hereinbefore described.

38. A method according to claim 15, substantially as hereinbefore described with reference to any of Examples VIII—XXXVI.

39. A method according to claim 28 substantially as hereinbefore described with reference to any of Examples XV—XIX or XXXII—XXXIV.

40. A method according to claim 15 wherein said crop is sugarcane.

41. A method according to claim 15 wherein said crop is oil palm, rubber, tea or coffee.

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