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(54) Title: HERBICIDE MIXTURE, METHOD FOR CONTROLLING UNDESIRABLE VEGETATION AND USE OF HERBICIDES

(57) Abstract: Disclosed is a synergic herbicide mixture comprising at least one sulfonylurea herbicide, particularly sulfometuron-methyl, together with diuron and hexazinone, or salts thereof. Also disclosed is a method for controlling undesirable vegetation by applying the herbicide mixture to the locus of the undesirable vegetation. This herbicide mixture is disclosed to effectively control a broad spectrum of weed species, including *Digitaria nuda*, with selectivity in crops, particularly sugarcane.

TITLE

HERBICIDE MIXTURE, METHOD FOR CONTROLLING UNDESIRABLE VEGETATION AND USE OF HERBICIDES

FIELD OF THE INVENTION

The present invention relates to a synergic mixture of active herbicides that are effective for the selective control of undesirable vegetation in useful crops, particularly sugarcane, to a method for weed control using said mixture of active herbicides, as well as to the use of said mixture for selective weed control, particularly of *Digitaria nuda*.

BACKGROUND OF THE INVENTION

Weed growth in useful crops causes significant yield reduction. The control of undesirable vegetation is therefore crucial to obtain high productivity in crops, and improved weed control is a continual objective in the agricultural field.

During periods of little rain precipitation, weeds and their seeds can be spread by winds, by activity of birds, by soil cultivation, etc. Furthermore herbicides applied during these periods are subject to degradation by sunlight and other weather conditions, and thus may not effectively control weeds when soil moisture increases and weed seeds germinate. In this situation the presence of undesirable vegetation and consequent problems for crops will only be noticed after the beginning of the rainy period, when weed control becomes more difficult, because during the rainy period, weeds grow quickly.

This problem affects many perennial crops, such as e.g. coffee, sugarcane, citrus, pasture, pine and eucalyptus.

Sugarcane crops, for instance, are especially affected by weeds, and weed control in sugarcane crops has been the object of many studies. Sugarcane is not replanted every year, and the harvest coincides with the beginning of the rain reduction period, favoring even more the dissemination of undesired vegetation due to crop harvesting activity and/or weather conditions, such as winds.

Furthermore, sugarcane crops occupy large areas, which can be difficult to treat simultaneously with herbicides. The situation has become more difficult due to expansion of sugarcane planting areas, which have been growing to support increased production of ethanol as an alternative fuel source. There is therefore an urgent need for herbicides that can be applied in the dry period to provide effective control of undesirable vegetation.

To address this need, new herbicide products have been developed during the past few years that can be applied during the dry period of the year, and in the pre- and post-emergence phase, both of the crop and of the undesirable vegetation. Nevertheless these new products still have deficiencies.

Herbicide active ingredients such as isoxaflutole and imazapic, which can be applied during the dry period for weed control, are useful only for controlling weeds before emergence, because they act on germinating weed seeds. Unfortunately these products can damage crops due to phytotoxicity, which prevents frequent reapplication. Such damage may become apparent only after the onset of rains. Therefore although these herbicides pre-emergently control a good spectrum of weed species, farmers must return to the field to physically remove weeds escaping control of the herbicides.

The importance of broad spectrum of weed control must be emphasized, not only due to the presence of both broadleaf (i.e. dicot) and narrow leaf (i.e. monocot) weeds, but also because of the increasing prevalence of weed species resistant to the most commonly used herbicides as result of extensive use of herbicides to control undesirable vegetation. Currently, many products commercially used do not provide effective control of a broad spectrum of weed species including *Digitaria nuda* Schumacher, which is becoming increasingly prevalent in the principal producing regions of sugarcane and other crops.

Another herbicide widely used in sugarcane and other crops is ametryn. However, this compound does not effectively control certain important weeds including *Brachiaria decumbens* Stapf (reclassified name: *Urochloa decumbens* (Stapf) R. Webster). Furthermore, it cannot be applied during the dry period.

Herbicides from the sulfonylurea group represent a class of compounds used in agriculture for controlling undesirable vegetation. They generically consist of a sulfonylurea link (-SO_2NHCONH-) joining two aromatic or heteroaromatic rings.

One of the sulfonylurea herbicides is sulfometuron-methyl, also known as methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate, which has been commercialized for industrial weed control and weed control along roadsides and rail lines, as well as a sugarcane ripener. This compound is specifically described in U.S. Patent 4,394,506 and can be prepared by means of the process disclosed therein.

Another well known herbicide compound is diuron, also known as 3-(3,4-dichlorophenyl)-1,1-dimethylurea. This compound is specifically described in U.S. Patents 2,655,445 and 2,768,971, and can be prepared by means of the process disclosed therein.

A third herbicide compound on the market is hexazinone, also known as 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazine-2,4-(1*H*,3*H*)-dione. This compound is specifically described by U.S. Patents 3,902,887, 3,850,924 and 3,983,116, and can be prepared by means of the processes disclosed therein.

However, these three herbicidal compounds when applied individually do not control a broad spectrum of important weeds and, depending on the application rate and stage of crop development, may cause crop phytotoxicity.

To provide a broader spectrum of undesirable vegetation control, mixtures of herbicide active ingredients are sometimes developed. To achieve superior effects, mixtures of herbicide active ingredients may also be developed to solve other specific technical problems, such as effective weed control from dry season application. Certain rare combinations of herbicidal active ingredients may provide a synergistic (i.e. greater than additive) herbicide effect on one or more important weeds or a safening (i.e. less than additive) effect on crop plants.

To develop highly effective herbicide mixtures, years of research and development are required, and mixtures of two or more herbicides do not always achieve all desired objectives.

The herbicides diuron and hexazinone, despite providing in combination a good spectrum of weed control, are not recommended for application during the dry period.

Hexazinone has also been commercialized in combination with clomazone. Although this mixture otherwise provides a good spectrum of weed control, it does not satisfactorily control *Brachiaria decumbens* and some broadleaf weed species.

Therefore, the development of an effective herbicide product for controlling undesirable vegetation, including broad and narrow leaf weeds, which can be satisfactorily applied both in the dry period and in the beginning of rainy period, reduces the need for repeated applications, and does not damage the crops of interest, is desirable. A new herbicidal mixture that can facilitate control of undesirable vegetation in crops has now been discovered.

SUMMARY OF THE INVENTION

The present invention relates to a mixture characterized by comprising at least one sulfonylurea herbicide, diuron and hexazinone, or salts thereof.

The present invention also relates to a herbicidal composition (i.e. final mixture) comprising the aforesaid mixture and at least one diluent. More particularly, the present invention relates to a herbicidal composition comprising the aforesaid mixture and at least one component selected from the group consisting of surfactants, solid diluents and liquid diluents.

The present invention also relates to a method for controlling undesirable vegetation, characterized by comprising the application of aforesaid mixture to the locus of the undesirable vegetation. More particularly, the present invention relates to a method for controlling the growth of undesired vegetation comprising contracting the vegetation or its environment with a herbicidally effective amount of a mixture comprising at least one sulfonylurea herbicide, diuron and hexazinone, or salts thereof (for example, as a herbicidal composition comprising the aforesaid mixture and at least one inert component).

The present invention also relates to the use of the aforesaid mixture for controlling broad or narrow leaf vegetation.

The present invention also relates to the use of a herbicide for controlling undesirable vegetation, characterized by being the use of a sulfonylurea herbicide to control *Digitaria nuda*.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having", "contains" or "containing" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be nonrestrictive regarding the number of instances (i.e. occurrences) of the element or component. Therefore "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

As referred to herein, the terms "broadleaf" and "broad leaf" used either alone or in phrases such as "broadleaf weed" means dicot or dicotyledon, a term used to describe a group of angiosperms characterized by embryos having two cotyledons. The term "narrow leaf" used either alone or in phrases such as "narrow leaf weed" means monocot or monocotyledon, a term used to describe a group of angiosperms characterized by embryos having one cotyledon. Grass weeds (family Poaceae) include many of the most agronomically important monocot weeds.

The term "sugarcane" refers to species of the genus *Saccharum* having a sucrose content useful for sugar production, particularly *S. officinarum* L., *S. barberi* Jesw., *S. robustum* Brandes, Jeswiet ex Grassl, *S. sinense* Roxb., *S. spontaneum* L. and *S. edule* Hassk., and hybrids and cultivars thereof.

As used in the present disclosure and claims, "locus of vegetation" refers to the vegetation and its environment (i.e. the area in which the vegetation grows or may grow).

The term "control" as used in the present disclosure and claims, means to prevent the appearance of undesirable vegetation or to reduce its growth or vigor.

"Phytotoxicity" in the context of the present invention relates to any effect of a herbicide that hinders the ordinary development of a crop plant. Phytotoxic effects of a herbicide typically reduce the growth of a crop plant and may even cause its death. Therefore low phytotoxicity is desirable to maintain healthy crop plants.

In the present disclosure and claims, the term "light soil" refers to soil that contains less than 15% of clay, "medium soil" refers to soil than contains from 15% to 30% of clay, and "heavy soil" refers to soil that contains more than 30% of clay.

The term “pre-emergence period” relates to the period before the emergence of foliage above ground. In contrast, the term “post-emergence period” related to the period after the emergence of foliage above ground. These two terms are often used regarding plants developing from seeds, but also relate to the development of foliage from plant parts at or below ground level, such as rhizomes or roots.

In commercial plantings, sugarcane is typically propagated from stem cuttings. After the first crop (known as the “plant crop”) of cane is cut for harvesting, new sprouts eventually appear from the rhizomes and roots, and these sprouts develop into new sugarcane stalks known as “ratoons”. After cutting the first sugarcane crop grown from cuttings, the cane regrowing from sprouts is known as “ratoon cane”, which produces a “ratoon crop”. Ratoon cane can be subsequently cut for harvesting and the process repeated until the sugarcane field is replanted. In the context of the present disclosure and claims, the term “pre-emergence ratoon cane” refers to the stage or period beginning with the cutting of a sugarcane crop so the plants are without foliage and ending with the appearance of sprouts. The term “post-emergence ratoon cane” refers to the stage or period beginning with the appearance of sprouts, which develop into ratoon cane stalks.

The terms “dry period”, “rain reduction period” or “dry season” according to the present invention correspond to the period of lowest average rain precipitation in the region where the crop is planted. These terms particularly relate to geographic regions having distinct wet and dry seasons. As an example, on the Brazilian Plateau (center south region of Brazil including the Cerrado savanna) and also in the southeast region of Brazil around São Paulo the dry season is generally considered to extend from about the month of May into September, particularly the months of June, July and August. As a further example, in the northeast region of Brazil the dry season is generally considered to be from October to January, particularly the months of October, November and December. More generally, the dry season may be defined as the period of the year during which the average, particularly historical average, daily rainfall is no more than about 2 mm, typically no more than about 1 mm, more typically no more than about 0.6 mm, and most typically no more than about 0.3 mm. The terms “rainy period” and “wet season” correspond to the period of the year during which average, particularly historical average, daily rainfall exceeds that during the dry season. The terms “beginning of the rainy period” or “semi-dry season” relate to the ending of the dry season and beginning of the wet season. During this period average daily rainfall is typically in the range from about 1 mm to about 3 mm. As an example, on the Brazilian Plateau and in the southeast Brazil region the beginning of wet season is generally considered to occur in the month of September. Therefore the combination of the dry period and the beginning of the rainy period on the Brazilian Plateau and in the southeast Brazil region is generally from about the month of May through September.

The term "synergic" as used in the present disclosure and claims refers to the herbicidal active ingredients cooperatively working together in the mixture of the invention to produce a result significantly superior to the results obtainable from the active ingredients separately. Synergic effects can include, for example, synergism (i.e. greater than expected additive effect) in controlling one or more weeds (i.e. undesirable vegetation) or a reduction of phytotoxicity (i.e. lessening of the negative effect) on crops, which is also unexpected and surprising. The reduction of phytotoxicity on crops is also known as "safening". Crop safening can allow greater herbicide application rates in crops to provide better weed control, including control of weeds species that are difficult to control at lower application rates. This facilitates an improved spectrum of weed control.

One skilled in the art recognizes that because in the environment and under physiological conditions salts of chemical compounds are in equilibrium with their corresponding nonsalt forms, salts share the biological utility of the nonsalt forms. Thus a wide variety of salts of the compounds in the mixture of the present invention are useful for control of undesired vegetation (i.e. are agriculturally suitable). These salts may include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. Salts may also include those formed with organic or inorganic bases such as pyridine, triethylamine or ammonia, or amides, hydrides, hydroxides or carbonates of sodium, potassium, lithium, calcium, magnesium or barium. Accordingly, the present invention relates to a mixture comprising at least one sulfonylurea herbicide, diuron and hexazinone, or agriculturally suitable salts thereof. Typically diuron and hexazinone are present not as salts in the present mixture. However, salts of sulfonylurea herbicides are readily prepared from bases and often agriculturally applied in this form. Therefore the present mixture often includes at least one sulfonylurea herbicide in the form of a salt thereof, which can also be described as an agriculturally suitable salt thereof.

The inventors of the present invention have discovered a mixture of three herbicidal components that is remarkably useful for controlling undesirable vegetation. This mixture comprises combination of at least one sulfonylurea herbicide, diuron and hexazinone, or salts thereof. The mixture controls a broad spectrum of weed species, advantageously including both broad and narrow leaf weeds. The mixture can be easily applied by conventional herbicide application methods and equipment. The mixture can be usefully applied both in the dry period and in the beginning of the rainy period during both the pre- and post-emergence of crops and undesirable vegetation. When applied appropriately, the present herbicidal mixture can provide useful weed control without significant phytotoxicity to crop plants. Depending upon selection of the sulfonylurea herbicide, the mixture can provide selective control of a broad spectrum of undesirable vegetation in useful crops, such as cotton, soy, coffee, sugarcane, citrus, maize, peanuts, wheat, pasture, pine, eucalyptus, and particularly sugarcane, with little phytotoxicity to the crop plants.

The inventors have discovered that mixture of the present invention advantageously provides a synergic effect for selective weed control in crops. Thus the present invention relates to a synergic mixture of herbicide components. Combinations of the three herbicide components (i.e. at least one sulfonylurea herbicide, diuron and hexazinone) provide broader spectrum of weed control due to the complementary addition of their individual weed control spectra. Furthermore the effects observed on weed species can be synergistic, i.e. provide greater than the expected additive effect such as calculated by the Colby Equation (see S. R. Colby, "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, **1967**, *15*(1), 20–22). The inventors have also discovered that in the present mixture, the combination of diuron and hexazinone surprisingly safens sulfonylurea herbicides on crop plants. This safening allows sulfonylurea herbicides to be applied to crops without unacceptable phytotoxicity at application rates higher than possible without diuron and hexazinone. Therefore the sulfonylurea can more effectively selectively control undesirable vegetation, including weed species otherwise difficult to control, in crops. The broad spectrum of control hinders the proliferation of tolerant weed species.

The following sulfonylurea herbicides are illustrative of those useful in the mixture of the present invention: amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, flucetosulfuron, flupyrsulfuron-methyl, flazasulfuron, foramsulfuron, halosulfuron-methyl, imazosulfuron, iodosulfuron-methyl, mesosulfuron-methyl, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-ethyl, rimsulfuron, sulfometuron-methyl, sulfosulfuron, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, trifloxysulfuron, triflusulfuron-methyl and tritosulfuron. Of note in the mixture of the present invention are sulfonylurea herbicides selected from the group consisting of amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, ethametsulfuron-methyl, flupyrsulfuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, metsulfuron-methyl, nicosulfuron, primisulfuron-methyl, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, triasulfuron, tribenuron-methyl and triflusulfuron-methyl (including mixtures thereof). Of particular note in the mixture in the present invention are sulfonylurea herbicides selected from the group consisting of azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, ethametsulfuron-methyl, flupyrsulfuron-methyl, metsulfuron-methyl, nicosulfuron, rimsulfuron, sulfometuron-methyl, thifensulfuron-methyl, tribenuron-methyl and triflusulfuron-methyl (including mixtures thereof). Also of note is the mixture of the present invention wherein the sulfonylurea herbicide component comprises one or more sulfonylurea herbicides other than metsulfuron-methyl, or does not include metsulfuron-methyl.

According to a particular embodiment of the present invention at least one sulfonylurea herbicide in the present mixture is selected from metsulfuron-methyl, rimsulfuron and sulfometuron-methyl (including mixtures thereof). These sulfonylurea herbicides are particularly useful in the present mixture for controlling a broad spectrum of weed species including *Digitaria nuda* with safety to sugarcane crops. A more particular embodiment of the present invention in this regard is the present mixture in which at least one sulfonylurea herbicide is selected from sulfometuron-methyl and rimsulfuron (including mixtures thereof).

According to a more particular embodiment of the present invention at least one sulfonylurea herbicide in the present mixture is sulfometuron-methyl. In a related embodiment, sulfometuron-methyl is the only sulfonylurea herbicide in the present mixture. Including sulfometuron-methyl in the present mixture has been discovered to provide excellent control of a broad spectrum of weed species including *Digitaria nuda*. This synergic effect can in some instances be synergistic. The diuron and hexazinone have also been unexpectedly discovered to effectively safen sulfometuron-methyl on sugarcane crops, so that a sufficient amount of the herbicide mixture can be applied to control a broad spectrum of weeds, including species such as *Digitaria nuda* which are otherwise difficult to control. Furthermore, including sulfometuron-methyl in the mixture has been discovered to provide long-lasting weed control, so that the mixture can be applied once during the dry period or at the beginning of the wet period, and good weed control is maintained throughout the wet period, thereby reducing need to reapply herbicides.

Typically, the weight ratio of the three essential components in the present mixture, i.e. the sulfonylurea herbicide component, diuron and hexazinone is about 12–17 : 500–700 : 150–190, respectively. According to an even more particular embodiment of the present invention, the mixture of active ingredients comprises about 12 g to 17 g of sulfonylurea herbicide (active ingredient) per kg of the final formulated mixture (i.e. composition), about 500 to 700 g of diuron per kg of the final formulated mixture and about 150 to 190 g of hexazinone per kg of the final formulated mixture. For example, in one embodiment the mixture comprises about 14.5 g of sulfonylurea herbicide, about 603 g of diuron and about 170 g of hexazinone per kg of the final formulated mixture.

The mixture of this invention will generally include the herbicide active ingredient components in compositions, i.e. formulations or final mixtures, with at least one additional component selected from the group consisting of surfactants, solid diluents and liquid diluents, which serves as a carrier. These carriers are also described as inert components. Inert components are components other than active ingredient components in the formulations. Inert components include surfactants, solid diluents and liquid diluents. Therefore the present mixture, when formulated (to produce a final mixture), is a composition characterized by comprising at least one inert component. The formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredients, mode of application and environmental factors such as soil type, moisture and temperature.

The mixtures of component (a) (i.e. the at least one sulfonylurea herbicide or salt thereof), component (b) (i.e. diuron or salt thereof) and component (c) (i.e. hexazinone or salt thereof) can be formulated in a number of ways, including:

(i) component (a), component (b) and component (c) can be formulated separately and applied separately or applied simultaneously in an appropriate weight ratio, e.g., as a tank mixture; or

(ii) component (a), component (b) and component (c) can be formulated together in the proper weight ratio.

Furthermore, additional ways include, for example, formulating component (b) and (c) together and formulating component (a) separately, and then applying the formulations separately or simultaneously in an appropriate weight ratio, such as in a tank mixture.

Useful formulations include both liquid and solid compositions (i.e. final mixtures). Liquid compositions include solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like, which optionally can be thickened into gels. The general types of aqueous liquid compositions are soluble concentrate, suspension concentrate, capsule suspension, concentrated emulsion, microemulsion and suspo-emulsion. The general types of nonaqueous liquid compositions are emulsifiable concentrate, microemulsifiable concentrate, dispersible concentrate and oil dispersion.

The general types of solid compositions are dusts, powders, granules, pellets, prills, pastilles, tablets, filled films (including seed coatings) and the like, which can be water-dispersible ("wettable") or water-soluble. Films and coatings formed from film-forming solutions or flowable suspensions are particularly useful for seed treatment. Active ingredient can be (micro)encapsulated and further formed into a suspension or solid formulation; alternatively the entire formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. An emulsifiable granule combines the advantages of both an emulsifiable concentrate formulation and a dry granular formulation. High-strength compositions are primarily used as intermediates for further formulation.

Sprayable formulations are typically extended in a suitable medium before spraying. Such liquid and solid formulations are formulated to be readily diluted in the spray medium, usually water. Spray volumes can range from about from about one to several thousand liters per hectare, but more typically are in the range from about ten to several hundred liters per hectare. Sprayable formulations can be tank mixed with water or another suitable medium for foliar treatment by aerial or ground application, or for application to the growing medium of the plant. Liquid and dry formulations can be metered directly into drip irrigation systems or metered into the furrow during planting.

Formulations (i.e. herbicidal compositions or final mixtures) according to the present invention comprise a mixture of at least one sulfonylurea herbicide, diuron and hexazinone, or salts thereof (i.e. active ingredient) in a herbicidally effective amount. These herbicidal compositions or final mixtures also comprise a least one inert component. More particularly the herbicidal compositions comprise at least one component selected from the group consisting of surfactants, solid diluents and liquid diluents. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Water-Dispersible and Water-soluble Granules, Tablets and Powders	0.001–90	0–99.999	0–15
Oil Dispersions, Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	1–50	40–99	0–50
Dusts	1–25	70–99	0–5
Granules and Pellets	0.001–99	5–99.999	0–15
High Strength Compositions	90–99	0–10	0–2

Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, gypsum, cellulose, titanium dioxide, zinc oxide, starch, dextrin, sugars (e.g., lactose, sucrose), silica, talc, mica, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Typical solid diluents are described in Watkins et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey.

Liquid diluents include, for example, water, *N*,*N*-dimethylalkanamides (e.g., *N*,*N*-dimethylformamide), limonene, dimethyl sulfoxide, *N*-alkylpyrrolidones (e.g., *N*-methylpyrrolidinone), ethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, propylene carbonate, butylene carbonate, paraffins (e.g., white mineral oils, normal paraffins, isoparaffins), alkylbenzenes, alkylnaphthalenes, glycerine, glycerol triacetate, sorbitol, triacetin, aromatic hydrocarbons, dearomatized aliphatics, alkylbenzenes, alkylnaphthalenes, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, acetates such as isoamyl acetate, hexyl acetate, heptyl acetate, octyl acetate, nonyl acetate, tridecyl acetate and isobornyl acetate, other esters such as alkylated lactate esters, dibasic esters and γ-butyrolactone, and alcohols, which can be linear, branched, saturated or unsaturated, such as methanol, ethanol, *n*-propanol, isopropyl alcohol, *n*-butanol, isobutyl alcohol, *n*-hexanol, 2-ethylhexanol, *n*-octanol, decanol, isodecyl alcohol, isooctadecanol, cetyl alcohol, lauryl alcohol, tridecyl alcohol, oleyl alcohol, cyclohexanol, tetrahydrofurfuryl alcohol, diacetone alcohol and benzyl alcohol. Liquid diluents also include glycerol esters of saturated and unsaturated fatty acids (typically C_6–C_{22}), such as plant seed and fruit oils (e.g, oils of olive, castor, linseed, sesame, corn (maize), peanut, sunflower, grapeseed, safflower, cottonseed, soybean, rapeseed, coconut and palm kernel), animal-sourced fats (e.g., beef tallow, pork tallow, lard, cod liver oil, fish oil), and mixtures thereof. Liquid diluents also include alkylated fatty acids (e.g., methylated, ethylated, butylated) wherein the fatty acids may be obtained by hydrolysis of glycerol esters from plant and animal sources, and can be purified by distillation. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950.

The solid and liquid compositions of the present invention often include one or more surfactants. When added to a liquid, surfactants (also known as "surface-active agents") generally modify, most often reduce, the surface tension of the liquid. Depending on the nature of the hydrophilic and lipophilic groups in a surfactant molecule, surfactants can be useful as wetting agents, dispersants, emulsifiers or defoaming agents.

Surfactants can be classified as nonionic, anionic or cationic. Nonionic surfactants useful for the present compositions include, but are not limited to: alcohol alkoxylates such as alcohol alkoxylates based on natural and synthetic alcohols (which may be branched or linear) and prepared from the alcohols and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof; amine ethoxylates, alkanolamides and ethoxylated alkanolamides; alkoxylated triglycerides such as ethoxylated soybean, castor and rapeseed oils; alkylphenol alkoxylates such as octylphenol ethoxylates, nonylphenol ethoxylates, dinonyl phenol ethoxylates and dodecyl phenol ethoxylates (prepared from the phenols and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); block polymers prepared from ethylene oxide or propylene oxide and reverse block polymers where the terminal blocks are prepared from propylene oxide; ethoxylated fatty acids; ethoxylated fatty esters and oils; ethoxylated methyl esters; ethoxylated tristyrylphenol (including those prepared from ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); fatty acid esters, glycerol esters, lanolin-based derivatives, polyethoxylate esters such as polyethoxylated sorbitan fatty acid esters, polyethoxylated sorbitol fatty acid esters and polyethoxylated glycerol fatty acid esters; other sorbitan derivatives such as sorbitan esters; polymeric surfactants such as random copolymers, block copolymers, alkyd peg (polyethylene glycol) resins, graft or comb polymers and star polymers; polyethylene glycols (pegs); polyethylene glycol fatty acid esters; silicone-based surfactants; and sugar-derivatives such as sucrose esters, alkyl polyglycosides and alkyl polysaccharides.

Useful anionic surfactants include, but are not limited to: alkylaryl sulfonic acids and their salts; carboxylated alcohol or alkylphenol ethoxylates; diphenyl sulfonate derivatives; lignin and lignin derivatives such as lignosulfonates; maleic or succinic acids or their anhydrides; olefin sulfonates; phosphate esters such as phosphate esters of alcohol alkoxylates, phosphate esters of alkylphenol alkoxylates and phosphate esters of styryl phenol ethoxylates; protein-based surfactants; sarcosine derivatives; styryl phenol ether sulfate; sulfates and sulfonates of oils and fatty acids; sulfates and sulfonates of ethoxylated alkylphenols; sulfates of alcohols; sulfates of ethoxylated alcohols; sulfonates of amines and amides such as *N,N*-alkyltaurates; sulfonates of benzene, cumene, toluene, xylene, and dodecyl and tridecylbenzenes; sulfonates of condensed naphthalenes; sulfonates of naphthalene and alkyl naphthalene; sulfonates of fractionated petroleum; sulfosuccinamates; and sulfosuccinates and their derivatives such as dialkyl sulfosuccinate salts.

Useful cationic surfactants include, but are not limited to: amides and ethoxylated amides; amines such as *N*-alkyl propanediamines, tripropylenetriamines and dipropylenetetramines, and ethoxylated amines, ethoxylated diamines and propoxylated amines (prepared from the amines and ethylene oxide, propylene oxide, butylene oxide or mixtures thereof); amine salts such as amine acetates and diamine salts; quaternary ammonium salts such as quaternary salts, ethoxylated quaternary salts and diquaternary salts; and amine oxides such as alkyldimethylamine oxides and bis-(2-hydroxyethyl)-alkylamine oxides.

Also useful for the present compositions (i.e. final mixtures) are mixtures of nonionic and anionic surfactants or mixtures of nonionic and cationic surfactants. Nonionic, anionic and cationic surfactants and their recommended uses are disclosed in a variety of published references including *McCutcheon's Emulsifiers and Detergents*, annual American and International Editions published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co.; Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964; and A. S. Davidson and B. Milwidsky, *Synthetic Detergents*, Seventh Edition, John Wiley and Sons, New York, 1987.

Compositions of this invention may also contain formulation auxiliaries and additives, known to those skilled in the art as formulation aids (some of which may be considered to also function as solid diluents, liquid diluents or surfactants). Such formulation auxiliaries and additives may control: pH (buffers), foaming during processing (antifoams such polyorganosiloxanes), sedimentation of active ingredients (suspending agents), viscosity (thixotropic thickeners), in-container microbial growth (antimicrobials), product freezing (antifreezes), color (dyes/pigment dispersions), wash-off (film formers or stickers), evaporation (evaporation retardants), and other formulation attributes. Film formers include, for example, polyvinyl acetates, polyvinyl acetate copolymers, polyvinylpyrrolidone-vinyl acetate copolymer, polyvinyl alcohols, polyvinyl alcohol copolymers and waxes. Examples of formulation auxiliaries and additives include those listed in *McCutcheon's Volume 2: Functional Materials*, annual International and North American editions published by McCutcheon's Division, The Manufacturing Confectioner Publishing Co.; and PCT Publication WO 03/024222.

The herbicide active ingredients are typically incorporated into the present compositions by dissolving the active ingredient in a solvent or by grinding in a liquid or dry diluent. Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. If the solvent of a liquid composition intended for use as an emulsifiable concentrate is water-immiscible, an emulsifier is typically added to emulsify the active-containing solvent upon dilution with water. Active ingredient slurries, with particle diameters of up to 2,000 μm can be wet milled using media mills to obtain particles with average diameters below 3 μm. Aqueous slurries can be made into finished suspension concentrates (see, for example, U.S. 3,060,084) or further processed by spray drying to form water-dispersible granules. Dry formulations usually require dry milling processes, which produce average particle diameters in the 2 to 10 μm range. Dusts and powders can be prepared by blending and usually grinding (such as with a hammer mill or fluid-energy mill). Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147–48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8–57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

For further information regarding the art of formulation, see T. S. Woods, "The Formulator's Toolbox – Product Forms for Modern Agriculture" in *Pesticide Chemistry and Bioscience, The Food–Environment Challenge*, T. Brooks and T. R. Roberts, Eds., Proceedings of the 9th International Congress on Pesticide Chemistry, The Royal Society of Chemistry, Cambridge, 1999, pp. 120–133. See also U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10–41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138–140, 162–164, 166, 167 and 169–182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1–4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81–96; Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989; and *Developments in formulation technology*, PJB Publications, Richmond, UK, 2000.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. These Examples illustrate three active ingredients formulated together in single compositions. However, as already discussed, the active ingredients can be similarly formulated separately and then later combined. Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be constructed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except where otherwise indicated.

Example A

High Strength Concentrate

sulfometuron-methyl	1.3%
diuron	76.4%
hexazinone	20.8%
silica aerogel	0.5%
synthetic amorphous fine silica	1.0%

Example B

Wettable Powder

sulfometuron-methyl	1.7%
diuron	48.7%
hexazinone	14.6%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%

Example C

Granule

sulfometuron-methyl	0.2%
diuron	7.7%
hexazinone	2.1%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%

Example D

Extruded Pellet

sulfometuron-methyl	0.4%
diuron	20.3%
hexazinone	4.3%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%

Example E

Emulsifiable Concentrate

sulfometuron-methyl	0.2%
diuron	7.7%
hexazinone	2.1%
polyoxyethylene sorbitol hexoleate	20.0%
C_6–C_{10} fatty acid methyl ester	70.0%

Example F

Granule

metsulfuron-methyl	0.2%
diuron	7.6%
hexazinone	2.2%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%

Example G

Extruded Pellet

rimsulfuron	0.5%
diuron	19.1%
hexazinone	5.4%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%

Thus the mixture of active ingredients according to the present invention can be made according to conventional processes and in any of the common agriculturally useful formulations, such as powders, granules, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates and the like. All of these formulation types are suitable to provide the synergic effect of the present mixture, which can also be described as a synergic mixture. According to a particular embodiment of the present invention, the mixture of active ingredients according the present invention is made in form of granules, more particularly water-dispersible granules.

According to an even more particular embodiment of the present invention, the mixture (i.e. synergic mixture) of herbicides consists of a mixture of separate formulations (i.e. separate compositions) wherein each of the separate formulations comprises one or two of the active ingredient components but not all three of the active ingredient components. The term "separate formulation" according to the present invention refers to a composition comprising one or two but not all three of the active ingredient components. For example, a separate formulation may comprise sulfometuron-methyl as the only herbicide active ingredient. A separate formulation may comprise diuron as the only herbicide active ingredient. A separate formulation may comprise hexazinone as the only herbicide active ingredient. A separate formulation may comprise both diuron and hexazinone as the only herbicide active ingredients. Products comprising the mixture of the present invention in which the active ingredients are separately formulated obviates the need for the farmer to prepare tank mixtures, which may be prohibited by agriculture, cattle-raising, environmental and health-regulating agencies. The separate formulations may have been previously publicly disclosed or even commercialized, which can reduce development and registration cost and need to sacrifice animals to obtain approval for new formulation products. Alternatively, the separate formulations according to the present invention may be new and not previously known or used by the public.

The mixture of the present invention may be simply a mixture of separate formulations, such as generally described in PCT Patent Publication WO 94/24861. In an embodiment of particular note, the mixture of the present invention is a homogeneous granule mixture according to the general teaching of U.S. Patent 6,022,552 and counterpart Brazilian Patent Application BR 9609282-3. This homogeneous granule mixture technology was invented by E. I. du Pont de Nemours and Company, and is now known to people skilled in the art as "blends" and "homogeneous mixtures". This formulation technology involves homogeneous mixtures of two or more groups of cylindrical granules comprising separate formulations, in which the granules satisfy size proportion requirements as described in U.S. Patent 6,022,552 and Brazilian Patent Application BR 9609282-3. Typically the cylindrical granules are prepared by extrusion methods, such as paste extrusion. The cylindrical granules can be sized by the method described in U.S. Patent 6,270,025 and counterpart Brazilian Patent PI9808331.7 to produce uniform particles having the required proportions. This homogenous mixture technology facilitates preparing particular mixtures with specific ratios of active ingredients that can be dispensed by pouring, volumetric and weight measurements and other techniques, while retaining the bulk composition in the dispensed samples.

According to an even more particular embodiment of the present invention, the mixture is prepared from separate granule formulations that have already been developed, in the amounts shown in the table below:

Concentration of active ingredient in the separate granule formulations	Amount of separate granule formulations to form an embodiment of the mixture of the present invention
Diuron (800 g/ kg) (e.g., KARMEX™, KARMEX™ XP)	753.9 g
Hexazinone (750 g/ kg) (e.g., STYLE™, VELPAR™ DF)	226.8 g
Sulfometuron-methyl (750 g/ kg) (e.g., CURAVIAL™, OUST™ 75WG, OUST™ XP)	19.3 g
TOTAL	1000 g

The sulfonylurea herbicide, diuron and hexazinone in the mixture of this invention can be further mixed with one or more other biologically active compounds or agents including herbicides, herbicide safeners, fungicides, insecticides, nematocides, bactericides, acaricides, growth regulators such as insect molting inhibitors and rooting stimulants, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants, plant nutrients, other biologically active compounds or entomopathogenic bacteria, virus or fungi to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such other biologically active compounds or agents are listed in *The Pesticide Manual, 13th Edition*, C. D. S. Tomlin, Ed., British Crop Protection Council, Farnham, Surrey, U.K., 2003 and *The BioPesticide Manual, 2nd Edition*, L. G. Copping, Ed., British Crop Protection Council, Farnham, Surrey, U.K., 2001. Combination of the sulfonylurea, diuron and hexazinone with other herbicides can broaden the spectrum of activity against additional weed species, and suppress the proliferation of any resistant biotypes. The other biologically active compounds or agents can be formulated together with the sulfonylurea herbicide, diuron and/or hexazinone or formulated separately and applied separately or simultaneously.

The amount of active ingredients applied in the present mixture to provide a certain level of control of undesirable vegetation depends upon a variety of factors including characteristics of the soil, and amount and types of undesirable vegetation. Although a wide range of application rates (i.e. herbicidally effective amount) of the present mixture can be used to provide a herbicidal effect, and as little as about 2 g total active ingredient per hectare can show useful herbicidal effects, commonly at least about 100 g total active ingredient per hectare, more commonly at least about 250 g total active ingredient per hectare, and most commonly at least about 500 g total active ingredient per hectare is applied. The amount is not limited, but typically no more than about 20 kg total active ingredient per hectare is applied. One skilled in the art can easily determine through simple experimentation the optimal amount to provide the desired level of weed control. Although the amount and variety of weeds to be controlled will affect optimal application rate, typically a formulated composition (i.e. final mixture) comprising about 14.5 g of sulfonylurea herbicide (e.g., sulfometuron-methyl), about 603 g of diuron and about 170 g of hexazinone per kg of formulated composition is applied at rate of about 1.3 to 1.7 kg (of formulated composition) per hectare on light soil, about 1.5 to 1.9 kg per hectare on medium soil, and about 1.7 to 2.3 kg per hectare on heavy soil.

According to the method of the present invention, the mixture (i.e. synergic mixture) of the active herbicides is applied in an area where undesirable vegetation grows or is believed likely to grow. This area may be the locus of a crop, but can also be an area without a crop. The mixture can be applied pre- and post-emergence of crops and pre- and post-emergence of weeds. Typically the present mixture is applied by spraying an aqueous suspension of the mixture prepared by diluting a combined formulation (i.e. final mixture) or a mixture of separate formulations comprising the sulfonylurea herbicide component, diuron and hexazinone with water (e.g., in a spray tank).

Supplemental surfactant adjuvants are recommended to be added to spray mixtures of many herbicide products used for weed control in crops such as sugarcane. The supplemental surfactant adjuvants are added to the aqueous spray mixtures to supplement the comparatively small amounts of dispersants and wetting agents present in the product formulations. Surprisingly, the inventors of the present mixture have discovered that such supplemental surfactant adjuvants are not needed in order to obtain good weed control by the present mixture, and moreover, supplemental surfactant adjuvants can increase the risk of injury to crops, e.g., sugarcane. Therefore an embodiment of note relates to a method for selective weed control in which the present mixture is not combined with a supplemental surfactant adjuvant in the aqueous mixture that is applied to the locus of the undesirable vegetation.

In one embodiment, before the weeds have emerged the mixture is applied to prevent weeds from later growing. To practice this embodiment in geographic regions having distinct wet and dry seasons, the mixture is preferably and conveniently applied during the rain reduction period (i.e. dry period) or during the beginning of the rainy period. This method provides both immediate and residual control of undesirable vegetation, without need to reapply herbicides during the rainy period. The mixture and method of the present invention may require application just once during the year, which reduces the time required and need for herbicide application equipment.

Preferably the present mixture, particularly wherein the sulfonylurea component comprises or consists of sulfometuron-methyl, is applied during the dry period, because dry period timing provides best crop tolerance even from broadcast applications of the mixture. Accordingly, in embodiments of the invention the present mixture is applied when the average, particularly historical average, daily rainfall is no more than about 2 mm, or no more than about 1 mm, or no more than about 0.6 mm, or no more than about 0.3 mm.

Examples for crops for application of the method of the present invention include cotton, soy, coffee, sugarcane, citrus, maize, peanuts, wheat, pasture, pine and eucalyptus. Of particular note is the use of the present mixture to control undesirable vegetation in perennial crops such as coffee, sugarcane, citrus, pasture, pine and eucalyptus. According to a specific embodiment of the present invention, the crop of interest is sugarcane.

In a particular embodiment of the present invention, the mixture of active ingredients is applied to the sugarcane crop during the dry period after the cane has been harvested by cutting. Applying the present mixture during this period has been discovered to allow greater application rates without subsequent injury to the sugarcane plants. Application of the present mixture during the dry period provides excellent weed control not only during the dry period but also during the following wet period.

During the pre-emergence ratoon cane stage, any methods to apply herbicides, including broadcast spray, can be used. During the post-emergence ratoon cane stage, the mixture of the invention is preferably applied in a directed spray application (i.e. "direct spot method) to avoid contact with the developing sugarcane shoots.

The method for controlling undesirable vegetation according to the present invention is especially advantageous for providing an excellent spectrum of broad and narrow leaf weed control with no significant injury to crops of interest. As an additional feature, the method of the present invention provides means to control weed species such as *Digitaria nuda* which are difficult to control with some current herbicide products.

Another aspect of the present invention involves the use of the mixture of herbicide active ingredients disclosed herein for the control of undesired vegetation and application of the mixture both during the dry and the beginning of the rainy periods, as already described. Furthermore the mixture as disclosed herein may be applied as a sugarcane ripener.

In the present mixture, the sulfonylurea herbicide component, particularly sulfometuron-methyl, rimsulfuron and/or metsulfuron-methyl, preferably sulfometuron-methyl and/or rimsulfuron, and more preferably sulfometuron-methyl, is the component contributing most to control of *Digitaria nuda*. Therefore an aspect of the present invention relates to the use of sulfonylureas, particularly sulfometuron-methyl, rimsulfuron, metsulfuron-methyl and mixtures thereof, preferably sulfometuron-methyl and/or rimsulfuron, and more preferably sulfometuron-methyl, for controlling *Digitaria nuda*. Because of the safening of sulfonylureas by diuron and hexazinone on crops discovered, these sulfonylureas are most useful in controlling *Digitaria nuda* when combined with diuron and hexazinone according to the present invention.

HERBICIDE TEST EXAMPLES

The following examples illustrate the synergic utility of the present mixture for control of undesirable vegetation. These examples are merely illustrative and do not limit the scope of the present invention in any way.

EXAMPLE 1 – COMPARATIVE

This greenhouse test was designed to evaluate greater-than-additive effects (i.e. synergism) in controlling *Digitaria nuda* from mixtures of sulfometuron-methyl with diuron and hexazinone according to the present invention.

Plastic pots (10-cm square) were filled to the rim with a sandy loam soil having pH of 6.1, 1.4% organic matter and a cation exchange capacity (CEC) of 5.7 milliequivalents per 100 grams (meq/100g). The soil was tamped firm to a uniform level of 2.5 cm below the rim of each pot. A measured amount of seeds of *Digitaria nuda* were scattered on the soil surface. Seeded pots were covered with approximately 50 mL of the same planting soil, tamped, and set on a greenhouse bench.

The same day the pots were treated preemergence with herbicides. The pots were sorted into test units prior to the herbicide application. Treatments were replicated three times. The application rates for this test were selected based on the recommended use rate of each compound. The herbicides were diluted in a measured amount of water and then mixed using a magnetic stir bar for 10 minutes before aliquots were taken to make individual treatment solutions. Sulfometuron-methyl (SMM) was in the form of the DuPont product OUST 75 WG, which is a wettable granule formulation containing 75 weight % active ingredient. A mixture of hexazinone and diuron in 11 : 39 weight ratio was in the form of the DuPont product VELPAR-K 60 WG, which is a wettable granule formulation containing 13.2 weight % hexazinone and 46.8 weight % diuron active ingredients. These products were applied alone and in combinations. Application rates of sulfometuron-methyl were 20, 25 and 30 g ai ha^{-1}, and application rates of the VELPAR-K mixture of hexazinone and diuron (132 g a.i. hexazinone + 468 g a.i. diuron / kg of formulated product) were 400, 800 and 1200 g total a.i. ha^{-1}. ("a.i." means active ingredient.) The surface of all pots was moistened with water just prior to spraying to hold the soil in place. The pots were then sprayed through a T-Jet 8002E nozzle using a stationary belt sprayer calibrated to deliver 281 L/ha at 234 kPa.

The pots were then placed in a greenhouse and watered thoroughly 2–3 times daily as needed. A balanced fertilizer solution was injected into the watering system to provide 218 ppm of nitrogen. Artificial lighting was used to supplement natural light to produce a 14 h photoperiod. Greenhouse temperatures were targeted for 27 °C in the day and 21 °C at night.

Control was visually evaluated relative to the control plants at 28 days after treatment (DAT). A numerical percent rating system was used to describe the response observed from each treatment on a scale of 0 to 100%, in which 0% indicates no response and 100% indicates plant death or near death. The reported results are the mean averages of the three replicates.

Colby's Equation was used to determine the herbicidal effects expected from the mixtures. Colby's Equation (Colby, S. R. "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations," *Weeds*, 15(1), pp 20–22 (1967)) calculates the expected additive effect of herbicidal mixtures, and for two active ingredients is of the form:

$$P_{a+b} = P_a + P_b - (P_a P_b / 100)$$

wherein P_{a+b} is the percentage effect of the mixture expected from additive contribution of the individual components,

P_a is the observed percentage effect of the first active ingredient at the same use rate as in the mixture, and

P_b is the observed percentage effect of the second active ingredient at the same use rate as in the mixture.

The observed and expected results are listed in Table 1.

TABLE 1

Effect of sulfometuron-methyl, and a mixture of diuron and hexazinone, alone and in combination on *Digitaria nuda*

Application Rate (g a.i./ha)			% Control	
Sulfometuron-methyl	Diuron	Hexazinone	Observed	Expected
20	–	–	67	–
25	–	–	87	–
30	–	–	100	–
–	312	88	20	–
–	624	176	30	–
–	936	264	77	–
25	312	88	93	90
25	624	176	100	91
25	936	264	100	97
–	–	–	0	–

This test showed mixing sulfometuron-methyl with diuron and hexazinone to provide greater control of *Digitaria nuda* than expected from additive effect calculated by the Colby Equation, which is consistent with synergistic response.

EXAMPLE 2 – COMPARATIVE

This greenhouse test was designed to evaluate safening of sulfometuron-methyl in mixtures with diuron and hexazinone according to the present invention. To facilitate this evaluation, strong baseline injury was obtained by broadcast spraying the treatments to contact the sugarcane foliage (i.e. post-emergence). To minimize crop injury in field crops in the post-emergence sugarcane phase, treatments are preferably directed applications to minimize contact with the sugarcane foliage.

Plastic pots (10-cm square) were filled to the rim with a sandy loam soil having pH of 6.1, 1.4% organic matter and a cation exchange capacity (CEC) of 5.7 milliequivalents per 100 grams (meq/100g). The soil was tamped firm to a uniform level of 6.4 cm below the rim of each pot. The sugarcane variety used in this test was the Brazilian variety RB-72-454 (*Saccharum officinarum* L). One sugarcane node was planted on the soil surface of each pot. The soil surface was then covered with about 5.1 cm of the same planting medium, tamped, and set on a greenhouse bench. The cuttings were grown in the greenhouse until the sugarcane was at the 2–3 leaf stage.

The pots were sorted into test units prior to the herbicide application. Treatments were replicated three times. The application rates for this test were selected based on the recommended use rate of each compound. The herbicides were diluted in a measured amount of water and then mixed using a magnetic stir bar for 10 minutes before aliquots were taken to make individual treatment solutions. Sulfometuron-methyl (SMM) was in the form of the DuPont product OUST 75 WG, which is a wettable granule formulation containing 75 weight % active ingredient. A mixture of hexazinone and diuron in 11 : 39 weight ratio was in the form of the DuPont product VELPAR-K 60 WG, which is a wettable granule formulation containing 13.2 weight % hexazinone and 46.8 weight % diuron active ingredients. These products were applied alone and in combinations. Application rates of sulfometuron-methyl were 20 and 30 g ai ha^{-1}, and the application rate of the VELPAR-K mixture of hexazinone and diuron (132 g a.i. hexazinone + 468 g a.i. diuron / kg of formulated product) was 1200 g total a.i. ha^{-1}. The surface of all pots was moistened with water just prior to spraying to hold the soil in place. The pots were then sprayed through a T-Jet 8002E nozzle using a stationary belt sprayer calibrated to deliver 281 L/ha at 234 kPa.

The pots were then placed in a greenhouse and watered thoroughly 2–3 times daily as needed. A balanced fertilizer solution was injected into the watering system to provide 218 ppm of nitrogen. Artificial lighting was used to supplement natural light to produce a 14 h photoperiod. Greenhouse temperatures were targeted for 27 °C in the day and 21 °C at night.

Plant injury was visually evaluated relative to the control plants at 47 days after treatment (DAT). A numerical percent rating system was used to describe the injury observed from each treatment on a scale of 0 to 100%, in which 0% indicates no response and 100% indicates plant death or near death. The reported results are the mean averages of the three replicates.

Because the combination of diuron and hexazinone caused no injury at the application rate tested, Colby's Equation is not needed to calculate the expected crop injury from mixtures of diuron and hexazinone with sulfometuron-methyl. The expected crop injury is the injury observed from sulfometuron-methyl applied alone.

The observed and expected results are listed in Table 2.

TABLE 2

Effect of sulfometuron-methyl, and a mixture of diuron and hexazinone, alone and in combination on sugarcane.

Application Rate (g a.i./ha)			% Phytotoxicity	
Sulfometuron-methyl	Diuron	Hexazinone	Observed	Expected
20	–	–	37	–
30	–	–	60	–
–	936	264	0	–
20	936	264	13	37
30	936	264	15	60
–	–	–	0	–

This test showed mixing sulfometuron-methyl with diuron and hexazinone to provide a remarkable reduction of injury to sugarcane.

EXAMPLE 3 – COMPARATIVE

In this greenhouse test, the mixture of sulfometuron-methyl, hexazinone and diuron in a ratio according to a particular embodiment of the present invention was tested in comparison with several commercially available herbicide products. These included the active ingredients sulfometuron-methyl (SMM), diuron, ametryn, a mixture of hexazinone and diuron in a weight ratio of 11 : 39 (hexazinone + diuron A) and a mixture of hexazinone and diuron in a weight ratio of 8 : 67 (hexazinone + diuron B).

Seeds of *Digitaria nuda* and *Digitaria horizontalis* were planted in plastic pots (10-cm square), and the plants were grown in a greenhouse for 9 to 14 days. When the plants reached the 3–4 leaf stage of growth, the plants were sorted into test units before herbicide application. *Digitaria nuda* was 15–17 cm and *Digitaria horizontalis* was 17–20 cm in height at the time of application. The surface of all the test units was moistened with water just prior to spraying to hold the soil in place and prevent loss of the herbicide-treated soil during handling. Formulated herbicides were diluted with water and sprayed on the plants using a stationary belt sprayer calibrated to deliver 281 L/ha at 234 kPa to provide the application rates listed in Table 3. Each herbicide treatment was replicated three times. After herbicide application, the test units were returned to the greenhouse.

At 28 days after treatment, the amount of control averaged over the plants of each treatment was rated by measuring the fresh weight of treated plants. The numerical response ratings were calculated as percent growth reduction relative to untreated check plants. Ratings are expressed on a 0 to 100 percent scale, wherein 0 means no weed control and 100 means complete control. The ratings are listed in Table 3.

The results of this test show sulfometuron-methyl alone controlling *Digitaria nuda* up to 76%. Moreover, sulfometuron-methyl did not significantly control *Digitaria horizontalis*.

The results show, additionally, the effect of herbicides diuron, ametryn, (hexazinone + diuron A), (hexazinone + diuron B) separately for the control of *Digitaria nuda* and *horizontalis*. Ametryn alone controlled *Digitaria nuda*, but it was not sufficiently effective for the control of *Digitaria horizontalis*.

The results also show that the mixture of sulfometuron-methyl, hexazinone and diuron according to the present invention is effective for controlling both *Digitaria nuda* and *Digitaria horizontalis*. The results presented in Table 3 show the synergic effect of the mixture of the present invention, because the % control of *Digitaria nuda*, which was 76% when sulfometuron-methyl was applied alone and less than 50% when diuron, (hexazinone + diuron A) or (hexazinone + diuron B) was applied, exceeded 80% from application of the mixture of the present invention. Thus the mixture of sulfometuron-methyl with hexazinone and diuron provided substantially better results, which characterizes one aspect of the synergy of the mixture of the present invention.

TABLE 3

DIGITARIA CONTROL TEST

			% Control	
	Active(s)	Rate (g a.i./ha)	DIGNU	DIGHO
(A)	SMM	2	43	19
(B)	SMM	4	35	25
(C)	SMM	8	54	11
(D)	SMM	15	64	19
(E)	SMM	30	76	24
(F)	diuron	1200	2	52
(G)	diuron	2400	20	78
(H)	ametryn	1000	58	42
(I)	ametryn	1500	78	50

(J)	ametryn	2000	80	44
(K)	hexazinone + diuron A	220 + 780	32	82
(L)	hexazinone + diuron A	330 + 1170	48	95
(M)	hexazinone + diuron B	167 + 1332	5	86
(N)	hexazinone + diuron B	223 + 1776	21	98
(O)	SMM + (hexazinone + diuron A)	8 + (220 + 780)	52	70
(P)	SMM + (hexazinone + diuron A)	15 + (220 + 780)	59	87
(Q)	SMM + (hexazinone + diuron A)	30 + (220 + 780)	64	78
(R)	SMM + (hexazinone + diuron A)	8 + (330 + 1170)	46	80
(S)	SMM + (hexazinone + diuron A)	15 + (330 + 1170)	65	75
(T)	SMM + (hexazinone + diuron A)	30 + (330 + 1170)	81	91
(U)	SMM + (hexazinone + diuron B)	8 + (167+1332)	61	85
(V)	SMM + (hexazinone + diuron B)	15 + (167+1332)	72	94
(W)	SMM + (hexazinone + diuron B)	30 + (167+1332)	82	96
(X)	SMM + (hexazinone + diuron B)	8 + (223+1776)	58	96
(Y)	SMM + (hexazinone + diuron B)	15 + (223+1776)	67	98
(Z)	SMM + (hexazinone + diuron B)	30 + (223+1776)	84	96

EXAMPLE 4 – COMPARATIVE

This test was conducted similarly to the test described in Example 3 above. The activity of different herbicide compounds (sulfometuron-methyl, rimsulfuron, metsulfuron-methyl, terbacil, hexazinone, ametryn and isoxaflutole) for the pre-emergence and post-emergence control of *Digitaria nuda* was tested by applying the active ingredients to the plants at different development stages. To provide plants at eight different growth stages at the time of treatment, seeds of *Digitaria nuda* were planted in pots on eight different days which were an average of 3 days apart. This allowed the test compounds to be applied on the same day to *Digitaria nuda* preemergence (Pre) and plants of 1 cm, 2 cm, 4 cm, 12 cm, 17 cm, 18 cm and 20 cm height. The effects were visually rated 7 days after treatment on a 0 to 100 percent scale, wherein 0 indicates no response and 100 indicates plant death or near death. The results are shown in Table 4.

The tests showed that the sulfonylurea herbicides sulfometuron-methyl, rimsulfuron and metsulfuron-methyl) are effective for controlling *Digitaria nuda* except at very late growth stages, but the other herbicides, including hexazinone, did not show the same efficacy. Furthermore, although all three of the sulfonylurea herbicides were efficacious for controlling *D. nuda*, sulfometuron-methyl and rimsulfuron were found to be substantially more effective than metsulfuron-methyl at lower application rates. As described elsewhere in the present disclosure, the utility of sulfonylureas such as sulfometuron-methyl for controlling *D. nuda* has now been discovered to be further improved by combination with diuron and hexazinone.

TABLE 4

CONTROL OF DIGITARIA NUDA

		Stage of Development at Time of Application							
	Treatment	Pre	1 cm	2 cm	4 cm	12 cm	17 cm	18 cm	20 cm
	Active ingredient – Rate (g a.i./ha)	*Digitaria nuda Control* (%)							
(1A)	sulfometuron-methyl – 8	100	80	75	75	90	80	<50	<50
(1B)	sulfometuron-methyl –16	100	95	95	97	97	80	<50	<50
(1C)	sulfometuron-methyl – 31	100	98	98	98	98	80	<50	<50
(1D)	sulfometuron-methyl – 62	100	98	99	98	98	85	70	<50
(2A)	rimsulfuron – 8	100	80	90	80	70	85	70	<50
(2B)	rimsulfuron – 16	100	80	95	85	80	85	75	<50
(2C)	rimsulfuron – 31	100	100	95	95	90	85	85	<50
(2D)	rimsulfuron – 62	100	100	95	95	95	90	80	<50
(3A)	metsulfuron-methyl – 8	100	80	80	75	70	70	60	<50
(3B)	metsulfuron-methyl – 16	100	85	80	60	75	75	60	<50
(3C)	metsulfuron-methyl – 31	100	90	90	95	95	80	75	<50
(3D)	metsulfuron-methyl – 62	100	95	95	90	90	85	75	75
(4A)	terbacil – 100	<50	100	100	60–70	<50	<50	<50	<50
(4B)	terbacil – 200	<50	100	100	100	<50	<50	<50	<50
(4C)	terbacil – 400	<50	100	100	100	100	60–70	<50	<50
(4D)	terbacil – 800	60	100	100	100	100	95	<50	75
(5A)	hexazinone – 100	<50	<50	<50	<50	<50	<50	<50	<50
(5B)	hexazinone – 200	<50	<50	<50	<50	<50	<50	<50	<50
(5C)	hexazinone – 400	<50	<50	<50	<50	<50	<50	<50	<50
(5D)	hexazinone – 800	<50	80	<50	<50	<50	<50	<50	<50
(6A)	ametryn – 1000	<50	100	100	100	100	100	<50	<50
(6B)	ametryn – 1500	<50	100	100	100	100	100	85	85
(6C)	ametryn – 2000	<50	100	<50	100	100	100	85	75
(7A)	isoxaflutole – 50	80	60–70	60–70	60–70	<50	<50	<50	<50
(7B)	isoxaflutole – 100	85	60–70	85	60–70	60	<50	<50	<50
(7C)	isoxaflutole – 150	85	80	80	60–70	60	<50	<50	<50

EXAMPLE 5 – COMPARATIVE

The efficacy of various herbicide treatments (a mixture of diuron, hexazinone and sulfometuron-methyl (SMM), imazapic, a mixture of clomazone and hexazinone, or isoxaflutole) was evaluated for the control of broadleaf weed tropical clover (*Richardia* *brasiliensis* Gomes) within 15, 30, 60, 90, 120, 150 and 180 days after treatment (DAT). The herbicide treatments were applied during the dry period to a sugarcane field on medium soil after the sugarcane had been harvested, i.e. the "pre-emergence ratoon cane" stage. These applications were pre-emergence to the weeds as well as pre-emergence to the sugarcane.

This test was conducted using an experimental design known in the art as "randomized complete block". This method involves randomly selecting the areas in the field to be treated. The herbicide treatments were prepared by diluting herbicide formulations with water, and the resulting aqueous mixtures were applied to the selected areas as a broadcast spray from a spray boom. Weeds in "cleared control" areas were periodically cut to prevent weed infestation. "Non-cleared control" areas were neither treated nor cut, so weed growth was not suppressed.

After 15, 20, 60, 90, 120, 150 and 180 days after treatment (DAT), the weed control effect was visually rated on a 0 to 100 percent scale promulgated by ALAM (Asociación Latinoamericana de Melezas) in 1974 in Cali, Colombia. In this scale, 0 means no weed control and 100 means complete control. In this scale, 61–70 may be considered sufficient for agriculture. The results are listed in Table 5.

Because the test started at the end of the dry period, when there was little weed growth, the results are reported to be 100% during first 15 days for all of the herbicides.

The tests with active materials (1), (2) and (3) relate to the mixture of the present invention. The results demonstrate the excellent efficiency of the mixture of the present invention for the control of *Richardia brasiliensis*, because it provided 100% control even after 180 days, clearly showing it to be more effective than other active ingredients in commercial herbicide products. The mixture of the invention provided better efficacy that the mixture of clomazone and hexazinone (5) as well as imazapic (4) and isoxaflutole (6), which are active ingredients in products recommended for application during the dry period.

TABLE 5

EFFICACY EVALUATIONS FOR THE WEED TROPICAL CLOVER

	Active ingredient	Application Rate (g a.i./ha)	Formulation Dose (g/ha)	Percent Control of *Richardia brasiliensis*						
				Days After Treatment (DAT)						
				15	30	60	90	120	150	180
(1)	diuron + hexazinone + SMM	784 + 221 + 19	1300	100	100	98	96	95	95	95
(2)	diuron + hexazinone + SMM	905 + 255 + 22	1500	100	100	98	95	95	95	95

(3)	diuron + hexazinone + SMM	1025 + 289 + 25	1700	100	100	100	100	100	100	100
(4)	imazapic	98	140	100	100	98	99	98	98	98
(5)	clomazone + hexazinone	800 + 200	2000	100	98	94	90	88	88	85
(6)	isoxaflutole	150	200	100	98	96	89	85	85	85
(7)	cleared control	–	–	100	100	100	100	100	100	100
(8)	non-cleared control	–	–	0	0	0	0	0	0	0

EXAMPLE 6 – COMPARATIVE

In this test, herbicide treatments containing a mixture of diuron, hexazinone and sulfometuron-methyl, a mixture of clomazone and hexazinone, or isoxaflutole were applied to a sugarcane field on light soil during the "pre-emergence ratoon cane" period. The field was infested with seeds of the grass weeds *Digitaria horizontalis* Willd. and *Brachiaria decumbens* Stapf and the broadleaf weeds *Portulaca oleracea* L. and *Amaranthus deflexus* L. The herbicide treatments were applied before emergence of these weeds. This test was conducted using four replications and a "randomized complete block" design with blocks 3 m wide by 10 m long. The treatments were applied by diluting formulated products with water, and the resulting aqueous mixtures were applied to the selected areas as a broadcast spray from a spray boom attached to a carbon dioxide-pressurized precision backpack sprayer system.

The results were evaluated at 97, 120 and 135 days after treatment (DAT) for control of *Digitaria horizontalis* and *Portulaca oleracea*, and 80, 97, 120 and 135 days after treatment for control of *Brachiaria decumbens* and *Amaranthus deflexus*. Control of weeds was visually determined on a 0 to 100 percent scale described by Frans, R. R. Talbert, D. Marx and H. Crowley, **1986**, "Experimental design and techniques for measuring and analyzing plant response to weed control practices", pp. 37–38 in N. D. Camper (ed.) *Research Methods in Weed Science, 3rd Ed.*, Southern Weed Sci. Soc., Champaign, IL. In this scale, 0 means no weed control, 100 means complete control, and about 80 may be considered the minimum sufficient for agriculture. Sugarcane injury was visually determined on a 1 to 5 scale promulgated by ALAM (Asociaciôn Latinoamericana de Melezas) in 1974 in Cali, Colombia. In this scale, 1 means normal plants equal to the control, and 5 means fully dead plants. Weed control results are listed in Table 6A, and sugarcane injury results are listed in Table 6B.

Tables 6A and 6B confirm that the mixture of the present invention is more useful than previously developed herbicide products, because it achieves an excellent spectrum of weed control, while reducing phytotoxicity to sugarcane.

TABLE 6A

EFFECT OF TREATMENTS ON WEEDS

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	Formulation Dose (kg /ha)	Percent Control					
				Digitaria horizontalis			*Portulaca oleracea*		
				DAT			DAT		
				97	120	135	97	120	135
(1)	diuron + hexazinone + sulfometuron-methyl	905 + 255 + 22	1.5	100	99	100	100	99	100
(2)	diuron + hexazinone + sulfometuron-methyl	1025 + 289 + 25	1.7	100	100	100	100	100	100
(3)	diuron + hexazinone + sulfometuron-methyl	1146 + 323 + 28	1.9	100	99	100	100	99	100
(4)	clomazone + hexazinone	720 + 180	1.8	100	99	100	100	100	100
(5)	clomazone + hexazinone	800 + 200	2.0	100	100	100	100	100	100
(6)	clomazone + hexazinone	1000 + 250	2.5	100	100	100	100	100	100
(7)	isoxaflutole	150	0.2	100	100	99	99	100	98
(8)	control	–	–	0	0	0	0	0	0

TABLE 6A – Continued

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	Percent Control							
			Brachiaria decumbens				*Amaranthus deflexus*			
			DAT				DAT			
			80	97	120	135	80	97	120	135
(1)	diuron + hexazinone + sulfometuron-methyl	905 + 255 + 22	100	100	100	99	100	100	100	100
(2)	diuron + hexazinone + sulfometuron-methyl	1025 + 289 + 25	100	100	98	98	100	100	100	100
(3)	diuron + hexazinone + sulfometuron-methyl	1146 + 323 + 28	100	100	99	97	100	100	100	100
(4)	clomazone + hexazinone	720 + 180	100	100	99	97	100	100	100	100
(5)	clomazone +	800 + 200	100	100	99	98	100	100	99	99

	hexazinone									
(6)	clomazone + hexazinone	1000 + 250	100	100	100	99	100	100	100	100
(7)	isoxaflutole	150	100	100	97	96	100	100	99	98
(8)	control	–	0	0	0	0	0	0	0	0

TABLE 6B

EFFECT OF TREATMENTS ON SUGARCANE

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	Formulation Dose (kg /ha)	Phytotoxicity DAT				
				45	80	97	120	135
(1)	diuron + hexazinone + sulfometuron-methyl	905 + 255 + 22	1.5	1	1	1	1	1
(2)	diuron + hexazinone + sulfometuron-methyl	1025 + 289 + 25	1.7	1	1	1	1	1
(3)	diuron + hexazinone + sulfometuron-methyl	1146 + 323 + 28	1.9	1	1	2	2	2
(4)	clomazone + hexazinone	720 + 180	1.8	1	1	1	1	2
(5)	clomazone + hexazinone	800 + 200	2.0	1	1	1	1	2
(6)	clomazone + hexazinone	1000 + 250	2.5	1	1	1	1	2
(7)	isoxaflutole	150	0.2	2	2	2	3	3
(8)	control	–	–	1	1	1	1	1

EXAMPLE 7 – COMPARATIVE

In this test, herbicide treatments containing a mixture of diuron, hexazinone and sulfometuron-methyl, a mixture of clomazone and hexazinone, or isoxaflutole were applied to a field on medium soil at the time of the year when sugarcane in the surrounding area had been cut and not yet sprouted (the pre-emergence ratoon cane period) and annual weeds had not yet germinated.

Seeds of the grass weeds *Brachiaria decumbens* Stapf (reclassified as *Urochloa decumbens* (Stapf) R. Webster), *Panicum maximum* Jacq. (reclassified as *Urochloa maxima* (Jacq.) R. Webster), *Brachiaria plantaginea* (Link) A.S. Hitchc. (reclassified as *Urochloa plantaginea* (Link) R. Webster) and *Digitaria nuda* Schumacher and broadleaf weeds *Sida rhombifolia* L., *Euphorbia heterophylla* L. and *Ipomoea hederifolia* L. were planted in parallel rows in 1 m wide by 50 m long beds. Herbicide treatments were applied in bands perpendicular to the rows, so that each herbicide treatment was applied to each of the rows containing weed seeds.

The results were evaluated 65 days after treatment. Control of weeds was visually determined on a 0 to 100 percent scale, wherein 0 means no weed control and 100 means complete control. In this scale, about 80 may be considered the minimum sufficient for agriculture. The results are listed in Table 7. These results again confirm the mixture of the present invention provides excellent breadth of weed control compared to the other herbicides tested.

TABLE 7

EFFECT OF TREATMENTS ON WEEDS

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	% Control			
			Brachiaria decumbens	*Panicum maximum*	*Brachiaria plantaginea*	*Digitaria nuda*
(1)	sulfometuron-methyl	5	0	20	20	30
(2)	sulfometuron-methyl	10	0	85	90	70
(3)	sulfometuron-methyl	20	50	100	99	90
(4)	sulfometuron-methyl	30	70	100	100	95
(5)	hexazinone	200	0	20	0	0
(6)	diuron + hexazinone	936 + 264	80	100	100	0
(7)	ametryn	1000	10	20	20	75
(8)	hexazinone + sulfometuron-methyl	200 + 5	10	99	85	30
(9)	hexazinone + sulfometuron-methyl	200 + 7.5	10	99	85	60
(10)	hexazinone + sulfometuron-methyl	200 + 10	40	95	95	70
(11)	hexazinone + sulfometuron-methyl	200 + 15	30	95	95	90
(12)	hexazinone + sulfometuron-methyl	200 + 20	60	98	100	95
(13)	hexazinone + sulfometuron-methyl	200 + 30	85	98	100	98
(14)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 5	95	100	100	50
(15)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 10	95	100	100	70
(16)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 20	99	100	100	80
(17)	diuron + hexazinone	936 + 264 + 30	99	100	100	95

	+ sulfometuron-methyl					
(18)	amicarbazone	1400	85	85	100	20
(19)	control	–	0	0	0	0

TABLE 7 – Continued

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	% Control		
			Sida rhombifolia	*Euphorbia heterophylla*	*Ipomoea hederifolia*
(1)	sulfometuron-methyl	5	20	75	30
(2)	sulfometuron-methyl	10	90	85	75
(3)	sulfometuron-methyl	20	100	98	95
(4)	sulfometuron-methyl	30	97	98	98
(5)	hexazinone	200	90	90	90
(6)	diuron + hexazinone	936 + 264	100	75	100
(7)	ametryn	1000	20	20	30
(8)	hexazinone + sulfometuron-methyl	200 + 5	99	99	99
(9)	hexazinone + sulfometuron-methyl	200 + 7.5	99	99	99
(10)	hexazinone + sulfometuron-methyl	200 + 10	99	99	99
(11)	hexazinone + sulfometuron-methyl	200 + 15	99	99	99
(12)	hexazinone + sulfometuron-methyl	200 + 20	100	99	99
(13)	hexazinone + sulfometuron-methyl	200 + 30	99	99	99
(14)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 5	99	97	99
(15)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 10	100	98	99
(16)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 20	100	99	99
(17)	diuron + hexazinone + sulfometuron-methyl	936 + 264 + 30	100	99	99
(18)	amicarbazone	1400	100	100	99
(19)	control	–	0	0	0

EXAMPLE 8 – COMPARATIVE

In this test, herbicide treatments containing a mixture of diuron, hexazinone and sulfometuron-methyl, isoxaflutole, a mixture of clomazone and hexazinone, a mixture of diuron and hexazinone, or sulfometuron-methyl were applied to a sugarcane field on light soil during the "pre-emergence ratoon cane" period. The field was infested with seeds of the weeds *Sida rhombifolia* L., *Amaranthus deflexus* L. and *Portulaca oleracea* L. The herbicide treatments were applied before emergence of these weeds. This test was conducted using four replications and a "randomized complete block" design. The herbicide treatments were prepared by diluting herbicide formulations with water, and the resulting aqueous mixtures were applied to the selected areas as a broadcast spray.

The results were evaluated for both sugarcane phytotoxicity and weed control at 95 days after treatment. Both sugarcane crop phytotoxicity and weed control were visually determined on a 0 to 100 percent scale. For crop phytotoxicity, about 30% may be considered the commercially acceptable upper limit of injury without economic loss. Sugarcane phytotoxicity results are listed in Table 8A, and weed control results are listed in Table 8B.

Table 8B shows all of the herbicide treatments providing excellent control of *Sida rhombifolia*, *Amaranthus deflexus* and *Portulaca oleracea* in this test. The control plots showed a low infestation of these weeds, which facilitated their control.

The results in Table 8A show some of the treatments caused noticeable sugarcane phytotoxicity. While the treatments of sulfometuron-methyl alone caused 10 to 15% injury even at application rates as low as 30 g a.i./ha, combinations with mixtures of diuron and hexazinone eliminated the phytotoxicity. Thus these results show that the synergic mixture of the present invention surprisingly reduces the phytotoxic effect of sulfometuron-methyl while retaining excellent control of weeds.

Although mixtures of diuron and hexazinone were shown to be safe to sugarcane, the treatments using isoxaflutole and a mixture of clomazone and hexazinone caused up to 15% injury. The injury symptoms caused by isoxaflutole included chlorosis, leaf whitening and suppression of cane development. Although 15% injury is presently considered commercially acceptable, it is nevertheless undesirable.

TABLE 8A

SUGARCANE PHYTOTOXICITY RESULTS

	Treatments (Active ingredients)	Application Rate (g a.i./ha)	Formulation Dose (g /ha)	% Phytotoxicity	
				Average	Variation
(1)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 15	1500 + 20	0	0
(2)	(diuron + hexazinone) + sulfometuron-	(702 + 198) +	1500 + 27	0	0

	methyl	20			
(3)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 25	1500 + 33	0	0
(4)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 30	1500 + 40	0	0
(5)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 15	1700 + 20	0	0
(6)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 20	1700 + 27	0	0
(7)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 25	1700 + 33	0	0
(8)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 30	1700 + 40	0	0
(9)	isoxaflutole	135	180	15	15 – 15
(10)	clomazone + hexazinone	800 + 200	2000	12	10 – 15
(11)	diuron + hexazinone	796 + 224	1700	0	0
(12)	sulfometuron-methyl	30	40	11	10 – 15
(13)	sulfometuron-methyl	60	80	12	10 – 15
(14)	control	–	–	0	0

TABLE 8B

WEED CONTROL

	Treatments (Active ingredients)	Application Rate (g a.i./ha)	% Control		
			Sida rhombifolia	*Amaranthus deflexus*	*Portulaca oleracea*
(1)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 15	100	100	100
(2)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 20	100	100	100
(3)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 25	100	100	100
(4)	(diuron + hexazinone) + sulfometuron-methyl	(702 + 198) + 30	100	100	100
(5)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 15	100	100	100
(6)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 20	100	100	100
(7)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 25	100	100	100
(8)	(diuron + hexazinone) + sulfometuron-methyl	(796 + 224) + 30	100	100	100

(9)	isoxaflutole	135	100	100	100
(10)	clomazone + hexazinone	800 + 200	100	100	100
(11)	diuron + hexazinone	796 + 224	100	100	100
(12)	sulfometuron-methyl	30	99	100	100
(13)	sulfometuron-methyl	60	100	100	100
(14)	control	–	0	0	0

EXAMPLE 9 – COMPARATIVE

In this test, herbicide treatments containing imazapic, isoxaflutole, a mixture of hexazinone and clomazone or a mixture of hexazinone, diuron and sulfometuron-methyl were applied to a field with heavy soil at the time of the year when *Sorghum halepense* (L.) Pers. had not yet emerged and sugarcane had been cut and not yet sprouted (pre-emergence ratoon cane stage). The test was conducted using a "randomized complete block" design. The herbicide treatments were prepared by diluting herbicide formulations with water, and the resulting aqueous mixtures were applied to the selected areas as a broadcast spray.

The results were evaluated 100 days after treatment. Control of *Sorghum halepense* was visually determined using a 0 to 100 percent scale, wherein 0 means no weed control and 100 means complete control. The results are shown in Table 9.

The results show the present invention is useful for the control of *Sorghum halepense*, because it provided more than 80% control even after 100 days. This was significantly better control than provided by the other previously developed products.

TABLE 9

CONTROL OF *SORGHUM HALEPENSE*

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	Formulation Dose (g/ha)	% Control
(A)	imazapic	140	200	70
(B)	isoxaflutole	150	200	72
(C)	hexazinone + clomazone	220 + 880	2200	65
(D)	hexazinone + diuron + sulfometuron-methyl	255 + 905 + 22	1500	69
(E)	hexazinone + diuron + sulfometuron-methyl	289 + 1025 + 25	1700	75
(F)	hexazinone + diuron + sulfometuron-methyl	323 + 1146 + 28	1900	84
(G)	hexazinone + diuron +	357 + 1266 +	2100	81

	sulfometuron-methyl	30		

EXAMPLE 10 – COMPARATIVE

In this test, herbicide treatments containing a mixture of hexazinone, diuron and sulfometuron-methyl, isoxaflutole, imazapic, or a mixture of hexazinone and clomazone were applied to a field with medium soil at the time of the year when *Spermacoce latifolia* Aubl. had not yet emerged and sugarcane had been cut and not yet sprouted (pre-emergence ratoon cane stage). The test was conducted using a "randomized complete block" design. The herbicide treatments were prepared by diluting herbicide formulations with water, and the resulting aqueous mixtures were applied to the selected areas as a broadcast spray.

The results were evaluated 82 days after treatment. Control of *Spermacoce latifolia* was visually determined using a 0 to 100 percent scale, wherein 0 means no weed control and 100 means complete control. The results are shown in Table 10.

The results show the mixture of the present invention is useful for the control of *Sorghum halepense*, because it provided more than 90% control even after 82 days. This was significantly better control than provided by the other previously developed products.

TABLE 10

CONTROL OF *SPERMACOCE LATIFOLIA*

	Treatments (Active Ingredients)	Application Rate (g a.i./ha)	Formulation Dose (g/ha)	% Control
(A)	hexazinone + diuron + sulfometuron-methyl	255 + 905 + 22	1500	80
(B)	hexazinone + diuron + sulfometuron-methyl	289 + 1025 + 25	1700	87
(C)	hexazinone + diuron + sulfometuron-methyl	323 + 1146 + 28	1900	86
(D)	hexazinone + diuron + sulfometuron-methyl	357 + 1266 + 30	2100	90
(E)	hexazinone + diuron + sulfometuron-methyl	578 + 2050 + 49	3400	92
(F)	isoxaflutole	150	200	51
(G)	imazapic	140	200	62
(H)	hexazinone + clomazone	220 + 880	2200	83
(I)	control	–	–	0

As the person skilled in the art will realize in light of the above teachings, the scope of the invention allows numerous modifications and variations. It should therefore be understood in reading the attached claims that the invention can be embodied in ways besides those specifically described herein.

CLAIMS

What is claimed is:

1. A mixture characterized by comprising at least one sulfonylurea herbicide, diuron and hexazinone, or salts thereof.

2. The mixture of Claim 1, characterized by the sulfonylurea herbicide being selected from the group consisting of amidosulfuron, azimsulfuron, bensulfuron-methyl, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethametsulfuron-methyl, ethoxysulfuron, flucetosulfuron, flupyrsulfuron-methyl, flazasulfuron, foramsulfuron, halosulfuron-methyl, imazosulfuron, iodosulfuron-methyl, mesosulfuron-methyl, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron-methyl, prosulfuron, pyrazosulfuron-ethyl, rimsulfuron, sulfometuron-methyl, sulfosulfuron, thifensulfuron-methyl, triasulfuron, tribenuron-methyl, trifloxysulfuron, triflusulfuron-methyl and tritosulfuron.

3. The mixture of Claim 2, characterized by the sulfonylurea herbicide being selected from sulfometuron-methyl, rimsulfuron and/or metsulfuron-methyl.

4. The mixture of Claim 3, characterized by the sulfonylurea herbicide being sulfometuron-methyl.

5. The mixture of Claim 1, characterized by comprising about 12 g to 17 g of sulfonylurea, about 500 g to 700 g of diuron and about 150 g to 190 of hexazinone per kg of the mixture.

6. The mixture of Claim 5, characterized by comprising about 14.5 g of sulfonylurea, about 603 g of diuron and about 170 g of hexazinone per kg of the mixture.

7. The mixture of Claim 1, characterized by the mixture comprising at least one inert component.

8. The mixture of Claim 1, characterized by being in the form of powder, granules, pellets, solution, suspension, emulsion, wettable powder or emulsifiable concentrate.

9. The mixture of Claim 8, characterized by being in the form of granules.

10. The mixture of Claim 9, characterized by being in the form of water-dispersible granules.

11. The mixture of Claim 1, characterized by being a mixture of separate granule formulations, each one comprising one or two active ingredient components selected from at least one sulfonylurea herbicide, diuron and hexazinone.

12. The mixture of Claim 11, characterized by the separate granule formulations being in a homogeneous mixture.

13. The mixture of Claim 12, characterized by being a mixture of 753.9 g of a first formulation containing 800 g of diuron per kg, 226.8 g of a second formulation containing 750 g of hexazinone per kg and 19.3 g of a third formulation containing 750 g of sulfometuron-methyl per kg.

14. A method for controlling undesirable vegetation, characterized by comprising application of the mixture as defined in any one of Claims 1 to 13 to the locus where undesirable vegetation is to be controlled.

15. The method of Claim 14, characterized by comprising the application of the mixture to a crop of cotton, soy, coffee, sugarcane, citrus, maize, peanuts, wheat, pasture, pine or eucalyptus.

16. The method of Claim 15, characterized by comprising the application of the mixture to a crop of coffee, sugarcane, citrus, pine or eucalyptus.

17. The method of Claim 16, characterized by comprising the application of the mixture to a sugarcane crop.

18. The method of Claim 17, characterized by comprising the application of the mixture to the sugarcane crop in a pre-emergence ratoon cane period.

19. A method for controlling undesirable vegetation, characterized by comprising application of the mixture defined in Claims 5 or 6 in an amount of about 1.3 to 1.7 kg per hectare, wherein the locus of the undesirable vegetation comprises light soil.

20. A method for controlling undesirable vegetation, characterized by comprising application of the mixture defined in Claims 5 or 6 in an amount of about 1.5 to 1.9 kg per hectare, wherein the locus of the undesirable vegetation comprises medium soil.

21. A method for controlling undesirable vegetation, characterized by comprising application of the mixture defined in Claims 5 or 6 in an amount of about 1.7 to 2.3 kg per hectare, wherein the locus of the undesirable vegetation comprises heavy soil.

22. The method of Claim 14, characterized by comprising the application of the mixture during a dry period.

23. The method of Claim 14, characterized by comprising the application of the mixture when the historical average daily rainfall is no more than about 2 mm.

24. The method of Claim 23, characterized by comprising the application of the mixture when the historical average daily rainfall is no more than about 1 mm.

25. The method of any one of Claims 22, 23 or 24, characterized by comprising the application of the mixture to a sugarcane crop in a pre-emergence ratoon cane stage.

26. The method of Claim 14, characterized by comprising the application of the mixture during the beginning of a rainy period.

27. The method of Claim 26, characterized by comprising the application of the mixture to a sugarcane crop during a pre-emergence ratoon cane period.

28. The method of Claim 26, characterized by comprising the application of the mixture to a sugarcane crop during the post-emergence ratoon cane period by directed application avoiding contact with sugarcane foliage.

29. The method of Claim 14, characterized by the undesirable vegetation comprising broad or narrow leaf vegetation.

30. The method of Claim 29, characterized by the undesirable vegetation comprising *Digitaria nuda*.

31. The use of a herbicide mixture, characterized by being the use of the mixture as defined by any one of Claims 1 to 13 for controlling undesirable broad or narrow leaf vegetation.

32. The use of Claim 31, characterized by being for the control of *Digitaria nuda*.

33. The use of a herbicide for the control of undesirable vegetation, characterized by being the use of a sulfonylurea herbicide for the control of *Digitaria nuda*.

34. The use of Claim 33, characterized by the sulfonylurea herbicide being selected from sulfometuron-methyl, rimsulfuron, metsulfuron-methyl and mixtures thereof.

35. The use of Claim 34, characterized by the sulfonylurea herbicide being selected from sulfometuron-methyl, rimsulfuron and mixtures thereof.

36. The use of Claim 35, characterized by the sulfonylurea herbicide being sulfometuron-methyl.