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(54) Title: SALTS OF CARBOXYLIC ACID HERBICIDES

(57) Abstract: Amine salts of certain herbicides that in free acid form include at least one carboxylic acid moiety are described. Herbicide salts comprising the cation of various imidazole, piperazine, piperidine, and morpholine compounds are provided. The herbicide amine salts described are suitable for formulation into herbicidal application mixtures and/or stable concentration compos-
itions that exhibit acceptable volatility characteristics upon application.



SALTS OF CARBOXYLIC ACID HERBICIDES

FIELD OF THE INVENTION

[0001] The present invention generally relates to various salts of carboxylic acid herbicides. In particular, the present invention is directed to amine salts of certain herbicides that in free acid form include at least one carboxylic acid moiety. The herbicide amine salts are suitable for formulation into herbicidal application mixtures and/or stable concentrate compositions that exhibit acceptable volatility characteristics upon application.

BACKGROUND OF THE INVENTION

[0002] Various herbicides in free acid form, such as many auxin herbicides, have at least one carboxylic acid moiety. Auxin herbicides having at least one carboxylic acid moiety include 3,6-dichloro-2-methoxybenzoic acid (dicamba); 2,4-dichlorophenoxyacetic acid (2,4-D); 4-(2,4 dichlorophenoxy)butanoic acid (2,4-DB); 2-(2,4-dichlorophenoxy)propanoic acid (dichloroprop); 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA); 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB); 4-amino-3,6-dichloro-2-pyridinecarboxylic acid (aminopyralid); 3,6-dichloro-2-pyridinecarboxylic acid (clopyralid); 2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid (fluroxypyr); [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid (triclopyr); 2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop); 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid (picloram); 3,7-dichloro-8-quinolinecarboxylic acid (quinclorac); and 6-amino-5-chloro-2-cyclopropyl-4-pyrimidinecarboxylic acid (aminocyclopyrachlor). In particular, dicamba and 2,4-D have proven to be effective auxin herbicides.

[0003] Generally, synthetic auxin herbicides such as dicamba and 2,4-D mimic or act like natural auxin plant growth regulators. Auxin herbicides appear to affect cell wall plasticity and nucleic acid metabolism, which can lead to uncontrolled cell division and growth. The injury symptoms caused by auxin herbicides include epinastic bending and twisting of stems and petioles, leaf cupping and curling, and abnormal leaf shape and venation.

[0004] In order to provide enhanced solubility and increased herbicide loading for greater ease in formulation, conventional dicamba and other carboxylic acid auxin herbicide products are typically formulated as water-soluble salt solutions. For example, CLARITY (available from BASF) is a formulation containing the diglycolamine salt of dicamba and BANVEL (available from Arysta LifeScience North America LLC) is a formulation containing the dimethylamine salt of dicamba.

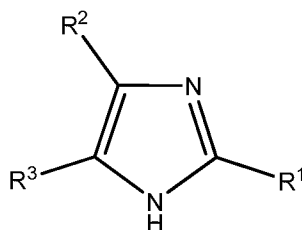
[0005] Off-site movement is sometimes associated with auxin herbicides. Volatile auxin herbicides like dicamba and 2,4-D can, under certain conditions of application, volatilize into the surrounding atmosphere and migrate from the application site to adjacent crop plants, such as soybeans and cotton, where contact damage to sensitive plants can occur. Typical symptoms of injury to crop plants include leaf cupping, leaf malformation, leaf necrosis, terminal bud kill and/or delayed maturity.

[0006] Some strategies to reduce herbicide volatilization have focused on encapsulation. In one approach, dicamba is absorbed into solid phase natural or synthetic polymers. However, the resulting particle sizes are typically not suitable for spray application and therefore limited to granular drop application. Micro-encapsulation in a polymer shell is also known in the art, but the relatively high solubility of dicamba and its salts precludes successful use of the technology in aqueous suspensions, and commercial dicamba micro-encapsulation products have not been developed.

[0007] Thus, a need persists for the identification of alternative salts of carboxylic acid herbicides that are suitable for formulation into herbicidal application mixtures and/or concentrate compositions that exhibit acceptable stability and compatibility characteristics. Preferably, the carboxylic acid herbicide salts exhibit low volatility in herbicide compositions that are efficacious, yet non-phytotoxic to sensitive crops located in areas adjacent to the target site and resist adverse effects to their volatility characteristics when tank mixed with other co-herbicides such as glyphosate.

SUMMARY OF THE INVENTION

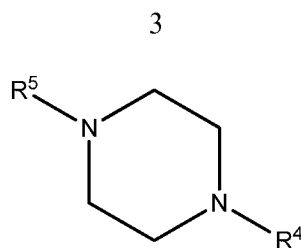
[0008] The present invention is directed to herbicide salts comprising an anion of a carboxylic acid herbicide and a cation of a compound selected from the group consisting of:
(a) Formula I:



Formula I

wherein R¹, R² and R³ are independently hydrogen or substituted or unsubstituted hydrocarbyl;

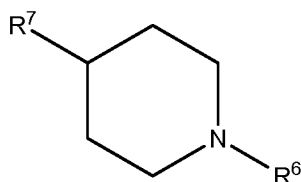
(b) Formula II:



Formula II

wherein R^4 and R^5 are independently hydrogen or substituted or unsubstituted hydrocarbyl, provided that when R^5 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl;

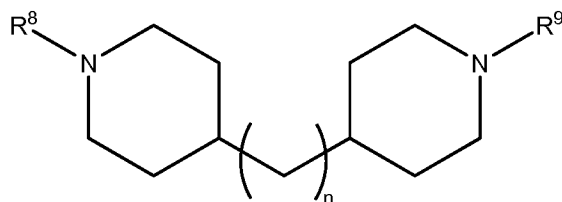
(c) Formula III:



Formula III

wherein R^6 is hydrogen, substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted heteroaryl and R^7 is hydrogen, oxo, or unsubstituted or substituted hydrocarbyl, provided that when R^6 is an unsubstituted C_1 - C_6 alkyl, then R^7 is not an aminoalkyl or when R^7 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^6 is not an aminoalkyl;

(d) Formula IV:

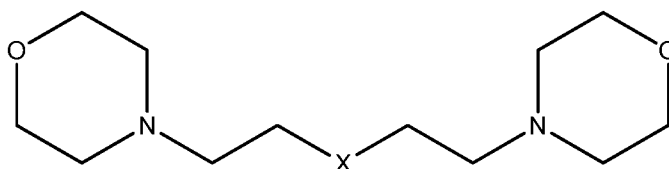


Formula IV

wherein n is from 1 to about 20, from 1 to about 10, from about 3 to about 10, or from about 3 to about 6 (e.g., 3) and R^8 and R^9 are independently any substituent as defined for R^7 ;

(e) Formula V:

4



Formula V

wherein X is O, NR¹⁰ or S and R¹⁰ is hydrogen or C₁₋₆ alkyl; and tautomers and mixtures thereof.

[0009] The present invention is further directed to herbicidal application mixtures comprising the herbicidal salts described herein useful for killing or controlling the growth of unwanted plants.

[0010] Other objects and features will be in part apparent and in part pointed out hereinafter.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] In general, the present invention is directed to amine salts of carboxylic acid herbicides which, in free acid form, have at least one carboxylic acid moiety.

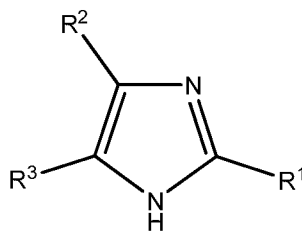
[0012] In accordance with the present invention, amine salts of carboxylic acid herbicides are provided that are suitable for formulation into herbicidal application mixtures and/or concentrate compositions that exhibit acceptable stability and compatibility characteristics. Herbicide salts are provided that are suitable for preparing stable, highly loaded herbicidal solutions, concentrates and/or emulsion concentrates. In accordance with some preferred embodiments, the herbicidal amine salts are selected so as to exhibit relatively low volatility. As compared to conventional herbicide salts known in the art, it is believed that some of the preferred herbicide salts of the present invention provide enhanced protection from offsite movement while maintaining comparably effective herbicidal efficacy on unwanted plants located in the target area. Further, herbicides salts are provided that are stable and resist adverse effects to their volatility characteristics upon mixing or formulating with other ingredients such as co-herbicides (e.g., glyphosate or glufosinate).

[0013] Typically, a herbicide salt of the present invention is derived from a carboxylic acid herbicide and a base compound (e.g., amine). For example, in one method, herbicide in free acid form is mixed with an amine base in water or other suitable solvent. As recognized by those skilled in the art, formation of the herbicide salt results from proton exchange between the carboxylic acid moiety and base.

[0014] The herbicide salts of the present invention comprise a carboxylate anion of a carboxylic acid herbicide. For example, in various embodiments, the herbicide salt may comprise the carboxylate anion of a herbicide selected from the group consisting of 3,6-dichloro-2-methoxybenzoic acid (dicamba); 2,4-dichlorophenoxyacetic acid (2,4-D); 4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB); 2-(2,4-dichlorophenoxy)propanoic acid (dichloroprop); 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA); 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB); 4-amino-3,6-dichloro-2-pyridinecarboxylic acid (aminopyralid); 3,6-dichloro-2-pyridinecarboxylic acid (clopyralid); 2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid (fluroxypyr); [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid (triclopyr); 2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop); 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid (picloram); 3,7-dichloro-8-quinolinecarboxylic acid (quinclorac); 6-amino-5-chloro-2-cyclopropyl-4-pyrimidinecarboxylic acid (aminocyclopyrachlor) and combinations thereof. In certain embodiments, the herbicide salt comprises the carboxylate anion of 3,6-dichloro-2-methoxybenzoic acid (dicamba) or 2,4-dichlorophenoxyacetic acid (2,4-D).

[0015] In accordance with the present invention, the herbicide salts further comprise a cation of various imidazole compounds, piperazine compounds, piperidine compounds, and morpholine compounds. Accordingly, as discussed in detail below, in various embodiments, the herbicide salt comprises an anion of a carboxylic acid herbicide and a cation of a compound selected from the group consisting of imidazole derivatives, piperazine derivatives, piperidine derivatives, and morpholine derivatives and mixtures thereof.

[0016] In particular embodiments, the herbicide salt of the present invention comprises a cation of an imidazole compound of Formula I:

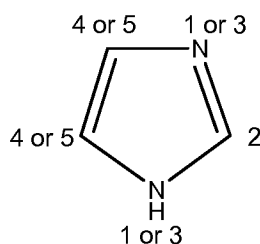


Formula I

wherein R^1 , R^2 and R^3 (i.e., the 2-, 4-, and/or 5- positions, respectively, as shown below) are independently hydrogen or substituted or unsubstituted hydrocarbyl. In accordance with some embodiments of the present invention, the cation derived from a compound of Formula I is a 2-,

4-, and/or 5-substituted imidazole cation (i.e., at least one of R^1 , R^2 and R^3 are independently substituted or unsubstituted hydrocarbyl).

[0017] In general, the naming of imidazole moieties discussed herein follows conventional organic chemistry nomenclature. For purposes of clarity, the ring positions on an imidazole ring are numbered as shown below.



The carbon atom between the two nitrogen atoms is referred to as the 2-position. The two nitrogen atoms adjacent the 2-position carbon atom are each referred to as either the 1 or 3 position, and the remaining two carbon atoms are referred to as either the 4- or 5-position. These positions are determined according to the naming convention which uses the lowest possible numbers for the substituents. Further, it is recognized that tautomers of imidazole moieties may exist in equilibrium in solution. For simplicity, when discussing imidazole moieties herein, only one tautomeric form is named or shown, but it is understood that such name or structure represents the other tautomer(s) as well.

[0018] Without being bound by theory, in some instances, selection of higher hydrocarbyl substituents that are relatively more hydrophobic are believed to enhance the low volatility characteristics of the herbicide salt (e.g., ethyl is preferable over methyl and so on). However, should an aqueous herbicidal solution or formulation of the salt be desired, the substituents are also selected to ensure sufficient water solubility. Accordingly, in various embodiments, R^1 , R^2 and R^3 are independently hydrogen, substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

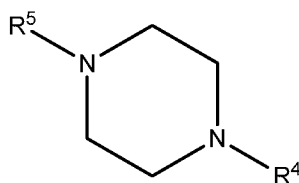
[0019] In some embodiments, R^1 is a substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In these and other embodiments, R^1 is a substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_{10} alkanol, substituted or unsubstituted C_5 - C_{10} cycloalkyl, substituted or unsubstituted C_3 - C_{10} heterocycloalkyl,

substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In some embodiments, R^1 is a C_1 - C_6 alkyl (preferably C_2 - C_6 alkyl), C_1 - C_6 alkanol, C_5 - C_6 cycloalkyl, or aryl. Still in other embodiments, R^1 is a C_1 - C_6 alkyl (preferably methyl, ethyl, isopropyl) or aryl (preferably phenyl).

[0020] Further, in various embodiments, R^2 and R^3 are independently hydrogen, substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_{10} alkanol, substituted or unsubstituted C_5 - C_{10} cycloalkyl, substituted or unsubstituted C_3 - C_{10} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In some embodiments, R^2 and R^3 are independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl. In these and other embodiments, R^2 and R^3 are independently hydrogen or substituted or unsubstituted C_1 - C_6 alkyl and more preferably C_1 - C_6 alkyl such as methyl or ethyl.

[0021] When R^1 , R^2 and/or R^3 of Formula I is a substituted group such as substituted hydrocarbyl, substituted alkyl, substituted alkanol, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl, the substituted group preferably includes one or more substituents selected from group consisting of alkyl, alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino. Even more preferably, these substituted groups are substituted with one or more substituents selected from group consisting of C_{1-6} alkyl, C_{1-6} alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino.

[0022] In other embodiments, the herbicide salt of the present invention comprises a cation of a piperazine compound. In particular, the herbicide salt comprises a cation of a compound of Formula II:



Formula II

wherein R^4 and R^5 are independently hydrogen or substituted or unsubstituted hydrocarbyl, provided that when R^5 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl.

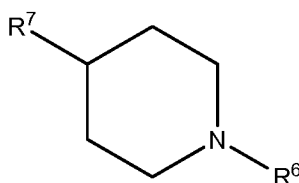
[0023] In some embodiments, only one nitrogen atom is substituted on the piperazine ring (e.g., R^5 is hydrogen). In these embodiments, R^4 is a substituted or unsubstituted C_1 - C_{20}

alkyl (other than an aminoalkyl), substituted or unsubstituted C₁-C₂₀ alkanol, substituted or unsubstituted C₅-C₂₀ cycloalkyl, substituted or unsubstituted C₃-C₂₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In these and other embodiments, R⁴ is a substituted or unsubstituted C₁-C₁₀ alkyl (other than an aminoalkyl), substituted or unsubstituted C₁-C₁₀ alkanol, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In some embodiments, R⁴ is a substituted or unsubstituted C₁-C₆ alkyl (other than an aminoalkyl), substituted or unsubstituted C₁-C₆ alkanol, or substituted or unsubstituted C₅-C₆ cycloalkyl. In particular embodiments, R⁴ is a C₁-C₆ alkyl (preferably ethyl, propyl, butyl, pentyl, or hexyl), C₁-C₆ alkanol (preferably hydroxyethyl), or a C₅-C₆ cycloalkyl (preferably cyclohexyl).

[0024] In other embodiments, both nitrogen atoms of the piperazine ring are substituted (i.e., R⁴ and R⁵ are not hydrogen). In these embodiments, R⁴ and R⁵ are independently substituted or unsubstituted C₁-C₂₀ alkyl, substituted or unsubstituted C₁-C₂₀ alkanol, substituted or unsubstituted C₅-C₂₀ cycloalkyl, substituted or unsubstituted C₃-C₂₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl, provided that when R⁵ is an unsubstituted C₁-C₆ alkyl, then R⁴ is not an aminoalkyl or when R⁴ is an unsubstituted C₁-C₆ alkyl, then R⁵ is not an aminoalkyl. In these and other embodiments, R⁴ and R⁵ are independently substituted or unsubstituted C₁-C₁₀ alkyl, substituted or unsubstituted C₁-C₁₀ alkanol, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl, provided that when R⁵ is an unsubstituted C₁-C₆ alkyl, then R⁴ is not an aminoalkyl or when R⁴ is an unsubstituted C₁-C₆ alkyl, then R⁵ is not an aminoalkyl. In some embodiments, R⁴ and R⁵ are independently C₁-C₆ substituted or unsubstituted alkyl, C₁-C₆ substituted or unsubstituted alkanol, substituted or unsubstituted C₅-C₆ cycloalkyl or substituted or unsubstituted C₃-C₆ heterocycloalkyl, provided that when R⁵ is an unsubstituted C₁-C₆ alkyl, then R⁴ is not an aminoalkyl or when R⁴ is an unsubstituted C₁-C₆ alkyl, then R⁵ is not an aminoalkyl. In particular embodiments, R⁴ and R⁵ are independently a C₁-C₆ alkyl (preferably methyl, ethyl, propyl, or butyl), C₁-C₆ alkanol (preferably hydroxyethyl), or a C₅-C₆ cycloalkyl (preferably cyclohexyl). In certain embodiments, the R⁴ and R⁵ are the same substituent (e.g., R⁴ and R⁵ are both methyl). In various embodiments, R⁴ and R⁵ are not aminoalkyl.

[0025] When R^4 and/or R^5 of Formula II is a substituted group such as substituted hydrocarbyl, substituted alkyl, substituted alkanol, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl, the substituted group preferably includes one or more substituents selected from group consisting of alkyl, alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino. Even more preferably, these substituted groups are substituted with one or more substituents selected from group consisting of C_{1-6} alkyl, C_{1-6} alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino.

[0026] In other embodiments, the herbicide salt of the present invention comprises a cation of a piperidine compound. In particular, the herbicide salt comprises a cation of a compound of Formula III:



Formula III

wherein R^6 is substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted heteroaryl and R^7 is hydrogen, oxo, or unsubstituted or substituted hydrocarbyl, provided that when R^6 is an unsubstituted C_1 - C_6 alkyl, then R^7 is not an aminoalkyl or when R^7 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^6 is not an aminoalkyl.

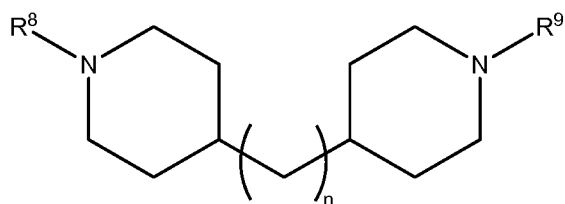
[0027] In various embodiments, R^6 is a substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_{10} alkanol, substituted or unsubstituted C_5 - C_{10} cycloalkyl, substituted or unsubstituted C_3 - C_{10} heterocycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted heteroaryl, provided that when R^6 is an unsubstituted C_1 - C_6 alkyl, then R^7 is not an aminoalkyl or when R^7 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^6 is not an aminoalkyl. In these and other embodiments, R^6 is a substituted or unsubstituted C_1 - C_6 alkyl, substituted or unsubstituted C_1 - C_6 alkanol, C_5 - C_6 cycloalkyl, C_3 - C_6 heterocycloalkyl, aryl or alkylaryl, provided that when R^6 is an unsubstituted C_1 - C_6 alkyl, then R^7 is not an aminoalkyl or when R^7 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^6 is not an aminoalkyl. In particular embodiments, R^6 is a C_1 - C_6 alkyl (preferably methyl, ethyl, propyl, isobutyl), C_1 - C_6 alkanol (preferably hydroxyethyl),

C₃-C₆ heterocycloalkyl (preferably piperdyl), aryl (preferably phenyl), or alkylaryl (preferably benzyl), provided that when R⁶ is an unsubstituted C₁-C₆ alkyl, then R⁷ is not an aminoalkyl. In various embodiments, R⁶ is not an aminoalkyl.

[0028] Further, in various embodiments, R⁷ is hydrogen, oxo, substituted or unsubstituted C₁-C₂₀ alkyl, substituted or unsubstituted C₅-C₂₀ cycloalkyl, substituted or unsubstituted C₃-C₂₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. More particularly, in these and other embodiments R⁷ is hydrogen, oxo, substituted or unsubstituted C₁-C₁₀ alkyl, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl. In certain embodiments, R⁷ is hydrogen or oxo. In various embodiments, R⁷ is not an aminoalkyl.

[0029] When R⁶ and/or R⁷ of Formula III is a substituted group such as substituted alkyl, substituted alkanol, substituted cycloalkyl, substituted heterocycloalkyl, substituted aryl, and substituted heteroaryl, the substituted group preferably includes one or more substituents selected from group consisting of alkyl, alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino. Even more preferably, these substituted groups are substituted with one or more substituents selected from group consisting of C₁₋₆ alkyl, C₁₋₆ alkoxy, hydroxyl, oxy, phenyl, carboxyl, and amino.

[0030] In various embodiments, the herbicide salt of the present invention comprises a cation of a bispiperidine compound. In particular, the herbicide salt comprises a cation of a compound of Formula IV:

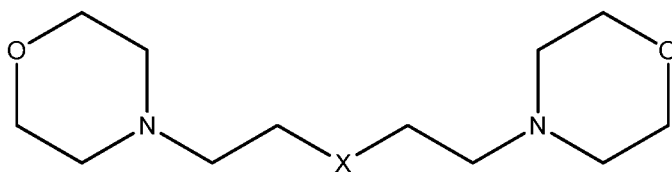


Formula IV

wherein n is from 1 to about 20, from 1 to about 10, from about 3 to about 10, or from about 3 to about 6 (e.g., 3) and R⁸ and R⁹ are independently any substituent as defined above for R⁷ in Formula III. For example, in various embodiments, R⁸ and R⁹ are each methyl or hydrogen.

[0031] In other embodiments, the herbicide salt of the present invention comprises a cation of a bismorpholine compound. In particular, the herbicide salt comprises a cation of a compound of Formula V:

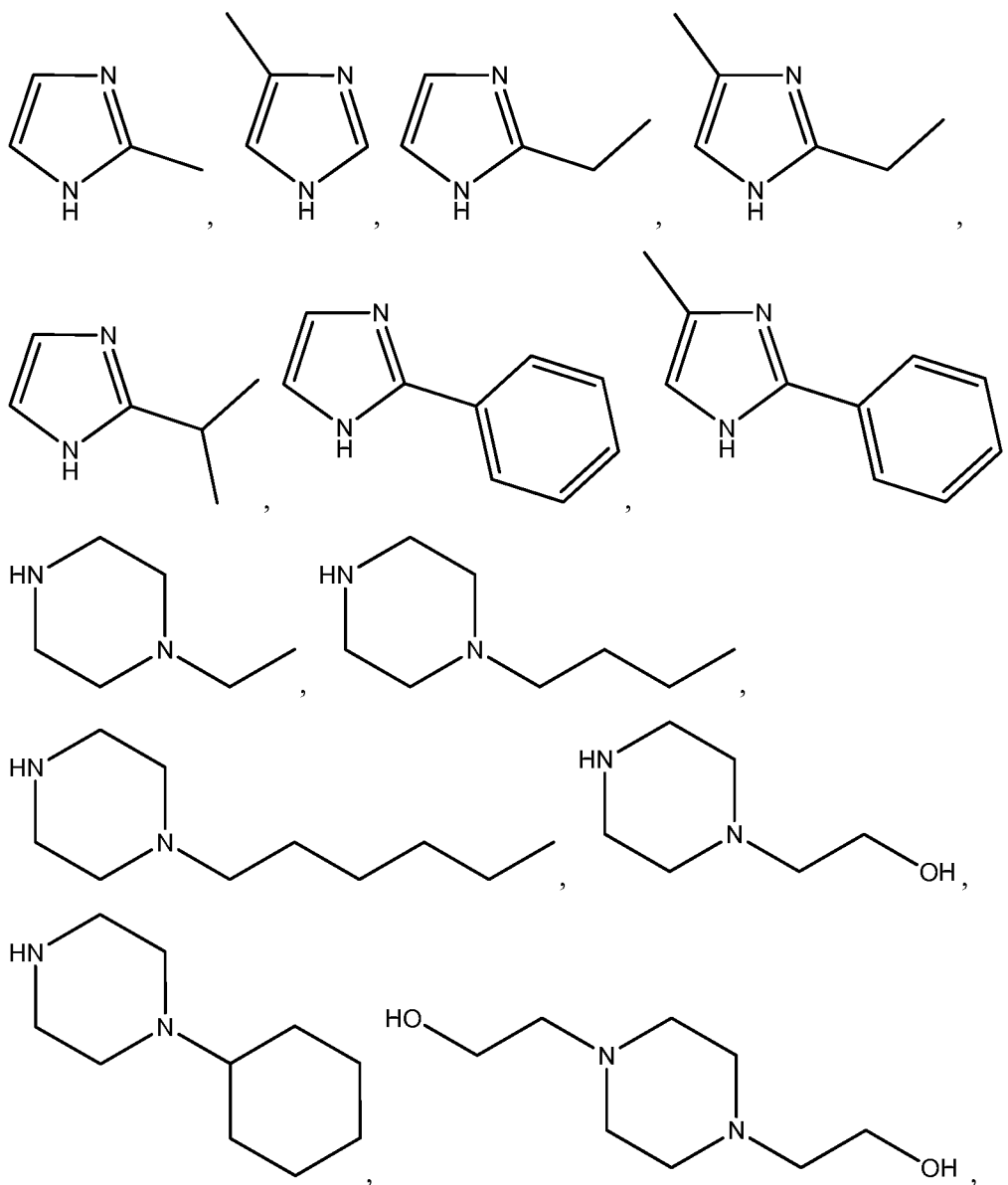
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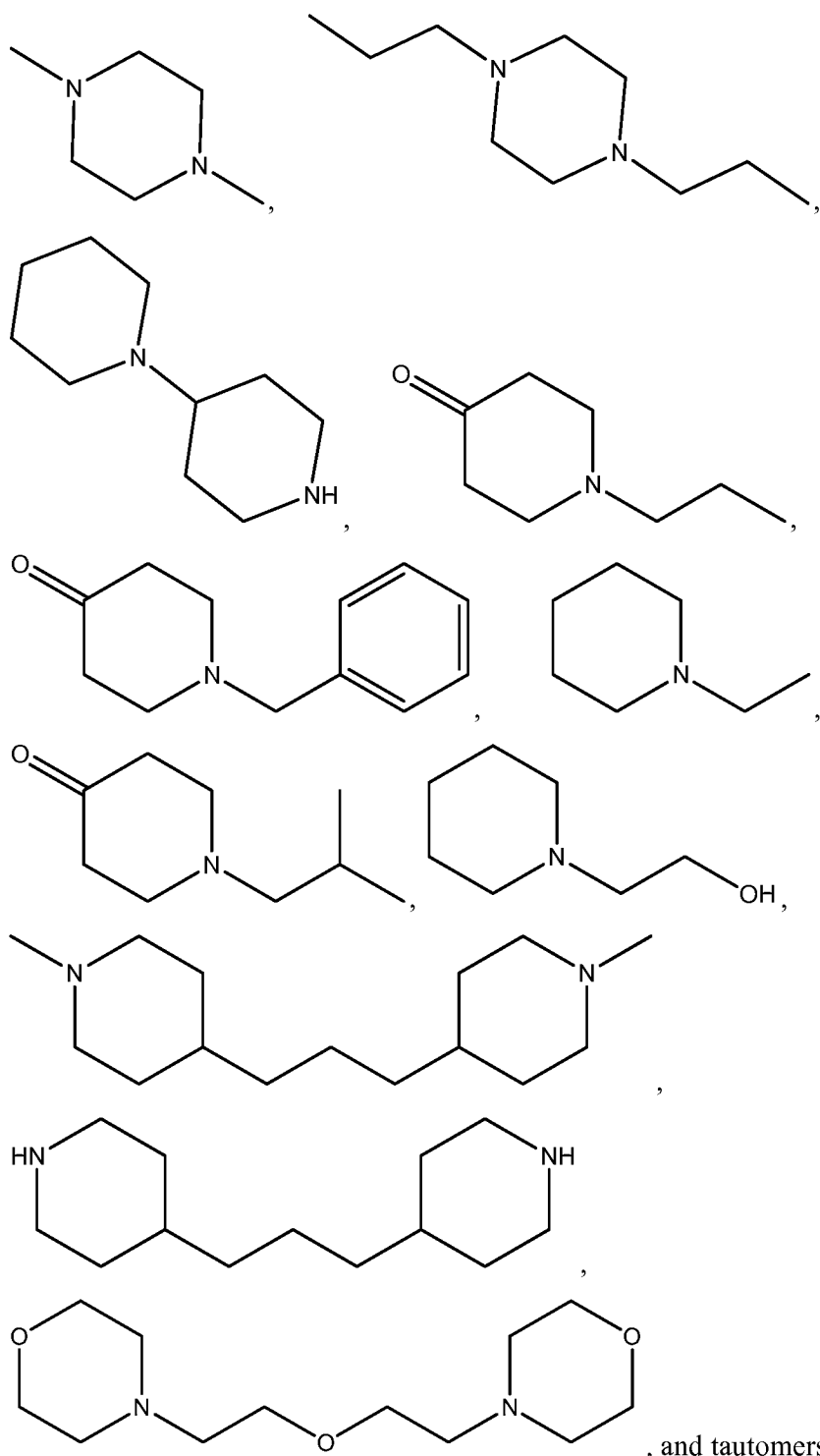
Formula V

wherein X is O, NR¹⁰ or S and R¹⁰ is hydrogen or C₁₋₆ alkyl.

[0032] In certain embodiments, the herbicide salt of the present invention comprises a cation of a compound selected from the group consisting of:



12



[0033] The herbicide salts may be derived from carboxylic acid herbicides and a base compound (e.g., amine). As noted above, in one method, herbicide in free acid form is mixed with an amine in water or other suitable solvent.

[0034] Typically, when preparing the herbicide salts of the present invention from a carboxylic acid herbicide containing a single carboxylic acid moiety and a base compound containing a single amine functional group susceptible to forming a cation, equimolar or excess base is used. However, when using some base compounds that contain more than a single amine functional group (e.g., di- and tri-amines), equimolar or excess base compound may be unnecessary. With carboxylic acid herbicides containing more than one carboxylic acid moiety and/or base compounds containing more than one amine functional group, the relative proportions of base compound and herbicide free acid are adjusted as necessary. Accordingly, in various embodiments, the molar ratio of the base compound to carboxylic acid herbicide is typically at least about 0.4:1, at least about 0.5:1, at least about 0.6:1, at least about 0.7:1, at least about 0.8:1, at least about 0.9:1, at least about 1:1, at least about 1.1:1, at least about 1.2:1, at least about 1.3:1, at least about 1.4:1, at least about 1.5:1, at least about 1.6:1, at least about 1.7:1, at least about 1.8:1, at least about 1.9:1, or at least about 2:1. In these and other embodiments, the molar ratio of the base compound to carboxylic acid herbicide may range from about 0.4:1 to about 2:1, from about 0.5:1 to about 2:1, from about 0.7:1 to about 2:1, from about 0.8:1 to about 1.8:1, from about 1:1 to about 2:1, from about 1.2:1 to about 1.8:1, from about 0.5:1 to about 1.5:1, or from about 1:1 to about 1.5:1.

[0035] Stated in other terms, equimolar or excess cations (i.e., proton-accepting groups) are typically provided when preparing the herbicide salts of the present invention. Accordingly, in various embodiments the molar ratio of cations to carboxylic acid herbicide anions (i.e., proton-donating groups) is at least about 1:1, at least about 1.1:1, at least about 1.2:1, at least about 1.3:1, at least about 1.4:1, at least about 1.5:1, at least about 1.6:1, at least about 1.7:1, at least about 1.8:1, at least about 1.9:1, or at least about 2:1. In these and other embodiments, the molar ratio of cations to carboxylic acid herbicide anions may range from about 1:1 to about 2:1, from about 1:1 to about 1.8:1, from about 1.1:1 to about 2:1, from about 1.2:1 to about 1.8:1, or from about 1:1 to about 1.5:1.

[0036] In certain instances, water-soluble herbicide salts are desirable so that aqueous herbicidal solutions or formulations can be prepared. Accordingly, in various embodiments, the herbicide amine salts in accordance with the present invention are water-soluble such that they may be dissolved in an aqueous solution or formulated in an aqueous solution concentrate. In other instances, water-insoluble herbicide salts may be desirable. Therefore, in accordance with other embodiments, the herbicide salts in accordance with the

present invention are water-insoluble such that they may be dissolved in an organic solvent or incorporated into an emulsion concentrate or suspension.

[0037] Suspensions of water-insoluble herbicide salts can be made by milling or grinding the dry herbicide salt in a milling machine such as an Eiger mill to the desired particle size (e.g., under 10 μm). Other adjuvants such as defoaming agents, dispersants, and stabilizers may be added during the milling process. Subsequently, the milled or ground herbicide salt particles are mixed with a liquid medium to form the suspension.

[0038] The herbicide salts of the present invention may be used in the preparation of herbicide formulations further comprising one or more additional co-herbicides. Co-herbicides include other carboxylic acid herbicides and salts thereof (e.g., auxin herbicide salts as previously described). Co-herbicides also include acetyl CoA carboxylase (ACCase) inhibitors, acetolactate synthase (ALS) or acetohydroxy acid synthase (AHAS) inhibitors, photosystem II inhibitors, photosystem I inhibitors, protoporphyrinogen oxidase (PPO or Protox) inhibitors, carotenoid biosynthesis inhibitors, enolpyruvyl shikimate-3-phosphate (EPSP) synthase inhibitor, glutamine synthetase inhibitor, dihydropteroate synthetase inhibitor, mitosis inhibitors, 4-hydroxyphenyl-pyruvate-dioxygenase (4-HPPD) inhibitors, synthetic auxins, auxin transport inhibitors and nucleic acid inhibitors, salts and esters thereof; racemic mixtures and resolved isomers thereof; and combinations thereof. Specific examples of possible co-herbicides include 2,4-D, aminocyclopyrachlor, mecoprop, mecoprop-P, triclopyr, acetochlor, acifluorfen, alachlor, atrazine, azafenidin, bifenox, butachlor, butafenacil, carfentrazone-ethyl, diuron, dithiopyr, flufenpyr-ethyl, flumiclorac-pentyl, flumioxazin, fluoroglycofen, fluthiacet-methyl, fomesafen, glyphosate, glufosinate, imazethapyr, lactofen, metazochlor, metolachlor (and S-metolachlor), metribuzin, oxadiargyl, oxadiazon, oxyfluorfen, pretilachlor, propachlor, propisochlor, pyraflufen-ethyl, sulfentrazone and thenylchlor, and salts and esters thereof; racemic mixtures and resolved isomers thereof, and combinations thereof. In some embodiments, the co-herbicide is a photosystem II inhibitor selected from, for example, ametryn, amicarbazone, atrazine, bentazon, bromacil, bromoxynil, chlorotoluron, cyanazine, desmedipham, desmetryn, dimefuron, diuron, fluometuron, hexazinone, ioxynil, isoproturon, linuron, metamitron, methibenzuron, metoxuron, metribuzin, monolinuron, phenmedipham, prometon, prometryn, propanil, pyrazon, pyridate, siduron, simazine, simetryn, tebuthiuron, terbacil, terbumeton, terbuthylazine and trietazine, salts and esters thereof, and mixtures thereof. In another embodiment, the co-herbicide is a 4-HPPD inhibitor selected from, for

example, mesotrione, isoxaflutole, benzofenap, pyrazolynate, pyrazoxyfen, sulcotrione, tembotrione, and tropamezone.

[0039] In accordance with another embodiment, the co-herbicide is a graminicide selected from butoxydim, clethodim, cycloxydim, sethoxydim, tepraloxydim, tralkoxydim, profoxydim, haloxyfop, propaquizafop and the C₁₋₄ alkyl and propargyl esters of clodinafop, cyhalofop, diclofop, fenoxaprop, fluazifop, fluazifop-P, haloxyfop, quizalofop and quizalofop-P (e.g., quizalofop-ethyl or quizalofop-P-ethyl, clodinafop-propargyl, cyhalofop-butyl, diclofop-methyl, fenoxaprop-P-ethyl, fluazifop-P-butyl, haloxyfop-methyl, haloxyfop-R-methyl).

[0040] In various embodiments, the herbicide salts of the present invention (e.g., salts of dicamba and/or 2,4-D) are used in the preparation of an herbicidal formulation containing glyphosate or glufosinate or salts or esters thereof as a co-herbicide.

[0041] The herbicide salts of the present invention may be used in the preparation of concentrate, tank mix or ready-to-use (RTU) formulations. Tank mix and RTU formulations comprising one or more of the herbicide salts of the present invention and optionally one or more co-herbicides typically comprise from about 0.1 g a.e./L to about 50 g a.e./L total herbicide loading while concentrate formulations typically comprise from about 50 to about 750 g a.e./L, from about 300 to about 750 g a.e./L, from about 350 to about 750 g a.e./L, from about 400 to about 750 g a.e./L, from about 450 to about 750 g a.e./L, or even from about 500 to about 750 g a.e./L total herbicide loading (for example, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, or even 750 g a.e./L, and ranges thereof). In co-herbicide formulations, the weight ratio on an acid equivalent basis of the carboxylic acid herbicide amine salt to the total co-herbicide is typically no greater than about 50:1, for example, about 50:1, 25:1, 10:1, 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, 1:5 or even about 1:10 and ranges thereof (e.g., from about 50:1 to about 1:10, from about 50:1 to about 1:5, from about 50:1 to about 1:1, from about 50:1 to about 3:1, from about 50:1 to about 5:1, from about 50:1 to about 10:1, from about 25:1 to about 1:1, or from about 25:1 to about 3:1, on an acid equivalent basis).

[0042] The herbicide salts of the present invention may be formulated with other conventional adjuvants, excipients or additives known to those skilled in the art. These other additives or ingredients may be introduced into the compositions of the present invention to provide or improve certain desired properties or characteristics of the formulated product. Hence, the herbicidal composition may further comprise one or more additional ingredients selected from, without limitation, surfactants, foam-moderating agents, preservatives or anti-microbials, antifreeze agents, solubility-enhancing agents, dispersants, stabilizers, dyes, and

thickening agents. For example, in various embodiments, the herbicidal composition comprising an herbicidal salt of the present invention, further comprises a surfactant selected from the group consisting of alkoxyated tertiary etheramines, alkoxyated quaternary etheramines, alkoxyated etheramine oxides, alkoxyated tertiary amines, alkoxyated quaternary amines, alkoxyated polyamines, sulfates, sulfonates, phosphate esters, alkyl polysaccharides, alkoxyated alcohols, and combinations thereof. The weight ratio of the carboxylic acid herbicide amine salt acid equivalent to surfactant can be readily determined by those skilled in the art (e.g., from about 1:1 to about 20:1, from about 2:1 to about 10:1 or from about 3:1 to about 8:1).

[0043] Application mixtures of the herbicides salts of the present invention may be prepared by dissolving the salts in water or other suitable solvent or by suitable dilution of a concentrate composition and applying to the foliage of unwanted plants by methods known in the art. The application mixture is applied to the foliage of a plant or plants at an application rate sufficient to give a commercially acceptable rate of weed control. This application rate is usually expressed as amount of herbicide per unit area treated, e.g., grams acid equivalent per hectare (g a.e./ha). Depending on plant species and growing conditions, the period of time required to achieve a commercially acceptable rate of weed control can be as short as a week or as long as three weeks, four weeks or 30 days. Application mixtures of the herbicides salts can be applied before planting, at planting, pre-emergence, or post-emergence to crop plants depending on the particular herbicide salt and crop plant.

[0044] Application mixtures prepared with the herbicide salts of the present invention may be applied to the foliage of crop plants and/or unwanted plants in the proximity of crop plants. Crop plants include hybrids, inbreds, and transgenic or genetically modified plants having specific traits or combinations of traits including, without limitation, herbicide tolerance (e.g., tolerant to carboxylic acid herbicides or other herbicides), *Bacillus thuringiensis* (Bt), high oil, high lysine, high starch, nutritional density, and drought resistance. Particular crop plants include, for example, corn, peanuts, potatoes, soybeans, canola, alfalfa, sugarcane, sugar beets, peanuts, grain sorghum (milo), field beans, rice, sunflowers, wheat and cotton. In various embodiments, the crop plant is selected from the group consisting of soybeans, cotton, peanuts, rice, wheat, canola, alfalfa, sugarcane, sorghum, and sunflowers. In other embodiments, the crop plant is selected from the group consisting of corn, soybean and cotton.

[0045] Herbicidal application mixtures prepared with herbicide salts of the present invention are particularly suited for application to transgenic plants having certain herbicide

tolerance traits. In some embodiments, the crop plants are resistant to carboxylic acid herbicides (e.g., dicamba and/or 2,4-D) and/or other herbicides (e.g., glyphosate). For example, an application mixture comprising a dicamba salt or 2,4-D salt of the present invention would be especially suited for applying to the foliage of auxin-susceptible plants growing in and/or adjacent to a field of crop plants comprising transgenic crop plants having a dicamba tolerance trait or 2,4-D tolerance trait, respectively. Further, a spray formulation comprising a carboxylic acid herbicide salt of the present invention and a co-herbicide comprising glyphosate or glufosinate (or salts thereof) would be especially suited for applying to the foliage of carboxylic acid herbicide-susceptible plants and plants susceptible to the co-herbicide growing in and/or adjacent to a field of crop plants comprising transgenic crop plants having stacked carboxylic acid herbicide tolerance trait and a glyphosate or glufosinate tolerance trait, respectively.

[0046] Herbicidal application mixtures containing a herbicide salt of the present invention can be applied pre-planting of the crop plant, such as from about two to about three weeks before planting herbicide-susceptible crop plants or crop plants not having a herbicide tolerance trait. Crop plants that are not susceptible to carboxylic acid herbicides or certain co-herbicides, (e.g., corn with respect to auxin herbicides), or plants having carboxylic acid herbicide tolerance and co-herbicide tolerance traits typically have no pre-planting restriction and the application mixture can be applied immediately before planting such crops. The application mixture can be applied at planting, pre-emergence, or post-emergence to crop plants to control carboxylic acid herbicides-susceptible weeds and, if a co-herbicide is present, co-herbicide-susceptible weeds in a field of the crop plants.

[0047] As mentioned above, volatility is a known problem of application mixtures containing salts of many carboxylic acid herbicides. Without being bound by theory, in some instances, the salts of the present invention are believed to provide desirable low volatility and reduced associated offsite movement. It has been discovered that significant decreases in volatility may be realized when using the herbicide salts of the present invention. An application mixture containing a herbicide salt of the present invention may provide greater than about 20%, 30%, 40%, 50%, 60%, 65%, 75%, 80%, or 85% reduction in volatility when compared to a similar conventional herbicide mixtures.

[0048] Volatility reduction may be quantified experimentally by methods known in the art. In one method the volatility of solutions containing a herbicide salt can be measured in the gas phase (air) via tube tests. In a tube test, a sample of the herbicide solution is placed in a test tube that has been modified to allow air flow through the tube. A selective collection

medium is attached to the outlet of the tube to collect volatilized herbicide. The collection medium is then analyzed for the respective herbicide. For further details see the Tube Test Protocol described in Example 2.

[0049] In another method, the volatility of solutions containing a herbicide salt can be evaluated by measuring herbicide concentrations in the gas phase (air) through air sampling in humidome plant growth chambers, which are maintained at constant temperature and humidity. For further details see the Humidome Protocol described in Example 2.

[0050] The term "hydrocarbyl" as used herein describes organic moieties consisting exclusively of the elements carbon and hydrogen and preferably containing 1 to about 50 carbon atoms, preferably 1 to about 30 carbon atoms, and even more preferably 1 to about 20 carbon atoms, including branched or unbranched, saturated or unsaturated and cyclic species. These moieties include alkyl, alkenyl, alkynyl, and aryl moieties optionally substituted with other aliphatic or cyclic hydrocarbon groups, such as alkaryl, alkenaryl and alkynaryl.

[0051] The term "substituted hydrocarbyl" as used herein describes hydrocarbyl moieties that are substituted with at least one atom other than carbon, including moieties in which a carbon chain or ring atom is substituted with a hetero atom such as nitrogen, oxygen, silicon, phosphorous, boron, sulfur, or a halogen atom. Unless otherwise stated, these substituents include halogen, heterocyclo, alkoxy, alkenoxy, alkynoxy, aryloxy, hydroxy, protected hydroxy, ketal, acyl, acyloxy, nitro, amino, amido, cyano, thiol, acetal, sulfoxide, ester, thioester, ether, thioether, hydroxyalkyl, urea, guanidine, amidine, phosphate, amine oxide, and quaternary ammonium salt.

[0052] Unless otherwise indicated, the alkyl groups described herein are preferably lower alkyl containing from 1 to 20 carbon atoms in the principal chain. They may be straight or branched chain or cyclic and include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, hexyl, 2-ethylhexyl, and the like.

[0053] The term "aryl" as used herein alone or as part of another group denote optionally substituted homocyclic aromatic groups, preferably monocyclic or bicyclic groups containing from 6 to 12 carbons in the ring portion, such as phenyl, biphenyl, naphthyl, substituted phenyl, substituted biphenyl or substituted naphthyl.

[0054] As used herein, the term "acid equivalent" or "a.e." refers to the amount of herbicide present without taking into account the weight of the counter-ion of the salt species present.

EXAMPLES

[0055] The following non-limiting examples are provided to further illustrate the present invention.

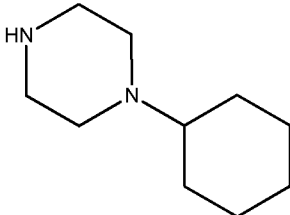
Example 1

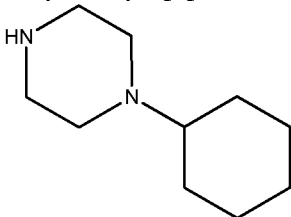
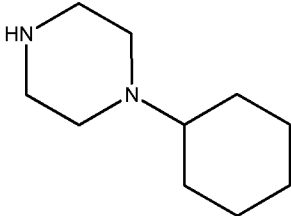
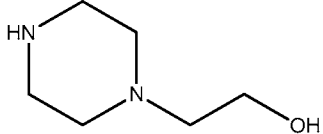
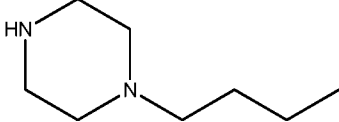
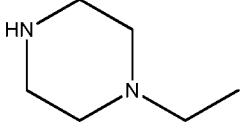
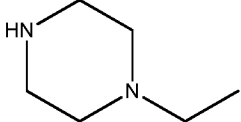
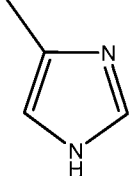
[0056] In this example, various salts of dicamba were prepared as described below with dicamba acid and various base compounds as listed below in Table 1.

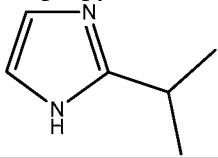
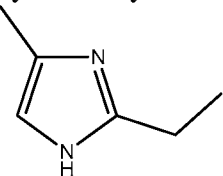
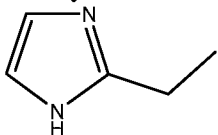
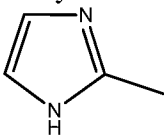
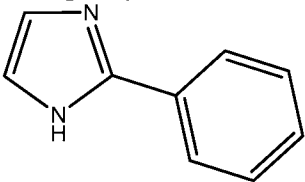
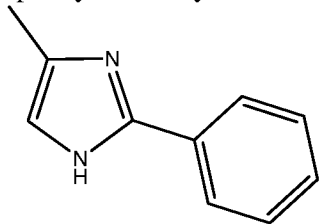
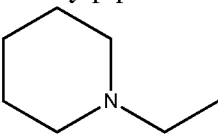
[0057] Various dicamba salts were prepared by mixing water and amine base reagents for a few minutes followed by addition of dicamba acid in one portion. The amount of dicamba acid added was pre-calculated based on the desired molar ratio of amine base compound to dicamba acid. The resulting mixtures were stirred for a period of time (e.g., from about 1 to about 24 hours) until all of the solids had dissolved by visual inspection. In some instances, heating of the reaction mixture was necessary to increase the reaction rate or facilitate completion of the reaction.

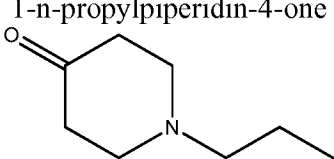
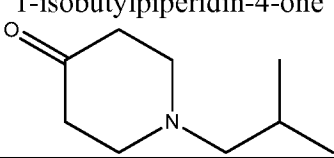
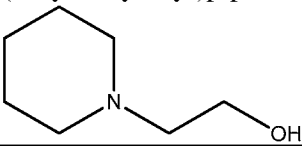
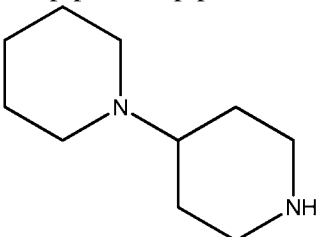
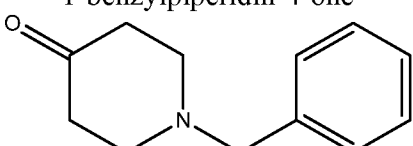
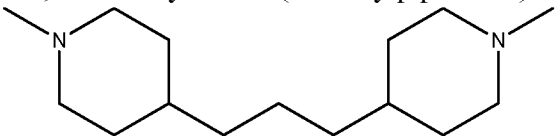
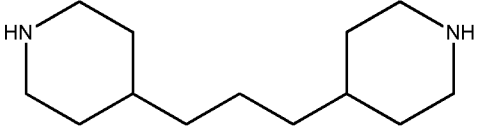
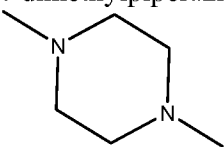
[0058] Various dicamba salts were also prepared according to the method described above, with the exception that the water was replaced by a suitable organic solvent (e.g., methanol). The amine base reagents and dicamba acid were dissolved in the solvent. The mixtures were stirred for at least for 2 hours in order to facilitate completion of the reaction. After reaction, the solvent was removed from the reaction mixture by either heating, application of vacuum, or the combination of both.

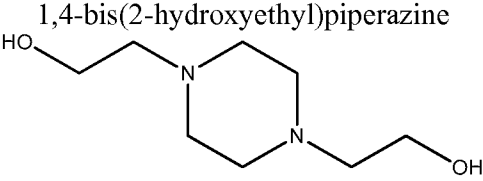
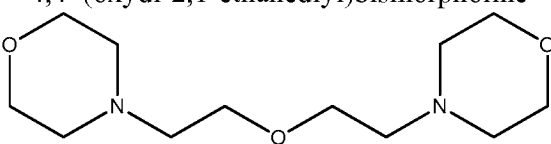
Table 1.

Salt No.	Base Compound	Approximate Base Compound to Dicamba Acid Molar Ratio	Solvent
1	1-cyclohexylpiperazine 	1:1	Methanol

Salt No.	Base Compound	Approximate Base Compound to Dicamba Acid Molar Ratio	Solvent
2	1-cyclohexylpiperazine 	0.67:1	Methanol
3	1-cyclohexylpiperazine 	1:1	Water
4	1-(2-hydroxyethyl)piperazine 	1:1	Water
5	1-n-butylpiperazine 	1:1	Water
6	1-ethylpiperazine 	1:1	Water
7	1-ethylpiperazine 	0.67:1	Water
8	4-methylimidazole 	1:1	Water

Salt No.	Base Compound	Approximate Base Compound to Dicamba Acid Molar Ratio	Solvent
9	2-isopropylimidazole 	1:1	Water
10	2-ethyl-4-methylimidazole 	1:1	Water
11	2-ethylimidazole 	1:1	Water
12	2-methylimidazole 	1:1	Water
13	2-phenylimidazole 	1:1	Methanol
14	2-phenyl-4-methylimidazole 	1:1	Methanol
15	1-ethylpiperidine 	1:1	Water

Salt No.	Base Compound	Approximate Base Compound to Dicamba Acid Molar Ratio	Solvent
16	1-n-propylpiperidin-4-one 	1.1:1	Water
17	1-isobutylpiperidin-4-one 	1:1	Water
18	1-(2-hydroxyethyl)piperidine 	1:1	Water
19	4-piperidinopiperidine 	0.5:1	Water
20	1-benzylpiperidin-4-one 	1:1	Methanol
21	4,4'-trimethylene-bis(1-methylpiperidine) 	0.5:1	Water
22	4,4'-trimethylenedipiperidine 	0.5:1	Water
23	1,4-dimethylpiperazine 	1:1	Water

Salt No.	Base Compound	Approximate Base Compound to Dicamba Acid Molar Ratio	Solvent
24	1,4-bis(2-hydroxyethyl)piperazine 	1:1	Water
25	4,4'-(oxydi-2,1-ethanediyl)bismorpholine 	0.69:1	Water

Example 2

[0059] In this example, various salts of dicamba prepared in Example 1 were selected for volatility testing. As described below, spray solutions containing the selected dicamba salts were prepared and subjected to volatility testing via the tube test and/or humidome protocols. Typically, the spray solutions containing the selected dicamba salts also contained potassium glyphosate co-herbicide. Aqueous test spray solutions containing selected salts of dicamba and potassium glyphosate were prepared by mixing a solution of dicamba salt with a solution of potassium glyphosate salt and adjusting the relative proportion and/or diluting with water to arrive at the desired concentration of dicamba and glyphosate.

Tube Test Protocol

[0060] To measure the dicamba concentration in the gas phase (air) volatilized from the spray solutions, 10 mL samples of each solution were placed into a 50 mL plastic centrifuge tube with one hole approximately 1/8 in (3.2 mm) diameter drilled into the tube at the mark between 20 mL and 30 mL lines. A 22 mm X 30 mm polyurethane foam (PUF), cut from a 76 mm length, available from SKC Inc., catalog # P22692, was placed into a glass tube of approximately 20 mm diameter with parafilm wrapped around the outside to obtain a snug fit into the top of the centrifuge tube. A hose was connected to the other end of the glass tube leading to a vacuum line. The air flow was regulated to approximately 2 L/min using a flow controller. Air was pulled through the tube at approximately 2 L/min for 24 hours. Note that the air conditions of flow rate, temperature, pressure and composition (e.g., relative humidity) are not narrowly critical as long as the various samples are analyzed under similar conditions.

For instance, air at from about 5°C to about 40°C, from about 0.5 to about 1.5 bar pressure, from about 0% to about 95% relative humidity, and at a flow rate of from about 0.1 to 10 L/min-mL sample could be suitably used for volatility analysis. In this test, the air pulled through the tubes was at about 35°C and about 40% relative humidity. The PUF was removed from the glass tube, extracted with 20 mL methanol and the resulting solution analyzed for dicamba concentration using liquid chromatography-mass spectroscopy (LC-MS) methods known in the art.

[0061] For comparison, samples of spray solutions containing 2 wt.% a.e. of the diglycolamine salt of dicamba (i.e., CLARITY) were also subjected to the tube test protocol. The comparison spray solution did not contain potassium herbicide co-herbicide.

[0062] The results of the tube tests are presented in Table 2. The reduction in volatility is calculated relative to the volatility of the samples containing the diglycolamine salt of dicamba.

Humidome Protocol

[0063] Humidomes were obtained from Hummert International (Part Nos 14-3850-2 for humidomes and 11-3050-1 for 1020 flat tray) and modified by cutting a 2.2 cm diameter hole on one end approximately 5 cm from the top to allow for insertion of a glass air sampling tube (22 mm OD) containing a polyurethane foam (PUF) filter. The sampling tube was secured with a VITON o-ring on each side of the humidome wall. The air sampling tube external to the humidome was fitted with tubing that was connected to a vacuum manifold immediately prior to sampling.

[0064] The flat tray beneath the humidome was filled with 1 liter of sifted dry or wet 50/50 soil (50% Redi-Earth and 50% US 10 Field Soil) to a depth of about 1 cm. To measure the dicamba concentration in the gas phase (air) volatilized from the spray solutions, samples of the spray solutions were sprayed over the soil in the humidome using a track sprayer at a rate of 10 gallons per acre (GPA). To avoid contamination of the sides of the flat tray, each tray was nested in an empty tray prior to spraying.

[0065] The flat tray bottom containing the dicamba formulation on soil was covered with a humidome lid and the lid was secured with clamps. The assembled humidomes were placed in a temperature and humidity controlled environment and connected to a vacuum manifold through the air sampling line. Air was drawn through the humidome and PUF at a rate of 2 liters per minutes (LPM) for 24 hours at which point the air sampling was stopped.

The humidomes were then removed from the controlled environment and the PUF filter was removed. The PUF filter was extracted with 20 mL of methanol and the solution was analyzed for dicamba concentration using LC-MS methods known in the art.

[0066] For comparison, samples of spray solutions containing the diglycolamine salt of dicamba (i.e., CLARITY) at approximately the same weight percent a.e. as the tested dicamba salt sprays were subjected to the humidome tests. The comparison spray solution did not contain potassium herbicide co-herbicide.

[0067] The results of the humidome tests are presented in Table 2. The reduction in volatility is calculated relative to the volatility of the samples containing the diglycolamine salt of dicamba.

[0068] The results of the volatility tests show that the selected dicamba salts were significantly less volatile than the solutions containing DGA dicamba.

Table 2.

Dicamba Salt No.	Dicamba Salt Concentration (wt.% a.e.)	Potassium Glyphosate Concentration (wt.% a.e.)	Volatility Reduction Over DGA Dicamba Spray (%)	
			Tube Test	Humidome Test
3	2	6	75	--
4	2	6	69	--
5	2	6	70	--
6	2	6	83	--
7	2	6	42	--
9	0.6	0.9	--	63
9	0.6	1.2	--	67
9	2	6	65	--
10	10	--	88	--
10	2	6	72	--
10	0.6	0.9	--	86
10	0.6	1.2	--	85
10	2.4	4.8		86
11	0.6	0.9	--	67
11	0.6	1.2	--	60
11	2	6	67	--
12	0.6	0.9	--	46
12	0.6	1.2	--	50
14	0.6	0.9	--	92
16	2	6	20	--
17	2	6	57	--
19	2	6	23	--
20	2	6	42	--
22	2	6	60	--
22	0.6	0.9	--	68
23	2	6	23	--
24	2	6	57	--
24	0.6	0.9	--	76
25	2	6	70	--
25	0.6	.9	--	76

--: Not tested or not present

Example 3

[0069] In this example, the herbicidal effectiveness of selected dicamba salts prepared in accordance with Example 1 was evaluated in greenhouse testing. The herbicidal effectiveness data set forth herein report "Weed killing efficacy" as a percentage following a

standard procedure in the art which reflects a visual assessment of plant mortality and growth reduction by comparison with untreated plants, made by technicians specially trained to make and record such observations. Such measurements are relied upon and regularly reported by Monsanto Company in the course of its herbicide business.

[0070] The following procedure was used for testing compositions of this example to determine herbicidal effectiveness.

[0071] Seeds of velvetleaf (ABUTH) were planted in 85 mm square pots in a soil mix which was previously steam sterilized and prefertilized with a 14-14-14 NPK slow release fertilizer at a rate of 3.6 kg/m³. The pots were placed in a greenhouse with sub-irrigation. About one week after emergence, seedlings were thinned as needed, including removal of any unhealthy or abnormal plants, to create a uniform series of test pots.

[0072] The plants were maintained for the duration of the test in the greenhouse where they received a minimum of 14 hours of light per day. If natural light was insufficient to achieve the daily requirement, artificial light with an intensity of approximately 475 microeinsteins was used to make up the difference. Exposure temperatures were not precisely controlled but averaged about 27°C during the day and about 21°C during the night. Plants were sub-irrigated throughout the test to ensure adequate soil moisture levels.

[0073] Application of herbicide salt solutions were made by spraying with a track sprayer fitted with a 9501E nozzle calibrated to deliver a spray volume of approximately 38 liters per hectare (l/ha). After treatment, pots were returned to the greenhouse until ready for evaluation.

[0074] For evaluation of herbicidal effectiveness, all plants in the test were examined by a single practiced technician, who recorded percent control, a visual measurement of the effectiveness of each treatment by comparison with untreated plants. Weed killing efficacy of 0% indicates no effect, and efficacy of 100% indicates that all of the plants are completely dead. Control of 85% or more is in most cases considered acceptable for normal herbicide use. However, in greenhouse tests such as those for this example it is normal to apply compositions at rates which give less than 85% control, as this makes it easier to discriminate among compositions having different levels of effectiveness. The weed killing efficacy was evaluated 21 days after the treatment. The table below lists the results of three imidazolum dicamba salts compared to CLARITY. The results show there is no significant difference between the imidazolum dicamba salts and CLARITY for weed control.

Table 3.

Dicamba salt	Application rate (g a.e. /ha)		
	140	280	560
	Weed killing efficacy (%)		
diglycolamine dicamba (CLARITY)	43.3	68.8	86.7
2-ethyl-4-methyl imidazolium dicamba	30.0	62.5	83.3
2-methyl imidazolium dicamba	40.0	66.7	85.0
2-ethyl imidazolium dicamba	38.3	67.5	80.8

[0075] When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

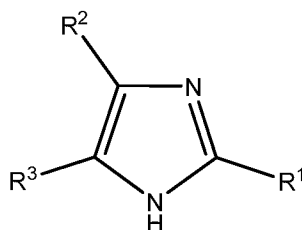
[0076] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0077] As various changes could be made in the above compositions and processes without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

WHAT IS CLAIMED IS:

1. A herbicide salt comprising an anion of a carboxylic acid herbicide and a cation of a compound selected from the group consisting of:

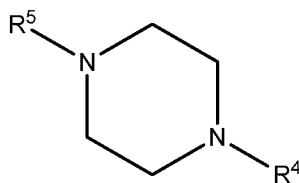
(a) Formula I:



Formula I

wherein R^1 , R^2 and R^3 are independently hydrogen or substituted or unsubstituted hydrocarbyl;

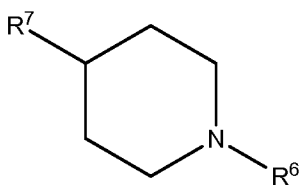
(b) Formula II:



Formula II

wherein R^4 and R^5 are independently hydrogen or substituted or unsubstituted hydrocarbyl, provided that when R^5 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl;

(c) Formula III:

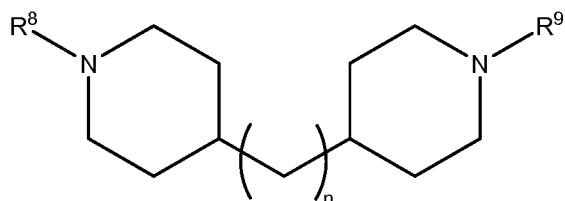


Formula III

wherein R^6 is hydrogen, substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted heteroaryl and R^7 is hydrogen, oxo, or unsubstituted or substituted hydrocarbyl, provided that when R^6 is an unsubstituted C_1 - C_6 alkyl, then R^7 is not an

aminoalkyl or when R^7 is hydrogen or an unsubstituted C_1 - C_6 alkyl, then R^6 is not an aminoalkyl;

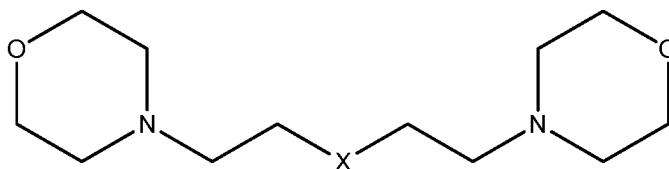
(d) Formula IV:



Formula IV

wherein n is from 1 to about 20, from 1 to about 10, from about 3 to about 10, or from about 3 to about 6 (e.g., 3) and R^8 and R^9 are independently any substituent as defined for R^7 ;

(e) Formula V:



Formula V

wherein X is O, NR^{10} or S and R^{10} is hydrogen or C_{1-6} alkyl; and tautomers and mixtures thereof.

2. The herbicide salt of claim 1 comprising a cation of the compound of Formula I.

3. The herbicide salt of claim 1 or 2 wherein R^1 , R^2 and R^3 are independently hydrogen, substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

4. The herbicide salt of any of claims 1 to 3 wherein R^1 is a substituted or unsubstituted C_1 - C_{20} alkyl, substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

5. The herbicide salt of any of claims 1 to 4 wherein R^1 is a substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_{10} alkanol, substituted or unsubstituted C_5 - C_{10}

cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

6. The herbicide salt of any of claims 1 to 5 wherein R¹ is a C₁-C₆ alkyl, C₁-C₆ alkanol, C₅-C₆ cycloalkyl, or aryl.

7. The herbicide salt of any of claims 1 to 6 wherein R¹ is a C₁-C₆ alkyl or aryl.

8. The herbicide salt of any of claims 1 to 7 wherein R¹ is methyl, ethyl, isopropyl, or phenyl.

9. The herbicide salt of any of claims 1 to 8 wherein R² and R³ are independently hydrogen, substituted or unsubstituted C₁-C₁₀ alkyl, substituted or unsubstituted C₁-C₁₀ alkanol, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

10. The herbicide salt of any of claims 1 to 9 wherein R² and R³ are independently hydrogen or substituted or unsubstituted C₁-C₁₀ alkyl.

11. The herbicide salt of any of claims 1 to 10 wherein R² and R³ are independently hydrogen or substituted or unsubstituted C₁-C₆ alkyl.

12. The herbicide salt of any of claims 1 to 11 wherein R² and R³ are independently hydrogen or C₁-C₆ alkyl.

13. The herbicide salt of any of claims 1 to 12 wherein R² and R³ are independently hydrogen or methyl.

14. The herbicide salt of claim 1 comprising a cation of the compound of Formula II.

15. The herbicide salt of any of claims 1 to 14 wherein R⁴ and R⁵ are independently substituted or unsubstituted C₁-C₂₀ alkyl, substituted or unsubstituted C₁-C₂₀ alkanol, substituted or unsubstituted C₃-C₂₀ cycloalkyl, substituted or unsubstituted C₁-C₂₀ heterocycloalkyl,

substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl, provided that when R^5 is an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl.

16. The herbicide salt of any of claims 1 to 15 wherein R^4 and R^5 are independently substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_{10} alkanol, substituted or unsubstituted C_5 - C_{10} cycloalkyl, substituted or unsubstituted C_3 - C_{10} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl provided that when R^5 is an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl.

17. The herbicide salt of any of claims 1 to 16 wherein R^4 and R^5 are independently C_1 - C_6 substituted or unsubstituted alkyl, C_1 - C_6 substituted or unsubstituted alkanol, substituted or unsubstituted C_5 - C_6 cycloalkyl or substituted or unsubstituted C_3 - C_6 heterocycloalkyl provided that when R^5 is an unsubstituted C_1 - C_6 alkyl, then R^4 is not an aminoalkyl or when R^4 is an unsubstituted C_1 - C_6 alkyl, then R^5 is not an aminoalkyl.

18. The herbicide salt of any of claims 1 to 17 wherein R^4 and R^5 are independently C_1 - C_6 alkyl, C_1 - C_6 alkanol, or C_5 - C_6 cycloalkyl.

19. The herbicide salt of any of claims 1 to 18 wherein R^4 and R^5 are independently methyl, ethyl, propyl, butyl, hydroxyethyl, or cyclohexyl.

20. The herbicide salt of any of claims 1 to 19 wherein R^5 is hydrogen.

21. The herbicide salt of claim 20 wherein R^4 is a substituted or unsubstituted C_1 - C_{20} alkyl (other than an aminoalkyl), substituted or unsubstituted C_1 - C_{20} alkanol, substituted or unsubstituted C_5 - C_{20} cycloalkyl, substituted or unsubstituted C_3 - C_{20} heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

22. The herbicide salt of claim 21 wherein R^4 is a substituted or unsubstituted C_1 - C_{10} alkyl (other than an aminoalkyl), substituted or unsubstituted C_1 - C_{10} alkanol, substituted or

unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

23. The herbicide salt of claim 22 wherein R⁴ is a substituted or unsubstituted C₁-C₆ alkyl (other than an aminoalkyl), substituted or unsubstituted C₁-C₆ alkanol, or substituted or unsubstituted C₅-C₆ cycloalkyl.

24. The herbicide salt of claim 23 wherein R⁴ is a C₁-C₆ alkyl, C₁-C₆ alkanol, or a C₅-C₆ cycloalkyl.

25. The herbicide salt of claim 24 wherein R⁴ is ethyl, propyl, butyl, pentyl, hexyl, hydroxyethyl, or cyclohexyl.

26. The herbicide salt of claim 1 comprising a cation of the compound of Formula III.

27. The herbicide salt of any of claims 1 to 26 wherein R⁶ is a substituted or unsubstituted C₁-C₁₀ alkyl, substituted or unsubstituted C₁-C₁₀ alkanol, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted heteroaryl.

28. The herbicide salt of any of claims 1 to 27 wherein R⁶ is a substituted or unsubstituted C₁-C₆ alkyl, substituted or unsubstituted C₁-C₆ alkanol, C₃-C₆ cycloalkyl, C₃-C₆ heterocycloalkyl, aryl or alkylaryl.

29. The herbicide salt of any of claims 1 to 28 wherein R⁶ is a C₁-C₆ alkyl, C₁-C₆ alkanol, C₃-C₆ heterocycloalkyl, aryl or alkylaryl.

30. The herbicide salt of any of claims 1 to 29 wherein R⁶ is methyl, ethyl, propyl, isobutyl, hydroxyethyl, benzyl, phenyl, or piperdyl.

31. The herbicide salt of any of claims 1 to 30 wherein R⁷ is hydrogen, oxo, substituted or unsubstituted C₁-C₂₀ alkyl, substituted or unsubstituted C₅-C₂₀ cycloalkyl, substituted or

unsubstituted C₃-C₂₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

32. The herbicide salt of any of claims 1 to 31 wherein R⁷ is hydrogen, oxo, substituted or unsubstituted C₁-C₁₀ alkyl, substituted or unsubstituted C₅-C₁₀ cycloalkyl, substituted or unsubstituted C₃-C₁₀ heterocycloalkyl, substituted or unsubstituted aryl, or substituted or unsubstituted heteroaryl.

33. The herbicide salt of any of claims 1 to 32 wherein R⁷ is hydrogen or oxo.

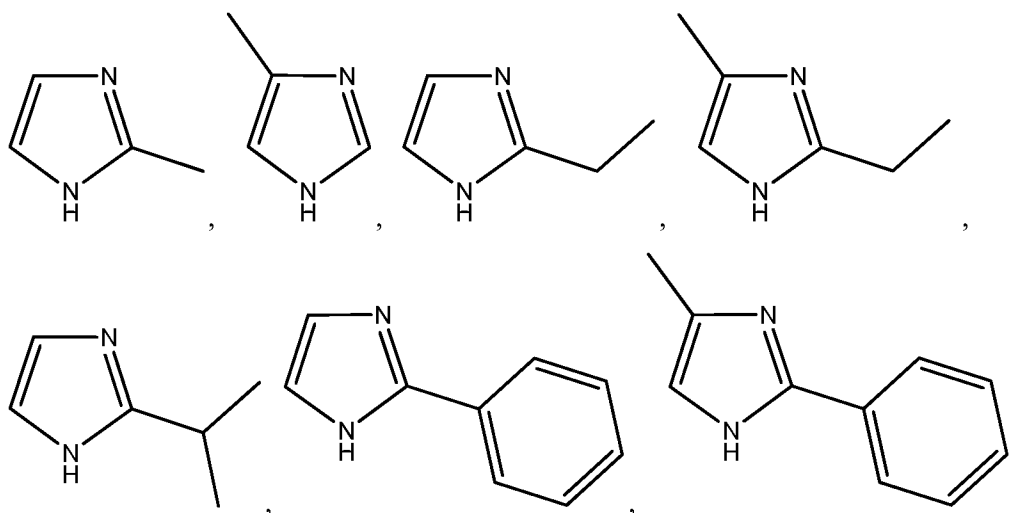
34. The herbicide salt of claim 1 comprising a cation of the compound of Formula IV.

35. The herbicide salt of any of claims 1 to 34 wherein n is from 1 to about 10, 3 to about 10, 3 to about 6, or 3.

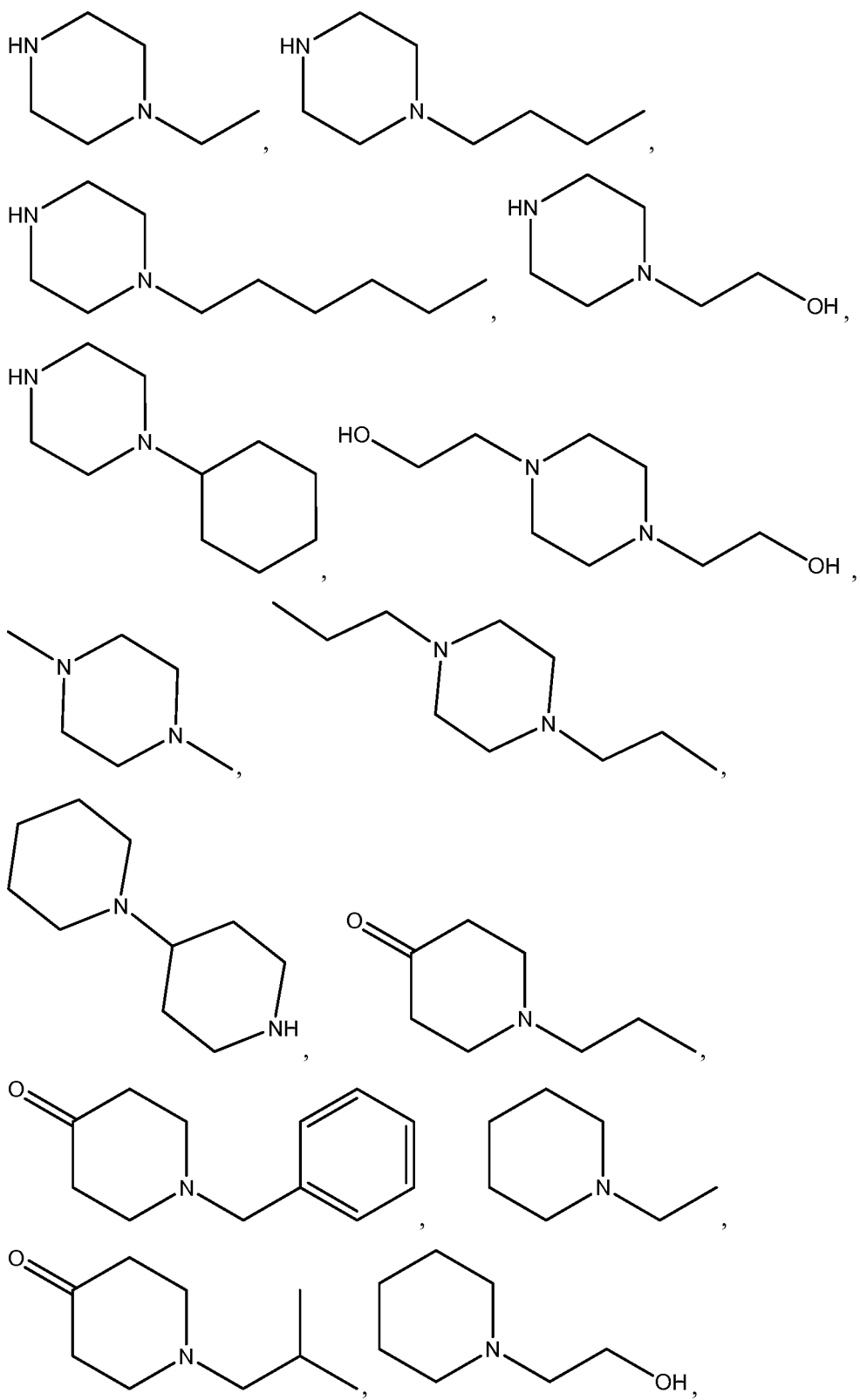
36. The herbicide salt of any of claims 1 to 35 wherein R⁸ and R⁹ are independently hydrogen or methyl.

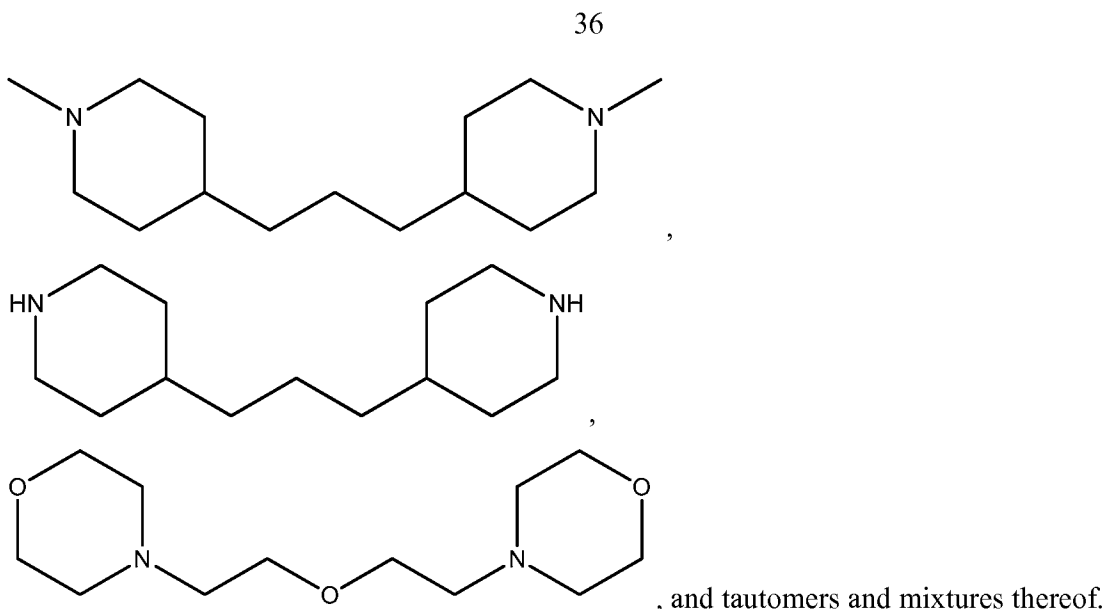
37. The herbicide salt of claim 1 comprising a cation of a compound of Formula V.

38. The herbicide salt of any of claims 1 to 37 comprising the cation of a compound selected from the group consisting of:



35





39. The herbicide salt of any of claims 1 to 38 wherein the carboxylic acid herbicide anion comprises the carboxylate anion of a herbicide selected from the group consisting of 3,6-dichloro-2-methoxybenzoic acid (dicamba); 2,4-dichlorophenoxyacetic acid (2,4-D); 4-(2,4-dichlorophenoxy)butanoic acid (2,4-DB); 2-(2,4-dichlorophenoxy)propanoic acid (dichloroprop); 2-(4-chloro-2-methylphenoxy)acetic acid (MCPA); 4-(4-chloro-2-methylphenoxy)butanoic acid (MCPB); 4-amino-3,6-dichloro-2-pyridinecarboxylic acid (aminopyralid); 3,6-dichloro-2-pyridinecarboxylic acid (clopyralid); 2-[(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid (fluroxypyr); [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid (triclopyr); 2-(4-chloro-2-methylphenoxy)propanoic acid (mecoprop); 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid (picloram); 3,7-dichloro-8-quinolinecarboxylic acid (quinclorac); 6-amino-5-chloro-2-cyclopropyl-4-pyrimidinecarboxylic acid (aminocyclopyrachlor) and combinations thereof.

40. The herbicide salt of any of claims 1 to 39 wherein the carboxylic acid herbicide anion comprises the carboxylate anion of 3,6-dichloro-2-methoxybenzoic acid (dicamba) or 2,4-dichlorophenoxyacetic acid (2,4-D).

41. A herbicidal application mixture useful for killing or controlling the growth of unwanted plants comprising the herbicidal salt of any one of the preceding claims.

42. The herbicidal application mixture of claim 41 further comprising at least one surfactant wherein the weight ratio of the herbicidal salt acid equivalent to surfactant is from about 1:1 to about 20:1, from about 2:1 to about 10:1 or from about 3:1 to about 8:1.

43. The herbicidal application mixture of claim 42 wherein the surfactant is selected from the group consisting of alkoxyated tertiary etheramines, alkoxyated quaternary etheramines, alkoxyated etheramine oxides, alkoxyated tertiary amines, alkoxyated quaternary amines, alkoxyated polyamines, sulfates, sulfonates, phosphate esters, alkyl polysaccharides, alkoxyated alcohols, and combinations thereof.

44. The herbicidal application mixture of any of claims 41 to 43 further comprising at least one co-herbicide.

45. The herbicidal application mixture of claim 44 wherein the co-herbicide is selected from the group consisting of auxin herbicides and salts thereof; acetyl CoA carboxylase (ACCase) inhibitors, acetolactate synthase (ALS) or acetohydroxy acid synthase (AHAS) inhibitors, photosystem II inhibitors, photosystem I inhibitors, protoporphyrinogen oxidase (PPO or Protox) inhibitors, carotenoid biosynthesis inhibitors, enolpyruvyl shikimate-3-phosphate (EPSP) synthase inhibitor, glutamine synthetase inhibitor, dihydropteroate synthetase inhibitor, mitosis inhibitors, 4-hydroxyphenyl-pyruvate-dioxygenase (4-HPPD) inhibitors, synthetic auxins, auxin transport inhibitors, nucleic acid inhibitors, and salts and esters thereof; racemic mixtures and resolved isomers thereof; and combinations thereof.

46. The herbicidal application mixture of claim 44 wherein the co-herbicide is selected from: 2,4-D, aminocyclopyrachlor, mecoprop, mecoprop-P, triclopyr, acetochlor, acifluorfen, alachlor, atrazine, azafenidin, bifenox, butachlor, butafenacil, carfentrazone-ethyl, diuron, dithiopyr, flufenpyr-ethyl, flumiclorac-pentyl, flumioxazin, fluoroglycofen, fluthiacet-methyl, fomesafen, glyphosate, glufosinate, imazethapyr, lactofen, metazochlor, metolachlor (and S-metolachlor), metribuzin, oxadiargyl, oxadiazon, oxyfluorfen, pretilachlor, propachlor, propisochlor, pyraflufen-ethyl, sulfentrazone and thenylchlor, and salts and esters thereof; racemic mixtures and resolved isomers thereof, and combinations thereof.

47. The herbicidal application mixture of any of claims 44 to 46 wherein the co-herbicide comprises glyphosate or a salt or ester thereof.

48. The herbicidal application mixture of any of claims 44 to 47 wherein the co-herbicide comprises glufosinate or a salt or ester thereof.

49. The herbicidal application mixture of any of claims 41 to 48 wherein the total herbicide concentration is at least 51, 55, 100, 150, 200, 250, 300, 350, 400, 450, 480, 500, 520, 540, 560, 580, 600, 620, 640, 660, 680 or 700 grams acid equivalent per liter.

50. The herbicidal application mixture of any of claims 41 to 49 wherein the weight ratio of the herbicidal salt to total co-herbicide is from about 50:1 to about 1:10, from about 50:1 to about 1:5, from about 50:1 to about 1:1, from about 50:1 to about 3:1, from about 50:1 to about 5:1, from about 50:1 to about 10:1, from about 25:1 to about 1:1, or from about 25:1 to about 3:1 on an acid equivalent basis.

51. A method of controlling unwanted plants comprising applying the herbicidal application mixture of any one of claims 41 to 50 to the unwanted plants.

52. A method of controlling carboxylic acid herbicide-susceptible plants growing in and/or adjacent to a field of crop plants comprising applying the herbicidal application mixture of any one of claims 41 to 50 to the foliage of the carboxylic acid herbicide-susceptible plants.

53. The method of claim 52 wherein the crop plant comprises a transgenic crop plant comprising a dicamba tolerance trait.

54. The method of claim 52 or 53 wherein the crop plant comprises a transgenic crop plant comprising a 2,4-D tolerance trait.

55. The method of any of claims 52 to 54 wherein the crop plant comprises a transgenic crop plant comprising a glyphosate tolerance trait.

56. The method of any of claims 52 to 55 wherein the crop plant comprises a transgenic crop plant comprising a glufosinate tolerance trait.

57. The method of any of claims 52 to 56 wherein the carboxylic acid herbicide-susceptible plants comprise auxin herbicide susceptible plants.