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(54) Stabilized aqueous formulations of sulfonylureas.

(57) An aqueous composition of a herbicidal sulfonylurea derivative or agriculturally suitable salt thereof is stabilised by an agriculturally suitable salt of a carboxylic or inorganic acid, present in an proportion of at least 3% up to the salt saturation limit of the aqueous solution.

EP 0 124 295 A2

Title BA-8539-A

STABILIZED AQUEOUS FORMULATIONS OF SULFONYLUREAS

Background of the Invention

This invention relates to stabilized aqueous compositions, said compositions comprising a sulfonylurea or its agriculturally suitable salt with an effective amount of a salt of a carboxylic or an inorganic acid, or with mixtures of such carboxylic or inorganic acid salts, provided that the solubility of carboxylic or inorganic acid salts at 5°C and a pH of about 6-10 is greater than or equal to 3% and further provided that the pH of a 0.1 molar solution of the carboxylic or inorganic acid salt is between 6 and 10.

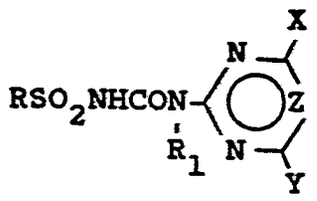
Sulfonylureas are known in the literature. For instance, U.S. Patents 4,127,405 and 4,169,719 teach herbicidal sulfonylureas. The aqueous suspension formulations of these herbicides are stabilized by the technique of the instant invention.

The above-mentioned patents and others disclose sulfonylureas which are highly effective as herbicides. There is however, a need to store agriculturally suitable formulations of such sulfonylureas for long periods of time after they are produced. Maintaining the stability of formulations of such herbicides is extremely important since an unstable formulation will be considerably less effective when utilized. That is to say, the active ingredient must be maintained intact in the formulation if herbicidal effect is to be maximized.

According to the instant invention, a formulation has been discovered, described below, which serves to maintain the stability of sulfonylurea herbicides.

Summary of the Invention

This invention relates to a stabilized aqueous suspension which comprises a compound of Formula I or its agriculturally suitable salt of Formula II with an effective amount of a salt of a carboxylic or an inorganic acid, or with mixtures of such carboxylic or inorganic acid salts, provided that the solubility of carboxylic or inorganic acid salts at 5°C and at pH 6-10 is greater than or equal to 3% and further provided that the pH of a 0.1 molar aqueous solution of the carboxylic or inorganic acid salt is between 6 and 10. All parts are by weight unless otherwise indicated.



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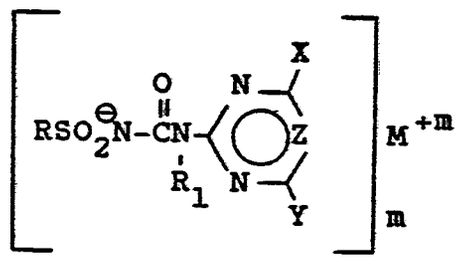
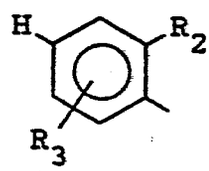
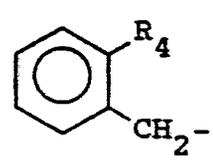
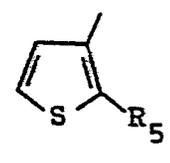


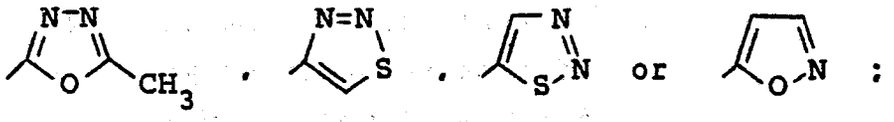
II

The concentration of the carboxylic or inorganic acid salt or salts in the composition is between 3% and the salt saturation limit of the aqueous solution. The values for the substituents are as follows:

R is  ,  or  :

R_1 is H or CH_3;

R_2 is F, Cl, Br, C_1-C_4 alkyl, $SO_2NR_6R_7$, $S(O)_nR_8$, $SO_2NCH_3(OCH_3)$, CO_2R_9, OSO_2R_{10}, OR_{11}, NO_2,



R_3 is H, F, Cl, Br, CH_3, OCH_3 or CF_3;

R_4 is Cl, NO_2 or CO_2R_{10};

R_5 is Cl, Br, $SO_2NR_6R_7$, $S(O)_nR_{10}$ or CO_2R_{10};

R_6 and R_7 are independently C_1-C_3 alkyl;

R_8 is C_1-C_3 alkyl or C_1-C_3 alkyl substituted by 1-5 atoms of F, Cl or Br;

R_9 is C_1-C_4 alkyl, $CH_2CH_2OCH_3$, CH_2CH_2Cl or $CH_2CH=CH_2$;

R_{10} is C_1-C_3 alkyl;

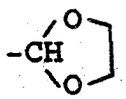
R_{11} is C_1-C_4 alkyl, $CH_2CH=CH_2$, $CH_2C\equiv CH$, or C_1-C_3 alkyl substituted with 1-5 atoms of F, Cl or Br;

n is 0 or 2;

Z is CH or N;

X is CH_3, OCH_3, Cl or $OCHF_2$;

Y is CH_3, OCH_3, $CH(OCH_3)_2$, $OCHF_2$ or



; and

M^{+m} is an agriculturally suitable cation; and

m is 1, 2, or 3;

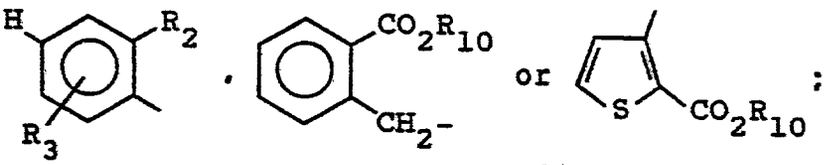
provided that when X is Cl then Z is CH and Y is OCH_3 or OCF_2H.

The compositions of this invention may contain more than one compound of Formula I or more than one compound of Formula II. In addition, the compositions may contain compounds of both Formula I and Formula II, simultaneously. The compositions of this invention may also optionally contain other herbicides.

Preferred for reasons of their greater stability and/or their more favorable physical properties are:

1) Compositions of the Generic Scope consisting of a compound of Formula I or a compound of Formula II wherein M is an ammonium, substituted ammonium or alkali metal ion and the counter ion of the carboxylic or inorganic acid salt is an ammonium, substituted ammonium or alkali metal ion.

2) Compositions of the Preferred 1 wherein

R is  ;

R_1 is H;

R_2 is Cl, CH_3, $SO_2N(CH_3)_2$, $S(O)_nR_8$, CO_2R_9, OSO_2R_{10}, OR_{11} or NO_2;

R_3 is H, Cl, CH_3, OCH_3 or CF_3;

R_8 is C_1-C_3 alkyl, CF_3, CF_2H or CF_2CF_2H;

R_9 is C_1-C_4 alkyl; and

R_{11} is C_1-C_4 alkyl, CF_3, CF_2H or CF_2CF_2H.

3) Compositions of the Preferred 2 wherein the compound is an agriculturally suitable salt of Formula II.

4) Compositions of the Preferred 3 wherein the cation of the compound of Formula II and the cation of the carboxylic or inorganic acid salt are identical.

5) Compositions of the Generic Scope wherein the concentration of the carboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

6) Compositions of the Preferred 1 wherein the concentration of the carboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

7) Compositions of the Preferred 2 wherein the concentration of the carboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

8) Compositions of the Preferred 3 wherein the concentration of the carboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

9) Compositions of the Preferred 4 wherein the concentration of the caboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

10) Compositions of the Generic Scope wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

11) Compositions of the Preferred 1 wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

12) Compositions of the Preferred 2 wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

13) Compositions of the Preferred 3 wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

14) Compositions of the Preferred 4 wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

Specifically preferred for reasons of their greatest stability and/or greatest utility are compositions containing compounds of Formula II selected from the agriculturally suitable salts of:

2-[[(4-chloro-6-methoxypyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoic acid, ethyl ester;

2-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino-carbonyl]aminosulfonyl]benzoic acid, methyl ester;

2-[[(4-6-dimethylpyrimidin-2-yl)aminocarbonyl]amino-sulfonyl]benzoic acid, methyl ester;

2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide;

2-[[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]amino-sulfonylmethyl]benzoic acid, methyl ester;

3-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino-carbonyl]aminosulfonyl[-2-thiophenecarboxylic acid methyl ester;

N-[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-2-hydroxybenzenesulfonamide, ethanesulfonate;

and compositions containing carboxylic or inorganic acid salts preferably selected from:

diammonium hydrogen phosphate:

ammonium acetate;

lithium acetate;

sodium acetate;

potassium acetate; or

sodium thiocyanate;

and compositions containing:

the ammonium salt of 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzene-sulfonamide and diammonium hydrogen phosphate.

Detailed Description of the Invention

This invention relates to stable and readily dispersible concentrated liquid suspensions of compounds of Formula I or their agriculturally suitable salts of Formula II in aqueous salt solutions. Compounds of Formula I are useful herbicides and their preparation is known in the art. See, for example,

U.S. Patents 4,127,405 and 4,169,719. Agriculturally suitable salts of Formula II are also useful herbicides and can be prepared by a number of ways known to the art. For example, metal salts can be made by treating the compounds of Formula I with a solution of an alkali metal salt having a sufficiently basic anion (e.g., hydroxide, alkoxide, carbonate or hydride). Ammonium and substituted ammonium salts can be made by similar techniques.

Salts of Formula II can also be prepared by exchange of one cation for another. Cationic exchange can be effected by direct treatment of an aqueous solution of a salt of Formula II (e.g., alkali metal or ammonium salt) with a solution containing the cation to be exchanged. This method is most effective when the desired salt containing the exchanged cation is insoluble in water and can be separated by filtration.

Exchange may also be effected by passing an aqueous solution of a salt of Formula II (e.g., an alkali metal or ammonium salt) through a column packed with a cation exchange resin containing the cation to be exchanged. In this method, the cation of the resin is exchanged for that of the original salt and the desired product is eluted from the column. This method is particularly useful when the desired salt is water-soluble.

Liquid concentrates are desirable because of the ease with which they can be measured, poured, handled or diluted in preparing aqueous slurries for spraying. Some of the compounds of Formula I and salts of Formula II do not have high solubility in water or other inexpensive solvents and moreover they are chemically unstable over long periods of time in many of these solvents. When dissolved in water alone, either partially or completely, hydrolysis and/or crystal growth

can occur in storage so that stable solutions or suspensions cannot be formulated.

It has been found that stabilized aqueous suspensions of compounds of Formula I or salts of Formula II can be prepared when the aqueous suspending medium contains ammonium, substituted ammonium or alkali metal salts of a carboxylic acid or an inorganic acid or mixtures of such salts provided that the solubility of those salts at pH 6-10 is greater than or equal to 3% at 5°C and further provided that the pH of a 0.1 molar aqueous solution of the carboxylic or inorganic acid salt is between 6 and 10.

The stabilization which is achieved with these compositions is evident in several ways. First, the chemical stability of the compounds of Formula I or the salts of Formula II in an aqueous suspension is markedly improved which allows formulation of such a suspension that is relatively stable in storage. Second, crystal growth of active ingredient is reduced and a controlled degree of flocculation is imparted to the particles of active herbicide which prevents formation of a hard-to-resuspend cake during storage. Third, the density of the suspending medium may be up to 30% higher than that of water which reduces the settling tendency of the suspended particles. Fourth, the dissolved salts act as an antifreeze which maintains the fluidity of the compositions at temperatures down to -6°C and below.

Another advantage of these compositions is that, although the compounds of Formula I and the salts of Formula II are relatively insoluble in the suspending medium, when diluted with water in the spray tank they quickly and completely dissolve at the more dilute spray concentrations, provided the pH of the spray solution is about 7.0 or above.

The salts which are preferred in the aqueous medium are ammonium, substituted ammonium or alkali metal salts of a carboxylic or an inorganic acid which are soluble in water at 3% or more at 5°C. The useful concentration range is from 3% to the saturation point at 5°C. The preferred salts of the invention will further possess a pH between 6 and 10 for a 0.1 molar aqueous solution. Examples of these salts are diammonium hydrogen phosphate, ammonium acetate, lithium acetate, sodium thiocyanate, sodium acetate, potassium acetate, or compatible mixtures of these. Diammonium hydrogen phosphate and sodium acetate are preferred for compositions containing the ammonium and sodium salts, respectively, of the salts of Formula II. The useful pH range of these compositions is 6-10 although 7-9 is preferred. In most cases, the salts described above will automatically produce a formulation with the desired pH. The anion of the carboxylic or inorganic acid salt may act as an acid acceptor and generate, in situ, the salt of Formula II from its corresponding conjugate acid. Utilizing this principle, one may prepare these compositions of the salts of Formula II directly from the conjugate acids of Formula I. If a higher or lower pH is desired, a small amount of acid or base can be added to the formulation. For example, with diammonium hydrogen phosphate, the pH can be lowered by addition of phosphoric acid or ammonium dihydrogen phosphate. The pH may be raised with ammonium hydroxide. The base or acid may have the same anion or cation as the salt but this is not a requirement.

The formulations of this invention contain e.g. about 1 to 50% (preferably 10 to 40%) of the compounds of Formula I or the salts of Formula II suspended in an aqueous solution which contains from 3% to the salt

saturation amounts of an agriculturally suitable salt of a carboxylic or an inorganic acid or mixtures thereof as described above. Preferred concentrations of these carboxylic or inorganic acid salts are in the range of about 10-40% in the aqueous phase. The formulation may also contain about 0.1% to 20% of surfactants. Higher ratios of surfactant to active ingredient are sometimes desirable and can be achieved by incorporation into the formulation or by tank mixing.

Among the surfactants used in these compositions are common wetting and dispersing agents such as trimethylnonyl polyethylene glycol ether, sodium alkylnaphthalenesulfonates, sodium alkylbenzenesulfonates, sodium dioctyl sulfosuccinate, sodium dodecyl sulfate, the ammonium and sodium salts of lignosulfonic acid and formaldehyde condensates of naphthalenesulfonic acid. More specific examples are sodium ligninsulfonate and ammonium ligninsulfonate.

Optionally, the formulations may also contain about 0.01-5.0% of thickening or suspending agents such as sodium carboxymethyl cellulose, polysaccharide gums, natural and refined smectite type clays and synthetic silicas.

The compositions of this invention may contain more than one compound of Formula I or more than one compound of Formula II. In addition, the compositions may contain compounds of both Formula I and Formula II, simultaneously. The compositions of this invention may also optionally contain other herbicides. The following herbicides are examples of materials which may be particularly useful in such combinations:

Common Name	Chemical Name
acifluorfen	5-[2-chloro-4-(trifluoromethyl)-phenoxy]-2-nitrobenzoic acid
alachlor	2-chloro-2',6'-diethyl-N-(methoxy-methyl)acetanilide
ametryn	2-(ethylamino)-4-(isopropylamino)-6-methylthio)-s-triazine
amitrole	3-amino-s-triazole
AMS	ammonium sulfamate
asulam	methyl sulfanilylcarbamate
atrazine	2-chloro-4-(ethylamino)-6-(isopropyl-amino)-s-triazine
barban	4-chloro-2-butynyl m-chlorocarbanilate
benefin	N-butyl-N-ethyl-α,α,α-trifluoro-2,6-dinitro-p-toluidine
bensulide	O,O-diisopropyl phosphorodithioate S-ester with N-(2-mercaptoethyl)-benzenesulfonamide
benzipram	3,5-dimethyl-N-(1-methylethyl)-N-(phenylmethyl)benzamide
benzoylprop	N-benzoyl-N-(3,4-dichlorophenoxy)-DL-alaine
bifenox	methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate
bromacil	5-bromo-3-sec-butyl-6-methyluracil
bromoxynil	3,5-dibromo-4-hydroxybenzonitrile
butachlor	N-(butoxymethyl)-2-chloro-2',6'-diethylacetanilide
butam	2,2-dimethyl-N-(1-methylethyl)-N-phenylmethyl)propanamide
buthidazole	3-[5-(1,1-dimethylethyl)-1,3,4-thia-diazol-2-yl]-4-hydroxy-1-methyl-2-imidazolidinone

Common Name	Chemical Name
butralin	4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine
cacodylic acid	hydroxydimethylarsine oxide
carbetamide	D-N-ethyllactamide carbanilate (ester)
CDAA	N-N-diallyl-2-chloroacetamide
CDEC	2-chloroallyl diethyldithiocarbamate
chloramben	3-amino-2,5-dichlorobenzoic acid
chlorbromuron	3-(4-bromo-3-chlorophenyl)-1-methoxy-1-methylurea
chloroxuron	3-[p-(p-chlorophenoxy)phenyl]-1,1-dimethylurea
chlorpropham	isopropyl m-chlorocarbanilate
cisanilide	cis-2,5-dimethyl-N-phenyl-1-pyrrolidinecarboxamide
CMA	calcium methanearsonate
cyanazine	2-[[4-chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile
cycloate	S-ethyl N-ethylthiocyclohexanecarbamate
cycluron	3-cyclooctyl-1,1-dimethylurea
cyperquat	1-methyl-4-phenylpyridinium
cyprazine	2-chloro-4-(cyclopropylamino)-6-(isopropylamino)-s-triazine
cyprazole	N-[5-(2-chloro-1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]cyclopropanecarboxamide
cypromid	3',4'-dichlorocyclopropanecarboxanilide
dalapon	2,2-dichloropropionic acid
dazomet	tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione

Common Name	Chemical Name
DCPA	dimethyl tetrachloroterephthalate
desmetryn	2-(isopropylamino)-4-(methylamino)-6-methylthio)-s-triazine
diallate	S-(2,3-dichloroallyl)diisopropylthiocarbamate
dicamba	3,6-dichloro-o-anisic acid
dichlobenil	2,6-dichlorobenzonitrile
dichlorprop	2-(2,4-dichlorophenoxy)propionic acid
diclofop	2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid
diethatyl	N-(chloroacetyl)-N-(2,6-diethylphenyl)glycine
difenzoquat	1,2-dimethyl-3,5-diphenyl-1H-pyrazolium
dinitramine	N^4,N^4-diethyl-α,α,α-trifluoro-3,5-dinitrotoluene-2,4-diamine
dinoseb	2-sec-butyl-4,6-dinitrophenol
diphenamid	N,N-dimethyl-2,2-diphenylacetamide
dipropetryn	2-(ethylthio)-4,6-bis(isopropylamino)-s-triazine
diquat	6,7-dihydrodipyrido[1,2-α:2',1'-c]-pyrazinediium ion
diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea
DMSA	disodium methanearsonate
endothall	7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid
erbon	2-(2,4,5-trichlorophenoxy)ethyl 2,2-dichloropropionate
ethafluralin	N-ethyl-N-(2-methyl-2-propenyl)-2,6-dinitro-4-(trifluoromethyl)benzenamine

Common Name	Chemical Name
ethofumesate	(±)-2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate
fenac	(2,3,6-trichlorophenyl)acetic acid
fenuron	1,1-dimethyl-3-phenylurea
fenuron TCA	1,1-dimethyl-3-phenylurea mono(trichloroacetate)
flamprop	N-benzoyl-N-(3-chloro-4-fluorophenyl)-DL-alanine
fluchloralin	N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)aniline
fluometuron	1,1-dimethyl-3-(α,α,α-trifluoro-m-tolyl)urea
fluorodifen	p-nitrophenyl α,α,α-trifluoro-2-nitro-p-tolyl ether
fluridone	1-methyl-3-phenyl-5-[3-(trifluoromethyl)phenyl]-4(1H)-pyridinone
fosamine	ethyl hydrogen (aminocarbonyl)phosphonate
glyphosate	N-(phosphonomethyl)glycine and agriculturally suitable salts thereof
hexaflurate	potassium hexafluoroarsenate
hexazinone	3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazin-2,4(1H,3H)-dione
ioxynil	4-hydroxy-3,5-diiodobenzonitrile
isopropalin	2,6-dinitro-N,N-dipropylcumidine
karbutilate	tert-butylcarbamic acid ester with 3-(m-hydroxyphenyl)-1,1-dimethylurea
lenacil	3-cyclohexyl-6,7-dihydro-1H-cyclopentapyrimidine-2,4(3H,5H)-dione
linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea
MAA	methanearsonic acid

Common Name	Chemical Name
MAMA	monoammonium methanearsonate
MCPA	[(4-chloro-o-tolyl)oxy]acetic acid
MCPB	4-[(4-chloro-o-tolyl)oxy]butyric acid
mecoprop	2-[(4-chloro-o-tolyl)oxy]propionic acid
mefluidide	N-[(2,4-dimethyl-5-[[(trifluoromethyl)sulfonyl]amino]phenyl]-acetamide
methalpropalin	N-(2-methyl-2-propenyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)benzenamide
metham	sodium methyldithiocarbamate
methazole	2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazolidine-3,5-dione
metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide
metribuzin	4-amino-6-tert-butyl-3-(methylthio)-as-triazin-5(4H)one
molinate	S-ethyl hexahydro-1H-azepine-1-carbothioate
monolinuron	3-(p-chlorophenyl)-1-methoxy-1-methylurea
monuron	3-(p-chlorophenyl)-1,1-dimethylurea
monuron TCA	3-(p-chlorophenyl)-1,1-dimethylurea mono(trichloroacetate)
MSMA	monosodium methanearsonate
napropamide	2-(α-naphthoxy)-N,N-diethylpropionamide
naptalam	N-1-naphthylphthalamic acid
neburon	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea
nitralin	4-(methylsulfonyl)-2,6-dinitro-N,N-dipropylaniline

Common Name	Chemical Name
nitrofen	2,4-dichlorophenyl p-nitrophenyl ether
nitrofluorfen	2-chloro-1-(4-nitrophenoxy)-4-(trifluoromethyl)benzene
norea	3-(hexahydro-4,7-methanoindan-5-yl)-1,1-dimethylurea
norflurazon	4-chloro-5-(methylamino)-2-(α,α,α-trifluoro-m-tolyl)-3(2H)-pyridazinone
oryzalin	3,5-dinitro-N^4,N^4-dipropylsulfanilamide
oxadiazon	2-tert-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)Δ^2-1,3,4-oxadiazolin-5-one
oxyfluorfen	2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene
paraquat	1,1'-dimethyl-4,4'-bipyridinium ion
PBA	chlorinated benzoic acid
pendimethalin	N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine
perfluidone	1,1,1-trifluoro-N-[2-methyl-4-(phenylsulfonyl)phenyl]methanesulfonamide
picloram	4-amino-3,5,6-trichloropicolinic acid
procyazine	2-[[4-chloro-6-(cyclopropylamino)-1,3,5-triazine-2-yl]amino]-2-methylpropanenitrile
profluralin	N-(cyclopropylmethyl)-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
prometon	2,4-bis(isopropylamino)-6-methoxy-s-triazine
prometryn	2,4-bis(isopropylamino)-6-(methylthio)-s-triazine
pronamide	3,5-dichloro(N-1,1-dimethyl-2-propynyl)benzamide

Common Name	Chemical Name
propachlor	2-chloro-N-isopropylacetanilide
propanil	3',4'-dichloropropionalide
propazine	2-chloro-4,6-bis(isopropylamino)-s-triazine
propham	isopropyl carbanilate
prosulfalin	N-[[4-(dipropylamino)-3,5-dinitrophenyl]sulfonyl]-S,S-dimethylsulfilimine
prynachlor	2-chloro-N-(1-methyl-2-propynyl)-acetanilide
secbumeton	N-ethyl-6-methoxy-N'-(1-methylpropyl)-1,3,5-triazine-2,4-diamine
siduron	1-(2-methylcyclohexyl)-3-phenylurea
simazine	2-chloro-4,6-bis(ethylamino)-s-triazine
simetryn	2,4-bis(ethylamino)-6-(methylthio)-s-triazine
TCA	trichloroacetic acid and its salts
tebuthiuron	N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea
terbacil	3-tert-butyl-5-chloro-6-methyluracil
terbuchlor	N-(butoxymethyl)-2-chloro-N-[2-(1,1-dimethylethyl)-6-methylphenyl]acetamide
terbuthylazine	2-(tert-butylamino)-4-chloro-6-(ethylamino)-s-triazine
terbutol	2,6-di-tert-butyl-p-tolyl methylcarbamate
terbutryn	2-(tert-butylamino)-4-(ethylamino)-6-methylthio)-s-triazine
tetrafluron	N,N-dimethyl-N'-[3-(1,1,2,2-tetrafluoroethoxy)phenyl]urea

Common Name	Chemical Name
thiobencarb	S-[(4-chlorophenyl)methyl] diethylcarbamothioate
triallate	S-(2,3,3-trichloroallyl)diisopropylthiocarbamate
trifluralin	α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
trimeturon	1-(p-chlorophenyl)-2,3,3-trimethylpseudourea
2,3,6-TBA	2,3,6-trichlorobenzoic acid and agriculturally suitable salts and esters thereof
2,4-D	(2,4-dichlorophenoxy)acetic acid and agriculturally suitable salts and esters thereof
2,4-DB	4-(2,4-dichlorophenoxy)butyric acid and agriculturally suitable salts and esters thereof
2,4-DEP	tris[2-(2,4-dichlorophenoxy)-ethyl] phosphite
methabenzthiazuron	1,3-dimethyl-3-(2-benzothiazolyl) urea
chlortoluran	N'-(3-chloro-4-methylphenyl)-N N-dimethylurea
isoproturan	N-(4-isopropylphenyl)-N'N'-dimethylurea
metoxuran	N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea

When an added herbicide is water-soluble, the pH of the resulting composition may need to be adjusted to lie within the range of 6 to 10. And further, water-soluble herbicides may act to replace, in part or in toto, the stabilizing inorganic and/or carboxylic acid salts.

The methods for making the stabilized compositions of this invention are well known and include ball-milling, bead-milling, sand-milling, colloid-milling and air-milling combined with high-speed blending.

A preferred technique for the preparation of stabilized compositions of Formula II involves suspending a compound of Formula I in water containing surfactants and thickening or suspending agents followed by neutralization with the desired base such as ammonium or sodium hydroxide to a pH of 6.0-10.0, preferably 7.0-9.0, followed by addition of the solid insolubilizing salt to the formulation with agitation. The technique of adding the insolubilizing salt is important. It is best to add the salt in increments to the neutralized conjugate acid in order to develop the precipitate more slowly; otherwise, a tacky solid or gum can form. The resulting suspension is then colloid-milled or bead-milled to a particle size of 1-20 microns, preferably 2-8 microns. The resulting stable aqueous suspension is suitable for use in herbicidal applications.

Example 1

2-Chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide	34.20%
sodium alkylnaphthalenesulfonate	2.00%
polysaccharide thickener	0.05%
magnesium aluminum silicate thickener	0.20%
diammonium hydrogen phosphate	16.05%
ammonium hydroxide solution (29% NH_3)	5.60%
water and impurities	balance

The sodium alkylnaphthalenesulfonate was dissolved in the water with stirring and the sulfonamide was added in increments and allowed to disperse well. To the dispersion was added the ammonium hydroxide to

form the salt of the sulfonamide. The resulting pH was 7.5. Stirring was continued while the diammonium hydrogen phosphate was added and allowed to dissolve (28.5% of solution). The polysaccharide and silicate thickeners were added and the resulting mixture was ground in a sand-mill to produce particles essentially under five microns in size. The pH of the composition was 7.8. On accelerated aging at 45°C for 3 weeks, the formulation did not settle appreciably and the suspended solids remained soft. The entire formulation could be easily fluidized by stirring or shaking. No detectible decomposition of active component occurred while a comparable composition containing no diammonium hydrogen phosphate showed 6% relative decomposition under the same conditions.

Example 2

The following example illustrates an in situ preparation of a composition of a salt of Formula II from the conjugate acid of Formula I.

2-Chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide	33.9%
sodium ligninsulfonate	2.0%
37.5% diammonium hydrogen phosphate solution	64.1%

The sodium ligninsulfonate and sulfonamide were added with stirring to the phosphate solution. The mixture then was ground in a sand-mill to give particles of essentially less than five microns. The pH of the composition was 8.25. A sample aged for 2 weeks at 45°C showed 0.47% relative decomposition of active component while a composition containing no phosphate showed 6.0% relative decomposition of the same component. No appreciable settling of the stabilized, aged composition was seen and it was easily fluidized with agitation.

Example 3

A stable suspension of the ammonium salt of the sulfonylurea, 2-[[(4-Chloro-6-methoxypyrimidin-2-yl)-aminocarbonyl]aminosulfonyl]benzoic acid, ethyl ester, was prepared as described in Example 2 using the same percentages of ingredients. The pH of the composition was 7.95. A sample aged for 2 weeks at 45°C showed a 0.4% relative decomposition of active component while a composition without phosphate showed 4.0% relative decomposition of the same component. Settling of the aged composition was slight and it was readily fluidized with agitation.

Example 4

2-[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]aminosulfonyl]benzoic acid, methyl ester	21.3%
sodium ligninsulfonate	1.11%
sodium hydroxide (50%)	4.48%
sodium acetate	18.71%
polysaccharide thickener	0.05%
water and impurities	balance

With stirring, the sodium ligninsulfonate and sodium hydroxide were dissolved in the water and the sulfonylurea was added in portions and allowed to react to form the water-soluble sodium salt. To the solution was added one-fourth of the sodium acetate and, 5 minutes later, another one-fourth. The remainder of the sodium acetate was added after precipitation of the sulfonylurea salt was observed to be occurring rapidly, after about 15 minutes. The percentage of sodium acetate in the aqueous phase was 25.0. The resulting composition was ground in a sandmill to produce particles essentially under five microns in size. The polysaccharide thickener was added several minutes before completion of the milling

operation. The pH of the composition was 9.03. On aging at 45°C for 3 weeks, suspended solids did not settle and the formulation could be readily fluidized with shaking. No detectable decomposition of active ingredient occurred while a composition without acetate showed 30% decomposition over the same accelerated aging period.

In the following examples, stable suspensions of sulfonylureas are prepared as described in Example 4 using salts as stabilizers against chemical decomposition and to prevent crystal growth:

Ex.	Sulfonylurea (neutral. agent)	Salt (% in H_2O)
5	A (NaOH)	sodium acetate (20)
6	B (NH_4OH)	ammonium acetate (30)
7	C (NaOH)	sodium thiocyanate (25)

A = 2-[[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoic acid, methyl ester.

B = 2-[[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-aminosulfonylmethyl]benzoic acid, methyl ester.

C = N-[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-2-hydroxybenzenesulfonamide, ethanesulfonate.

Example 8

3-[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]aminosulfonyl]-2-thiophenecarboxylic acid, methyl ester 12.0%

sodium alkylnaphthalenesulfonate	2.4%
lithium hydroxide-H_2O	1.3%
lithium acetate	29.2%
water and impurities	remainder

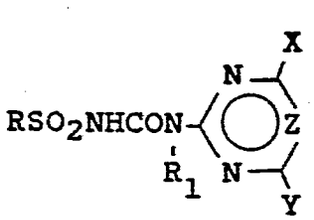
A stable suspension of the lithium salt of the sulfonylurea was prepared as described in Example 4. The lithium acetate concentration in the aqueous phase was 35%. The pH of the composition was 7.9. A sample aged at 45°C for 3 weeks showed no loss of active ingredient while the loss of the same ingredient from a composition without lithium acetate aged in the same manner was over 20%.

Example 9

The ammonium salt of the sulfonamide of Example 1 is air-milled to give a product with a particle size essentially less than five microns then dispersed with good agitation in a mixture of the remaining components of the formulation of Example 1. The suspension behavior and chemical stability are essentially as described in Example 1.

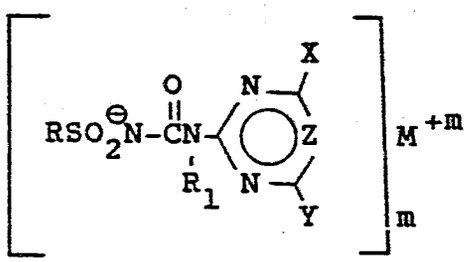
Claims:

1. A stabilized aqueous composition comprising an agriculturally suitable salt of a carboxylic or an inorganic acid, or mixtures of such carboxylic or inorganic acid salts, provided that the solubility of carboxylic or inorganic acid salts at 5°C and at pH 6-10 is greater than or equal to 3% and further provided that the pH of a 0.1 molar solution of the carboxylic or inorganic acid salt is between 6 and 10, and one or more compounds selected from



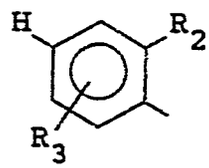
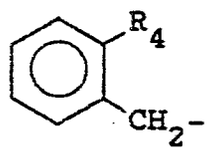
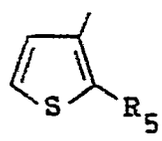
I

or



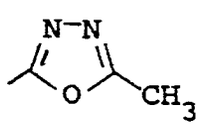
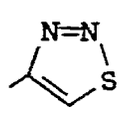
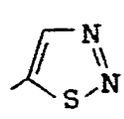
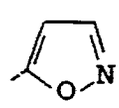
II

wherein the concentration of the carboxylic or inorganic acid salt or salts is between 3% and the salt saturation limit of the aqueous solution, and

R is  ,  or  ;

R_1 is H or CH_3;

R_2 is F, Cl, Br, C_1-C_4 alkyl, $SO_2NR_6R_7$, $S(O)_nR_8$, $SO_2NCH_3(OCH_3)$, CO_2R_9, OSO_2R_{10}, OR_{11}, NO_2,

 ,  ,  or  ;

R_3 is H, F, Cl, Br, CH_3, OCH_3 or CF_3;

R_4 is Cl, NO_2 or CO_2R_{10};

R_5 is Cl, Br, $SO_2NR_6R_7$, $S(O)_nR_{10}$ or CO_2R_{10};

R_6 and R_7 are independently C_1-C_3 alkyl;

R_8 is C_1-C_3 alkyl or C_1-C_3 alkyl substituted by 1-5 atoms of F, Cl or Br;

R_9 is C_1-C_4 alkyl, $CH_2CH_2OCH_3$, CH_2CH_2Cl or $CH_2CH{=}CH_2$;

R_{10} is C_1-C_3 alkyl;

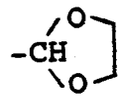
R_{11} is C_1-C_4 alkyl, $CH_2CH{=}CH_2$, $CH_2C{\equiv}CH$, or C_1-C_3 alkyl substituted with 1-5 atoms of F, Cl or Br;

n is 0 or 2;

Z is CH or N;

X is CH_3, OCH_3, Cl or $OCHF_2$;

Y is CH_3, OCH_3, $CH(OCH_3)_2$, $OCHF_2$ or



; and

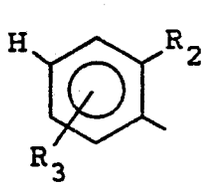
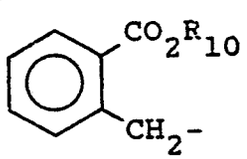
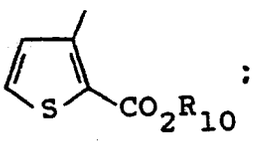
M^{+m} is an agriculturally suitable cation; and

m is 1, 2, or 3;

provided that when X is Cl then Z is CH and Y is OCH_3 or OCF_2H.

2. Compositions of Claim 1 wherein the counterion of the carboxylic or inorganic acid salt is an ammonium, substituted ammonium or alkali metal ion and when the compound is a salt of Formula II, then M is also an ammonium, substituted ammonium or alkali metal ion.

3. Compositions of Claim 2 wherein

R is  ,  or  ;

R_1 is H;

R_2 is Cl, CH_3, $SO_2N(CH_3)_2$, $S(O)_nR_8$, CO_2R_9, OSO_2R_{10}, OR_{11} or NO_2;

R_3 is H, Cl, CH_3, OCH_3 or CF_3;

R_8 is C_1-C_3 alkyl, CF_3, CF_2H or CF_2CF_2H;

R_9 is C_1-C_4 alkyl; and

R_{11} is C_1-C_4 alkyl, CF_3, CF_2H or CF_2CF_2H.

4. Compositions of Claim 3 wherein the compound is an agriculturally suitable salt of Formula II.

5. Compositions of Claim 4 wherein the cation of the compound of Formula II and the cation of the carboxyli or inorganic acid salt are identical.

6. Compositions of any of the preceding claims comprising a compound of Formula II wherein:

R_2 is F, Cl, Br, C_1-C_4 alkyl, $SO_2NR_6R_7$, $S(O)_nR_8$, $SO_2NCH_3(OCH_3)$, CO_2R_9, OSO_2R_{10}, OR_{11} or NO_2;

R_{11} is C_1-C_4 alkyl or C_1-C_3 alkyl substituted with 1-5 atoms of F, Cl or Br;

X is CH_3 or OCH_3;

Y is CH_3, OCH_3 or $CH(OCH_3)_2$;

or X may be Cl when Y is CH_3 or OCH_3.

7. Compositions of any of the preceding claims wherein the concentration of the carboxylic or inorganic acid salt or salts is greater than 10% and less than 40% or the salt saturation limit of the solution.

8. Compositions of any of the preceding claims wherein the salt or salts are selected from C_1-C_3 carboxylic acids and inorganic acid salts.

9. The composition of Claim 7 wherein the carboxylic or inorganic acid salt is selected from diammonium hydrogen phosphate, ammonium acetate, sodium acetate, lithium acetate, potassium acetate, or sodium thiocyanate.

10. The composition of any of the preceding claims comprising 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]benzenesulfonamide, ammonium salt with diammonium hydrogen phosphate.

11. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 2-[[(4-chloro-6-methoxypyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoic acid, ethyl ester.

12. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 2-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino-carbonyl]aminosulfonyl]benzoic acid, methyl ester.

13. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of N-[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-2-hydroxy-benzenesulfonamide, ethanesulfonate.

14. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 3-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl] aminosulfonyl]-2-thiophenecarboxylic acid, methyl ester.

15. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 2-[[(4,6-dimethylpyrimidin-2-yl)aminocarbonyl]-aminosulfonyl]benzoic acid, methyl ester.

16. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-aminocarbonyl]benzenesulfonamide.

17. The composition of any of Claims 1 to 9 wherein the compound of Formula II is an agriculturally suitable salt of 2-[[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-aminosulfonylmethyl]benzoic acid, methyl ester.

18. The composition of any of the preceding Claims with an additional herbicide which is not selected from I or II.

19. The composition of claim 1 wherein:

(a) the compound of Formula II is as defined in any of Claims 10 to 17:

(b) said salt of a carboxylic or inorganic acid is as defined in Claim 9 or is diammonium hydrogen phosphate when said compound of Formula II is the compound

defined in Claim 10;

(c) the concentration of said compound of Formula II is 10 to 40%;

(d) the concentration of said salt of a carboxylic or inorganic acid is greater than 10% and less than 40% or the salt saturation limit of the solution; and

(e) the pH of the composition is in the range 7 to

20. A modification of the composition of any of th preceding claims wherein said salt of a carboxylic or inorganic acid is replaced, in part or in toto, by one or more water soluble herbicides other than said compounds of Formula I or II.

21. A method for the preparation of a composition of any of Claims 1 to 20 which comprises forming an admixture in an aqueous medium of said agriculturally suitable salt of a carboxylic or inorganic acid and said one or more compounds selected from I and II, the concentration of the carboxylic or inorganic acid salt or salts being between 3% and the salt saturation limit of the aqueous solution.

22. A method for the preparation of a composition of any of Claims 1 to 20 which comprises

(i) suspending a compound of Formula I in water optionally containing surfactants and/or thickening or suspending agents;

(ii) optionally neutralising said mixture with base to a pH of 6.0 to 10.0 to obtain a salt of Formula II;

(iii) adding said agriculturally suitable salt of a carboxylic or inorganic acid, or mixture therefore; and

(iv) milling the mixture to obtain a slurry of desire particle size.

23. A method for the control of undesired vegetation by applying to the locus of such vegetation an effective amount of a herbicidal composition, characterise in

that said herbicidal composition comprises an aqueous dilution of the composition of any of Claims 1 to