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Stable solid formulations of cyclohexenone oxime ether herbicides

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(71) Applicant(s)
BASF Aktiengesellschaft

(72) Inventor(s)
Matthias Bratz; Karl-Friedrich Jager; Hans Ziegler; Rainer Berghaus

(74) Agent/Attorney
WATERMARK PATENT and TRADEMARK ATTORNEYS,Locked Bag 5,HAWTHORN VIC 3122

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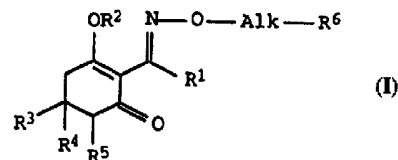
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(54) Title: STABLE SOLID FORMULATIONS OF CYCLOHEXENONE OXIME ETHER HERBICIDES (54) Bezeichnung: STABILE FESTFORMULIERUNGEN VON CYCLOHEXENONOXIMETHER-HERBIZIDEN (57) Abstract The invention concerns plant-protection formulations containing a cyclohexenone oxime ether of general formula (I) in which groups R¹ to R⁶ are as follows: R¹ is ethyl or propyl; R² is hydrogen or an equivalent of an agriculturally useful cation; R³ is 2-(thioethyl)propyl, tetrahydrothiopyran-3-yl, tetrahydrothiopyran-4-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl, 1-(methylthio)cyclopropyl, 5-(iso-propyl)isoxazol-3-yl, 2,5-dimethylpyrazol-3-yl, 2,3,6-trimethylphenyl or 2,4,6-trimethyl-3-butyrylphenyl; R⁴ and R⁵, independently of each other, are hydrogen, methyl or methoxycarbonyl; Alk is CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) or CH₂CH₂CH=CH; R⁶ is hydrogen, pyhenyl, halophenyl, dihalophenyl, phenoxy, halophenoxy or dihalophenoxy; plus a water-soluble basic salt of an acid with a pKs value greater than 5, but excluding alkali-metal hydroxides and alkali-metal carbonates. The invention also concerns the preparation of such formulations and their use as herbicides. (57) Zusammenfassung Pflanzenschutzwirkstoff-Formulierung, enthaltend einen Cyclohexenonoximether der allgemeinen Formel (I), in welcher die Reste R¹-R⁶ die folgenden Bedeutungen haben: R¹ Ethyl oder Propyl; R² Wasserstoff oder ein Äquivalent eines landwirtschaftlich brauchbaren Kations; R³ 2-(Thioethyl)propyl, Tetrahydrothiopyran-3-yl, Tetrahydrothiopyran-4-yl, Tetrahydropyran-3-yl, Tetrahydropyran-4-yl, 1-(Methylthio)cyclopropyl, 5-(iso-Propyl)isoxazol-3-yl, 2,5-Dimethylpyrazol-3-yl, 2,4,6-Trimethylphenyl oder 2,4,6-Trimethyl-3-butyrylphenyl; R⁴ und R⁵ unabhängig voneinander Wasserstoff, Methyl, Methoxycarbonyl; Alk CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) oder CH₂CH₂CH=CH; R⁶ Wasserstoff, Phenyl, Halogenphenyl, Dihalogenphenyl, Phenoxy, Halogenphenoxy oder Dihalogenphenoxy; und ein wasserlösliches basisches Salz einer Säure mit einem pKs-Wert größer als 5, wobei Alkalihydroxide und Alkalicarbonat ausgeschlossen sind, deren Herstellung und Verwendung als Herbizid.			



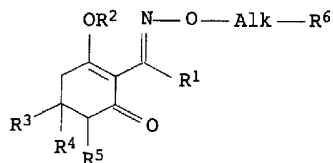
Stable solid formulations of cyclohexenone oxime ether herbicides

Abstract

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Crop protection active compound formulation [sic], comprising a cyclohexenone oxime ether of the general formula I

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where the radicals R¹-R⁶ have the following meanings:

R¹ is ethyl or propyl;

20

R² is hydrogen or an equivalent of an agriculturally utilizable cation;

R³ is 2-thioethylpropyl, tetrahydrothiopyran-3-yl, tetrahydrothiopyran-4-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl, 1-methylthiocyclopropyl, 5-isopropylisoxazol-3-yl, 2,5-dimethylpyrazol-3-yl, 2,4,6-trimethylphenyl or 2,4,6-trimethyl-3-butyrylphenyl;

25

30 R⁴ and R⁵ independently of one another are hydrogen, methyl or methoxycarbonyl;

Alk is CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) or CH₂CH₂CH=CH;

35 R⁶ is hydrogen, phenyl, halophenyl, dihalophenyl, phenoxy, halophenoxy or dihalophenoxy;

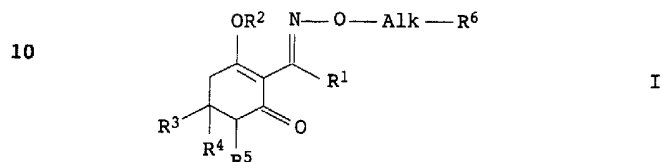
and a water-soluble basic salt of an acid having a pK_a of greater than 5, alkali metal hydroxides and alkali metal carbonates being
40 excluded, their preparation and use as herbicides are described.

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Stable solid formulations of cyclohexenone oxime ether herbicides

The present invention relates to crop protection active compound
5 formulation [sic], comprising a cyclohexenone oxime ether of the
general formula I



15 where the radicals R¹-R⁶ have the following meanings:

R¹ is ethyl or propyl;

20 R² is hydrogen or an equivalent of an agriculturally utilizable cation;

R³ is 2-thioethylpropyl, tetrahydrothiopyran-3-yl, tetrahydrothiopyran-4-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl,
25 1-methylthiocyclopropyl, 5-isopropylisoxazol-3-yl, 2,5-dimethylpyrazol-3-yl, 2,4,6-trimethylphenyl or 2,4,6-trimethyl-3-butyrylphenyl;

R⁴ and R⁵ independently of one another are hydrogen, methyl or
30 methoxycarbonyl;

Alk is CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) or CH₂CH₂CH=CH;

R⁶ is hydrogen, phenyl, halophenyl, dihalophenyl, phenoxy, halo-
35 phenoxy or dihalophenoxy;

and a water-soluble basic salt of an acid having a pK_a of greater than 5, their preparation and use as herbicides.

40 Cyclohexenone oxime ethers of the general formula I have been known as herbicides for a long time. Moreover, in small amounts they act as growth regulators.

The herbicidally active cyclohexenone oxime ethers of the general
45 formula I are disclosed, inter alia, in DE-A 24 39 104, DE-A 28 22 304, DE-A 38 08 072, DE-A 38 38 309, EP-A 046 860, EP-A 066 195, EP-A 071 707, EP-A 088 299, EP-A 088 301,



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EP-A 115 808, EP-A 125 094, EP-A 137 174, EP-A 142 741,
EP-A 177 913, EP-A 228 598, EP-A 230 235, EP-A 230 260,
EP-A 238 021, EP-A 243 313, EP-A 254 514, EP-A 319 835,
EP-A 456 068, EP-A 456 069, EP-A 456 112, EP-A 456 118,
5 U.S. 4,440,566, JP-A 54/191 945 and Proceedings Brit. Crop-
Protection Conference - weeds 1985, Vol. 1, pages 93-98.

The compounds are in general used in the form of water-dispersible powders (WP) or water-dispersible granules (WG), and also as
10 emulsifiable concentrates (EC). Some compounds of this class of substances are marketed as water-soluble formulations in which the active compound is present as the alkali metal salt. A disadvantage of the emulsifiable concentrates is that, beside the actual active compound, large amounts of organic solvents are also
15 applied during use. It has additionally been shown that the active compounds are unstable in organic solvents in the presence of emulsifiers or of water present in traces and decompose. These problems are described, for example, in EP 394 847 and EP 266 068.

20

Water-dispersible solid formulations (WPs or WGs) do avoid the use of organic solvents, but require a higher expenditure on preparation of the formulation.

25 The often low-melting or liquid active compounds must be absorbed on carrier material in order to be accessible to the necessary fine grinding. The addition of auxiliaries and carriers additionally leads to the fact that the active compound contents in the formulation have to precipitate to a low extent, which leads to
30 increased packaging and transportation costs. Examples of such formulations are found, inter alia, in EP 488 645.

Water-soluble formulations are also described. It is also seen here that the chemical instability of the cyclohexenone oxime
35 ethers stands in the way of a practical solution. A lithium salt, for example, is thus described in JP 62089 635. The preparation and the price of the lithium make this solution appear unattractive.

40 The preparation of various salts, among these salts of transition metals, by double decomposition is described in various applications. In practice, this process appears unsuitable as in the end sufficient stability is not achieved. (JP 59 1633 63, JP 8144 384, US 47 41 768, DE 3941160).

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The preferred manner of preparation of alkali metal salts is the extraction of the active compounds from organic solution with an aqueous solution of the alkali metal hydroxides (eg. DE 3941160).

- 5 It is an object of the present invention to develop storage-stable solid formulations of cyclohexenone oxime ethers of the general formula I and a process for their preparation.

We have found that this object is surprisingly achieved by the
10 crop protection active compound formulation described at the outset.

Water-soluble basic salts which are suitable for this purpose are:

- 15 Metaborates, phosphates, hydrogen phosphates, pyrophosphates, metasilicates, orthosilicates, tetraborates, sulfites, tripolyphosphates, polyphosphates, metaphosphates, citrates, tetrasodium EDTA, trisodium nitrilotriacetate, guanidine acetate, guanidine
20 carbonate, and mixtures of these.

Preferred cyclohexenone herbicides are:

- 2-(N-ethoxybutyrimidoyl)-5-(2-ethylthiopropyl)-3-hydroxy-2-cyclo-
25 hexenone-1-one [sic] (sethoxydim),
2-(1-allyloxyiminobutyl)-4-methoxycarbonyl-5,5-dimethyl-3-oxo-cyclohexenol (alloxydim),
2-(N-ethoxybutyrimidoyl)-5-(2-phenylthiopropyl)-3-hydroxy-2-cyclohexen-1-one [sic],
30 5-(2,4,6-trimethylphenyl)-3-hydroxy-2-[1-(ethoxyimino)propyl]-cyclohex-2-en-1-one (tralkoxydim),
2-(N-ethoxybutyrimidoyl)-3-hydroxy-5-(tetrahydropyran-3-yl)cyclohexen-1-one,
1-[1-ethoxyiminobutyl]-3-hydroxy-5-(tetrahydrothiopyran-3-yl)-
35 2-cyclohexen-1-one (cycloxydim),
2-[1-[(E)-3-chloroallyloxy]iminopropyl]-5-(2-ethylthiopropyl)-3-hydroxycyclohex-2-enone (clethodim),
2-(1-(3-chloroallyloxyiminobutyl)-5-(2-ethylthio)propyl)-3-hydroxycyclohex-2-enone (cloproxydim),
40 2-(1-(3-chloroallyloxy)iminopropyl)-5-(1,3-dimethylpyrazol-5-yl)-3-hydroxycyclohex-2-enone [sic],
2-(1-(3-chloroallyloxy)iminopropyl)-5-(1-thiomethylcyclopropyl)-3-hydroxycyclohex-2-enone,
2-(1-ethoxyiminopropyl)-5-(2,4,6-trimethyl-3-butyl phenyl)-
45 3-hydroxycyclohex-2-enone [sic] (butroxydim),
2-(1-(3-chloroallyloxy)iminopropyl)-5-(tetrahydropyran-4-yl)-3-hydroxycyclohex-2-enone,



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2-(1-(2-p-chlorophenoxypropyloxy)iminobutyl-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohex-2-enone or mixtures thereof.

Particularly preferred cyclohexenone herbicides are:

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Sethoxydim, cycloxydim, clethodim, tralkoxydim, butroxydim, 2-(1-(3-chloroallyloxy)iminopropyl)-5-(tetrahydropyran-4-yl)-3-hydroxycyclohex-2-enone, 2-(1-(2-p-chlorophenoxypropyloxy)iminobutyl-5-(tetrahydrothiopyran-3-yl)-3-hydroxy-cyclohex-2-en-10 one or mixtures thereof.

The cyclohexenone oxime ethers of the general formula I can be obtained during preparation as isomer mixtures, both E/Z isomer mixtures and enantiomer or diastereoisomer mixtures being possible. If desirable, the isomer mixtures can be separated by the methods customary for this purpose, eg. by chromatography or by crystallization.

The cyclohexenone oxime ethers of the general formula I can be 20 present in several tautomeric forms, which are all covered by the invention.

The cyclohexenone oxime ethers according to the invention are weak organic acids having pkas [sic] between 4 and 5. The low 25 solubility in water in the neutral range distinctly increases at basic pHs. It is thus possible by suitable combination of cyclohexenones with basic water-soluble substances (acid acceptors) to obtain water-soluble mixtures.

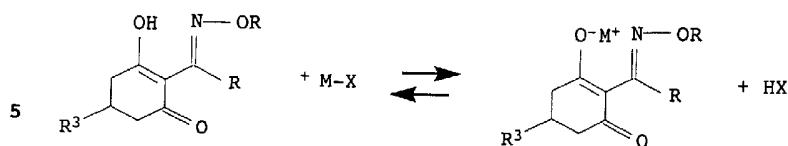
30 Beside the alkali metal hydroxides and alkali metal carbonates mentioned in the literature, basic water-soluble substances which are suitable for this purpose are those which are to be interpreted as alkali metal salts of those acids whose pka [sic] is greater than 5. The pka [sic] of the particular cyclohexenone is 35 preferably checked and then a basic substance is to be selected whose underlying pka [sic] is greater than that of the cyclohexenone.

It is to be expected that the following reaction commences in the 40 presence of water:

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A requirement for a clear solution then being formed is also that
10 the conjugate acid HX formed is also water-soluble.

Beside water-solubility, the mixtures of cyclohexenone and water-soluble basic salt (acid acceptor) according to the invention have a distinctly improved storage stability at elevated temperatures than, for example, the free active compounds or alkali metal salts which were obtained from the cyclohexenones with alkali metal hydroxides or alkali metal carbonates.

Adequate storage stability is an essential feature of commercially marketable and registrable crop protection agents.
20 Decreased decomposition of the active compound per se is also an economic advantage.

The following basic salts (acid acceptors) have proven suitable
25 for achieving the described water solubility and storage stability of the active compound:

Alkali metal metaborates, alkali metal tetraborates, alkali metal and ammonium metasilicates, trialkali metal and triammonium phosphates, alkali metal and ammonium hydrogen phosphates, alkali metal pyrophosphates, alkali metal tripolyphosphates, alkali metal sulfites, alkali metal citrates, tetrasodium EDTA, trisodium nitrilotriacetic acid [sic], guanidine carbonate and guanidine acetate, it being possible for the salts to be present in
35 anhydrous form or as hydrates.

Sodium metaborate, sodium metasilicate, trisodium phosphate, tetrasodium pyrophosphate, dipotassium hydrogen phosphate, guanidine carbonate, tetrasodium EDTA and trisodium nitrilotriacetic acid [sic] have proven particularly suitable.
40

The invention comprises solid water-soluble formulations, preferably in the form of powders or granules, which as the herbicidal component comprise a cyclohexenone oxime ether and a water-soluble basic salt. The proportion of the cyclohexenone oxime ether is from 5 to 95%, preferably from 10 to 85%, and the proportion of the basic salt is from 5 to 95%, preferably from 15 to
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90%, based on the sum of cyclohexenone oxime ether and basic salt.

In order to guarantee use in accordance with practice, it may be
5 necessary to add further formulation auxiliaries. These include,
for example, herbicidally active compounds, antidotes, water-sol-
uble salts, dispersants, wetting agents, binders, lubricants, ab-
sorptive carriers, antifoams, preservatives, colorants, pigments
or further adjuvants or surfactants customary in agricultural
10 practice.

Preferred basic water-soluble salts are: ammonium and alkali
metal metaborates, tetraborates, metasilicates, orthosilicates,
phosphates, hydrogen phosphates, pyrophosphates, tripolyphos-
15 phates, polyphosphates, sulfites, citrates, tetrasodium EDTA,
trisodium nitrilotriacetic acid [sic], guanidine carbonate and
guanidine acetate. The salts can be employed in anhydrous form
and in the form of their hydrates. If desired, mixtures of the
salts can be employed. The sodium and potassium salts are pre-
20 ferred. Additional water-soluble salts can be: sodium chloride,
potassium chloride, ammonium sulfate, sodium sulfate, potassium
sulfate and urea [sic], potassium carbonate and sodium carbonate.

Further herbicidally active compounds can be:

25 2,4-D, 2,4-DB, acetochlor, acifluorfen, aclonifen, alachlor, ali-
dochlor [sic], ametryn, amidosulfuron, amitrole, anilofos, asu-
lam, atrazine, azimsulfuron, aziprotryne, barban, benazolin,
benefin [sic], benfuresate, bensulfuron, bensulide, bentazone,
30 benzofenap, benzofluor, benzoylprop, benzthiazuron, bifenox, bi-
salafox, bromacil, bromobutide, bromofenoxim, bromoxynil, bumina-
fos, butachlor, butamifos, buten-achlor [sic], buthidazole,
butralin, buturon, butylate, cafenstrole, carbetamide, chloram-
ben, chlorbromuron, chlorbufam, chlorfenac, chloridazon, chlori-
35 muron, chlornitrofen, chlorophenprop [sic], chloroxuron, chlor-
propham, chlorsulfuron, chlorthal-dimethyl, chlorthiamid, chlor-
toluron, cinnemethylin, cinosulfuron, clodinafop, clomazone, clome-
prop, clopyralid, cumyluron, cyanazine, cycloate, cyclosulfamu-
ron, cycluron, cyhalofop, cyperquat, cyprazine, cyprazole, dala-
40 pon, desmedipham, desmetryn, di-allate, dicamba, dichlobenil,
dichlorprop, dichlorprop-P, diclofop, diethatyl, difenoxuron,
difenzoquat, diflufenican, dimefuron, dimethachlor, dimethame-
thryn [sic], dimethenamid, dinitramine, dinoseb, dinoseb [sic],
dinoterb, diphenamid, dipropetryn, diquat, dithiopyr, diuron,
45 DNOC, dymron, eglinazone, endothall [sic], EPTC, esprocarb, et-
halfluralin, ethametsulfuron, ethidimuron, ethiozin, ethofume-
sate, ethoxyfen, etobenzanid, fenoprop, fenoxaprop, fenoxaprop-p



- [sic], fenthiaprop, fenuron, flamprop, flazasulfuron, fluazifop, fluazifop-p [sic], fluchloralin, flumetsulam, flumiclorac, flumioxazin, flumipropyn, fluometuron, fluorbentranil, fluorochloridone, fluorodifen, fluoroglycofen, flupoxam, flupropacil, fluridone, fluroxyppyr, flurtamone, fomesafen, fosamine, furyloxyfen, 5 glufosinate-ammonium, glyphosate, halosulfuron, haloxyfop, haloxyfop [sic], haloxyfop-p [sic], hexazinone, imazamethapyr, imazapyr, imazaquin, imazethabenz, imazethapyr, imazosulfuron, ioxynil, isocarbamid, isopropalin, isoproturon, isouron, isoxaben, 10 isoxapyrifop, karbutilate, lactofen, lenacil, linuron, maleic hydrazide, MCPA, MCPB, mecoprop, mecoprop-P, mefenacet, mefluidide, metamitron, metazachlor, methabenzthiazuron, methazole, metobenzuron, metolachlor, metosulam, metoxuron, metribuzin, metsulfuron, minoterb, molinate, monalide, monolinuron, monuron, na- 15 propamide, nopropanilide [sic], naptalame [sic], NCC 330, neburon, nicosulfuron, nipyraclufen, nitralin, nitrofen, nitrofluorfen, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxyfluorfen, paraquat, pebulate, pendimethalin, perfluidone, phenisopham, phenmedipham, picloram, piperophos, PPG-1013, pretilachlor, 20 primisulfuron, procyzazine, prodiamine, profluralin, prometon, prometryn, propyzamide, propachlor, propanil, propaquizafop, propazine, propham, prosulfocarb, prosulfuron, prynachlor, pyrazolate, pyrazosulfuron, pyrazoxyfen, pyributicarb, pyridate, pyriithiobac, quinclorac, quinmerac, quizalofop, quizalofop-p [sic], 25 quizalofop [sic], rimsulfuron, secbumeton, siduron, simazine, simetryn, sulcotrione, sulfallate, sulfentrazone, sulfometuron-methyl, sulfosate, tebuthiuron, terbacil, terbucarb, terbutylchlor, terbumeton, terbutylazine, terbutryn, thiazopyr, thidiazimin, thifensulfuron-methyl, thiobencarb, tiocarbazil, tri-allate, 30 triasulfuron, triazofenamid, tribenuron, triclopyr, tridiphane, trietazine, trifluralin, triflusulfuron, trimeturon, vernolate, xylachlor or mixtures of these. The co-herbicides can be water-soluble or water-insoluble.
- 35 In the case of water-insoluble compounds, these are present as finely ground powders. It is additionally possible to introduce these into the formulation in the form of water-dispersible granules. In the case of water-soluble co-herbicides, these can be present in the form of the free acid or as its salt.
- 40 Dispersants or wetting agents which can be used, inter alia, are:
- Alkylarylsulfonates; phenylsulfonates; alkylsulfates [sic]; alkylsulfonates; alkyl ether sulfates; alkyl aryl ether sulfates; al- 45 kyl polyglycol ether phosphates; polyarylphenyl ether phosphates; alkylsulfosuccinates; olefinsulfonates; paraffinsulfonates; petroleum sulfonates; taurides; sarcosides; fatty acids; alkyl-



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- naphthalenesulfonic acids; naphthalenesulfonic acids; lignosulfonic acids; condensation products of sulfonated naphthalenes with formaldehyde; or with formaldehyde and phenol; lignin-sulfite waste liquor; including their alkali metal, alkaline earth metal, ammonium and amine salts; alkylphenol alkoxylates; alcohol alkoxylates; fatty amine alkoxylates; polyoxyethylene glycerol fatty acid esters; castor oil alkoxylates; fatty acid alkoxylates; fatty acid amide alkoxylates; fatty acid polydiethanolamides; lanolin ethoxylates; EO/PO block copolymers; fatty acid polyglycol esters; isotridecyl alcohol; fatty acid amides; methylcellulose; fatty acid esters; silicone oils; alkyl polyglycosides; glycerol fatty acid esters; alkyl phosphates; quaternary ammonium compounds, amine oxides; betaines and mixtures of these. The dispersants and wetting agents are known substances and are described in greater detail, for example, in: McCutchesons [sic] Emulsifiers & Detergents, MC Division, Glen Rock NJ; Stache, Tensid Taschenbuch [Surfactant Handbook], Hanser Verlag.

Binders which can be used are:

- 20 Polyvinylpyrrolidone, polyvinyl alcohol, carboxymethylcellulose, starch, vinylpyrrolidine [sic]/vinyl acetate copolymers and mixtures thereof.
- 25 Lubricants which can be used are: Mg stearate, Na stearate, talc, polyethylene glycol and mixtures thereof.

Absorptive carrier materials which can be used are:

- 30 Mineral earths such as silicic acids, silica gels, silicates, talc, kaolin, attaclay, limestone, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate and magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate and ureas, vegetable products such as grain flour, tree bark meal, wood meal and nutshell meal, cellulose powder, attapulgit, montmorillonite, mica, vermiculite, synthetic silicic acids, synthetic calcium silicates and mixtures thereof.
- 40 Suitable antifoams are, for example, silicone emulsions, long-chain alcohols, fatty acids, organofluorine compounds and mixtures thereof.



The formulation auxiliaries can be additionally used in the crop protection active compound formulation in a concentration from 0 to 95% by weight. If they are a constituent of the formulation, from 5 to 95% by weight have proven suitable.

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Further crop protection active compounds can be additionally used in a concentration from 0 to 90% by weight. If they are a constituent of the formulation, from 10 to 90% by weight have proven suitable. The % by weight mentioned relate to the total weight of 10 the crop protection active compound formulation.

The solid formulations according to the invention can be prepared in various manners known in principle to the person skilled in the art.

15

Suitable formulations are powders, granules, briquets, tablets and similar solid formulations. In addition to powders, granules are particularly preferred. The powders can be water-soluble or water-dispersible powders. The granules can be water-soluble or 20 water-dispersible granules for use in spray application or broadcasting granules for direct application. The average particle size of the granules is from 200 μ m to 2 mm.

Since these formulations are often hygroscopic substances, or 25 for reasons such as preventive user protection, the formulations can be packaged in water-soluble film bags. Preferably, a water vapor-impermeable outer covering such as polyethylene film, polyethylene-laminated paper or aluminum foil is additionally employed in the packaging.

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Suitable water-soluble films consist of the following materials:

Polyvinyl alcohol, cellulose derivatives such as methylcellulose or carboxymethylcellulose.

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The following preparation processes are suitable:

a) Active compound is solid

40

1) Mixing of active compound, basic salt and further auxiliaries, comminution if desired and subsequent agglomeration.

The processes of extruder granulation, disk granulation, fluidized bed granulation or mixer granulation, for 45 example, are suitable for agglomeration. If appropriate, the granules obtained are then dried.



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- 2) Mixing of active compound, basic salt and further auxiliaries, comminution if desired and subsequent compaction.

5 b) Active compound is an oil or a solid

- 1) Extraction of the cyclohexenone oxime ether dissolved in an organic solvent by means of an aqueous solution of the basic salt in the aqueous phase, then removal of the water.

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Suitable organic solvents are water-immiscible, or only partially miscible, solvents such as hydrocarbon [sic], aromatic hydrocarbons, halogenated aliphatic or aromatic hydrocarbons, ethers, carboxylic acid esters, carboxamides, ketones and alcohols.

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Spray drying, vacuum drying, fluidized bed drying and freeze drying, for example, are suitable for evaporating the water.

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The solids obtained in this way can then be additionally processed as under a).

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The aqueous solution thus obtained can furthermore be applied to an absorptive carrier material, eg. by spraying or mixing. Broadcasting granules, for example, can be obtained in this manner.

30 Formulation examples:

a) Test methods

- 35 The active compound content of the formulations was in each case determined by means of quantitative HPLC, and is indicated in percent.

Experiments on shelf life

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To investigate the shelf life, samples of the particular formulation are stored for a specific time at the particular temperature indicated in tightly closed glass vessels. The samples are then examined and compared with the comparison value at the start of storage (zero value). The active compound content is indicated as the relative proportion, based on the zero value (in percent).

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Experiments on dissolution behavior

2 g of the formulation are added in one portion to 100 ml of CIPAC standard water D which is stirred at about 100 rpm by means of a magnetic stirrer. The time which passes until the entire solid product has disintegrated or dissolved is taken.

b) Formulation experiments

The following compounds were used for formulation experiments:

Compound A: sethoxydim
Compound B: cycloxydim
Compound C: 2-(1-(3-chloroallyloxy)iminopropyl)-5-(tetrahydropyran-4-yl)-3-hydroxycyclohex-2-enone
Compound D: 2-(1-(2-p-chlorophenoxypropyloxy)iminobutyl-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohexenone

Comparison Example 1:

51.4 g of compound C (content 97%) are mixed with a mixture of 1 part of sodium carbonate and 1 part of sodium hydrogen carbonate (48.6 g) for 60 sec in an IKA laboratory mill (type M 20). The mixture is soluble in water within less than 5 min. The active compound content is 49.3%.

Example 1:

51.4 g of compound C (content 97%) are mixed with sodium metasilicate (48.6 g) for 60 sec in an IKA laboratory mill (type M 20). The mixture is soluble to give a clear solution in water within less than 5 min. The active compound content is 42%.

Example 2:

51.4 g of compound C and 48.6 [lacuna] of trisodium phosphate dodecahydrate are mixed as described in Ex. 1. Active compound content is 46%.

The storage stability at room temperature was observed for 3 months and compared.



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	Relative content of compound C after	
	1 month [%]	3 months [%]
Comparison Example 1	91	68
5 Example 1	100	95
Example 2	99	78

Comparison Example 2:

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500 g of active compound C are dissolved in 1,000 g of toluene. This solution is mixed with a solution of 58.5 g of sodium hydroxide in 650 g of water for 1 hour. After phase separation, the homogeneous aqueous phase is separated off and then dried to give granules in a laboratory fluidized bed granulator at an inlet temperature of the drying air of 120°C. The active compound content is 86.8%. The granules dissolve rapidly and completely on introducing into water.

20 Comparison Example 3:

92.3 g of active compound D were [sic] dissolved in 90 g of toluene. This solution is mixed with a solution of 7.66 g of sodium hydroxide solution in 100 g of water for 1 hour. After phase separation, the homogeneous aqueous phase is separated off, washed with MTB ether and then dried to give a solid product in a vacuum drying oven at a drying temperature of 40°C. The solid product has an active compound content of 87.1% and dissolves rapidly and completely on introducing into water.

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Comparison Example 4:

A 30% strength solution of active compound D in toluene is extracted with 2.5% strength NaOH. The aqueous phases are collected and dried at 70°C in a vacuum drying oven. The solid obtained has an active compound content of 84.6% and is soluble in water to give a clear solution within 2 min.

Example 3:

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50 ml of a 50% strength solution of compound A in tert-butyl methyl ether are shaken with a solution of 10.2 g of sodium metasilicate in 50 ml of water. After separating off the aqueous phase, the ether phase is washed with 30 ml of water. The combined aqueous phases are evaporated in vacuo at 70°C. The solid



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residue obtained is soluble to give a clear solution in water within 2 min. Active compound content: 70%.

Example 4:

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50 ml of a solution of cycloxydim (compound B) in Solvesso 150 (430 g/l) are extracted with a solution of 17.7 g of sodium metasilicate in 85 ml of water. After separating off the aqueous phase, the organic phase is washed with 30 ml of water and the combined aqueous phases are evaporated in vacuo at 70°C. The residue obtained is soluble in water to give a clear solution within 2 min. Active compound content: 57%.

Example 5:

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A mixture of sodium metaborate hydrate (48.6 g) and compound C (51.4 g) are [sic] first mixed in an IKA type M 20 universal mill and then treated successively with 7.2 ml of water. The material thus obtained is extruded using a basket extruder bench apparatus (Fitzpatrick Company Europe, type KAR 75) with a screen size of 0.8 mm. The granules obtained are dried at 60°C. Active compound content is 55%. The granules dissolve completely in water in less than 4 min.

25 Example 6:

A mixture of sodium phosphate dodecahydrate (58.9 g) and compound C (41.1 g) is extruded as described in Example 5 with addition of 3.8 ml of water. Active compound content: 52%. The granules dissolve in water to give a clear solution within 3 min.

Example 7:

A mixture of sodium metasilicate (48.6 g) and compound C (51.4 g) is extruded as described in Example 5 with addition of 25 g of water. Active compound content: 45%. The granules dissolve in water to give a clear solution within 2 min.

Example 8:

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A mixture of compound C (72%) and sodium metasilicate (28%) is mixed in an IKA type M 20 universal mill and made into a paste with addition of a total of 22.5 g of water. The material obtained is extruded as described in Example 5 and the granules obtained are dried at 60°C. Active compound content: 64%. The granules dissolve in water to give a clear solution within 2 min.



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Example 9:

217.5 g of active compound C are dissolved in 200 g of toluene. This solution is mixed with a solution of 82.5 g of sodium metasilicate in 300 g of water for 1 hour. After phase separation in a separating funnel, the homogeneous aqueous phase is separated off and then dried to give granules in a laboratory fluidized bed granulator (Combi Coater, Niro Aeromatic) at an inlet temperature of the drying air of 120°C.

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The active compound content is 64.2%. The granules dissolve rapidly and completely on introducing into water.

Example 10:

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16.0 g of sodium metasilicate and 84.82 g of active compound C are mixed and reacted in 100 g of water. An aqueous solution is formed. This is dried in a vacuum drying oven at a drying temperature of 70°C to give a solid product. The active compound content is 73.7%. The solid product dissolves rapidly and completely on introducing into water.

Example 11:

25 79.8 g of active compound D are dissolved in 100 g of toluene. This solution is mixed and reacted with a solution of 20.8 g of sodium metasilicate in 100 g of water for 1 hour. After allowing to stand, 3 phases are formed. The two lower, aqueous phases are separated off in a separating funnel and then dried at a drying temperature of 70°C in a vacuum drying oven to give a solid product having an active compound content of 78.7%. The solid product dissolves rapidly and completely on introducing into water.

35 Example 12:

88.75 g of active compound D are dissolved in 100 g of toluene. This solution is mixed and reacted with a solution of 11.6 g of sodium metasilicate in 100 g of water for 1 hour. After allowing to stand, 3 phases are formed. The two lower, aqueous phases are separated off in a separating funnel and then dried at a drying temperature of 70°C in a vacuum drying oven to give a solid product having an active compound content of 88.4%. The solid product dissolves rapidly and completely on introducing into water.



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Example 13:

Compound C (7.6 g) and bentazone sodium salt (84.7 g; content about 85%) are intimately mixed together with sodium metasilicate (7.7 g) in an IKA universal mill and then moistened with 8.5 ml of water. After extrusion of the material obtained, granules which are soluble in water to give a clear solution within 1 min are obtained. Active compound content (compound C): 6.8%.

10 Example 14:

84.7 g of Na bentazone, 7.6 g of compound C, 7.7 g of sodium metaborate and 6 ml of water are mixed and extruded as described in Example 13. The granules obtained are soluble in water to give a clear solution within 1 min.

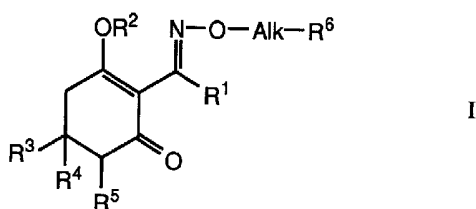
Active compound content (compound C): 6.5%.

20		Shelf life of formulation example, relative active compound content in %, storage time 30 d			
		20°C	30°C	40°C	50°C
25	Comparison Example				
	2	100	99	88	42
	3	100	98	88	40
	4	100	96	80	19
30	Example No.				
	4	100	100	96	96
	5	100	100	98	83
	6	100	99	99	87
	7	100	100	100	99
35	8	100	100	100	100
	9	100	100	100	78
	10	100	100	99	77
40	11	99	99	99	85
	12	99	99	99	90



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of preparing a storage-stable, water-soluble crop protection solid active compound formulation for controlling undesired vegetation comprising the step of combining a water-soluble basic salt of an acid having a pK_a of greater than 5, (alkali metal hydroxides and alkali metal carbonates being excluded) with a cyclohexenone oxime ether of the general formula I



where the radicals R¹-R⁶ have the following meanings:

- R¹ is ethyl or propyl;
- R² is hydrogen or an equivalent of an agriculturally utilisable cation;
- R³ is 2-thioethylpropyl, tetrahydrothiopyran-3-yl, tetrahydrothiopyran-4-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl, 1-methylthiocyclopropyl, 5-isopropylisoxazol-3-yl, 2,5-dimethylpyrazol-3-yl, 2,4,6-trimethylphenyl or 2,4,6-trimethyl-3-butyrylphenyl;
- R⁴ and R⁵ independently of one another are hydrogen, methyl or methoxycarbonyl;
- Alk is CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) or CH₂CH₂CH=CH;
- R⁶ is hydrogen, phenyl, halophenyl, dihalophenyl, phenoxy, halophenoxy or dihalophenoxy;
2. A method according to claim 1 wherein:
- R² is sodium;
- R³ is tetrahydrothiopyran-3-yl;
- R⁴ and R⁵ are both hydrogen;



Alk is $\text{CH}_2\text{CH}(\text{CH}_3)$;

and R^6 is p-fluorophenoxy or p-chlorophenoxy

3. A method according to claim 1 or 2 wherein the water-soluble basic salt is chosen from the group consisting of metaborate, phosphate, hydrogen phosphate, pyrophosphate, metasilicate, orthosilicate, tetraborate, sulfite, tripolyphosphate, polyphosphate, metaphosphate, tetrasodium EDTA, trisodium nitrilotriacetate, guanidine acetate, guanidine carbonate or mixtures thereof.

4. A method according to any one of the preceding claims wherein the water-soluble basic salt is chosen from the group consisting of alkali metal metaborate, alkali metal tetraborate, alkali metal and ammonium metasilicate, trialkali metal and triammonium phosphate, alkali metal and ammonium hydrogen phosphate, alkali metal pyrophosphate, alkali metal tripolyphosphate, alkali metal sulfite, alkali metal polyphosphate, tetrasodium EDTA, trisodium nitrilotriacetate, guanidine carbonate, guanidine acetate or mixtures thereof.

5. A method according to any one of the preceding claims wherein the crop protection active compound is a cyclohexenone oxime ether chosen from the group consisting of sethoxydim, cycloxydim, clethodim, tralkoxydim, butoxydim, 2-(1-(3-chloroallyloxy)iminopropyl)-5-(tetrahydropyran-4-yl)-3-(hydroxycyclohex-2-enone, 2-(1-(2-p-chlorophenoxypropyloxy)-iminobutyl)-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohex-2-enone or mixtures thereof.

6. A method according to any one of claims 1 to 4 wherein the cyclohexenone oxime ether is the sodium salt of 2-(1-(2-p-chlorophenoxypropyloxy)iminobutyl)-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohexenone.

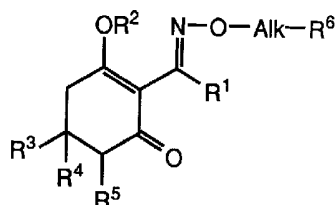
7. A method according to any one of the preceding claims which further comprises the addition of formulation auxiliaries.



8. A method according to any one of the preceding claims which comprises further crop protection active compounds.

9. A method according to any one of the preceding claims wherein the crop protection solid active compound formulation, comprises from 5 to 95% by weight of a cyclohexenone oxime ether of the general formula I,
from 5 to 95% by weight of a water-soluble basic salt,
from 0 to 95% by weight of a formulation auxiliary,
from 0 to 90% by weight of further crop protection active compounds.

10. A stable, water-soluble crop protection solid active compound formulation, comprising a cyclohexenone oxime ether of the general formula I



where the radicals R¹-R⁶ have the following meanings:

R¹ is ethyl or propyl;

R² is hydrogen or an equivalent of an agriculturally utilisable cation;

R³ is 2-thioethylpropyl, tetrahydrothiopyran-3-yl, tetrahydrothiopyran-4-yl, tetrahydropyran-3-yl, tetrahydropyran-4-yl, 1-methylthiocyclopropyl, 5-isopropylisoxazol-3-yl, 2,5-dimethylpyrazol-3-yl, 2,4,6-trimethylphenyl or 2,4,6-trimethyl-3-butyrylphenyl;

R⁴ and R⁵ independently of one another are hydrogen, methyl or methoxycarbonyl;

Alk is CH₂CH₂, CH₂CH(CH₃), CH₂CH=CH, CH₂CH=C(Cl) or CH₂CH₂CH=CH;

R⁶ is hydrogen, phenyl, halophenyl, dihalophenyl, phenoxy, halophenoxy or dihalophenoxy;

and a water-soluble basic salt of an acid having a pK_a of greater than 5, alkali metal hydroxides, alkali metal carbonates and ammonium salts being excluded.



11. A stable, water-soluble crop protection solid active compound formulation according to claim 10 wherein:

R² is sodium;

R³ is tetrahydrothiopyran-3-yl;

R⁴ and R⁵ are both hydrogen;

Alk is CH₂CH (CH₃); and

R⁶ is p-fluorophenoxy or p-chlorophenoxy.

12. A stable, water-soluble crop protection solid active compound formulation as claimed in claim 10, comprising, as crop protection active compound, a cyclohexenone oxime ether from the group consisting of sethoxydim, cycloxydim, clethodim, tralkoxydim, butoxydim, 2-(1-(3-chloroallyloxy)iminopropyl)-5-(tetrahydropyran-4-yl)3-hydroxycyclohex-2-enone, 2-(1-(2-p-chlorophenoxypropyloxy)-iminobutyl-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohex-2-enone or mixtures thereof.

13. A stable, water-soluble crop protection solid active compound formulation as claimed in claim 10 or 11 comprising the sodium salt of 2-(1-(2-p-chlorophenoxy)propyloxy)iminobutyl-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohexenone.

14. A stable, water-soluble crop protection solid active compound formulation as claimed in any one of claims 10 to 13, comprising as water-soluble salt a metaborate, phosphate, hydrogen phosphate, pyrophosphate, metasilicate, orthosilicate, tetraborate, sulfite, tripolyphosphate, polyphosphate, metaphosphate, tetrasodium EDTA, trisodium nitrilotriacetate, guanidine acetate, guanidine carbonate or mixtures thereof.

15. A stable, water-soluble crop protection solid active compound formulation as claimed in any one of claims 10 to 13, comprising as water-soluble basic salt an alkali metal metaborate, alkali metal tetraborate, alkali metal metasilicate, trialkali metal phosphate, alkali metal hydrogen phosphate, alkali metal



pyrophosphate, alkali metal tripolyphosphate, alkali metal sulfite, alkali metal polyphosphate, tetrasodium EDTA, trisodium nitrilotriacetate, guanidine carbonate, guanidine acetate or mixtures thereof.

16. A stable, water-soluble crop protection solid active compound formulation as claimed in any one of claims 10 to 15, furthermore comprising formulation auxiliaries.

17. A stable, water-soluble crop protection solid active compound formulation as claimed in any one of claims 10 to 16, comprising further crop protection active compounds.

18. A stable, water-soluble crop protection solid active compound formulation as claimed in any one of claims 10 to 17, comprising

from 5 to 95% by weight of a cyclohexenone oxime ether of the general formula I,

from 5 to 95% by weight of a water-soluble basic salt,

from 0 to 95% by weight of a formulation auxiliary,

from 0 to 90% by weight of further crop protection active compounds.

19. A process for preparing a crop protection solid active compound formulation as claimed in any one of claims 10 to 18, which comprises mixing a cyclohexenone oxime ether of the general formula I, the water-soluble basic salt, formulation auxiliaries if desired and further crop protection active compounds if desired, comminuting if desired and agglomerating or compacting.

20. A process for preparing a crop protection solid active compound formulation as claimed in any one of claims 10 to 18, which comprises dissolving a cyclohexenone oxime ether of the general formula I in an organic solvent, extracting with an aqueous solution of the water-soluble basic salt and then removing the water.



21. A process as claimed in claim 20, wherein the crop protection solid active compound formulation is comminuted if desired after removing the water and then agglomerated or compacted.

22. A process as claimed in claim 19 or 21, wherein extruder granulation, disk granulation, fluidised bed granulation or mixer granulation is used for agglomeration.

23. A process for controlling undesired vegetation, which comprises dissolving a herbicidally active amount of a crop protection solid active compound formulation as claimed in any one of claims 10 to 18 and allowing it to act on the crop plant, its habitat and/or on its seed.

24. A method according to claim 8 or 9, wherein the further crop protection active compound is glyphosate or a salt thereof.

25. A crop protection solid active compound formulation as claimed in claim 17 or 18, comprising glyphosate or a salt thereof as further crop protection active compound.

26. The sodium salt of 2-[1-(2-p-chlorophenoxypropyloxy) imino-butyl]-5-(tetrahydrothiopyran-3-yl)-3-hydroxycyclohexenone.

DATED this 10th day of March, 1999

BASE AKTIENGESELLSCHAFT

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290 BURWOOD ROAD
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