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(54) Title: HERBICIDAL COMPOSITION COMPRISING A MIXTURE OF A FIRST HERBICIDE AND PINOXADEN

(57) **Abstract**: The invention provides a herbicidal composition comprising a mixture of: (a) a first herbicide being a synthetic auxin herbicide (e.g. dicamba, MCPA or 2,4-D) or an acetolactate synthase (ALS) inhibitor herbicide (e.g. triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, sulfosulfuron, flupyrsulfuron-methyl, or pyroxsulam); wherein the first herbicide is present in the form of an aluminium salt; wherein the first herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and wherein the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden; and (b) pinoxaden. A further aspect of the invention also provides a method of reducing the antagonistic effect on the control of monocotyledonous weeds in non-oat cereals which is shown by a herbicidal mixture of either a synthetic auxin herbicide with pinoxaden or an ALS inhibitor herbicide with pinoxaden, which comprises applying a herbicidal composition according to the invention. The presence of the first herbicide in the form of an aluminium salt is thought to mitigate the antagonism of the grass-weed-herbicidal activity of pinoxaden which might otherwise occur.

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Herbicidal composition comprising a mixture of a first herbicide and pinoxaden

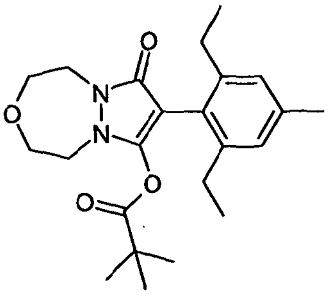
The present invention relates to a new herbicidal composition, e.g. for controlling weeds in crops of useful plants, especially in crops of cereals such as wheat and/or barley, which composition comprises (a) a first herbicide being a synthetic auxin herbicide or an ALS inhibitor herbicide, in form of a salt, and (b) the ACCase inhibitor herbicide pinoxaden.

It is known, for example, from R.J.A. Deschamps, A.I. Hsiao and W.A. Quick, Antagonistic effect of MCPA on fenoxaprop activity, Weed Sci. 38 (1990), pp. 62–66, that the commercially available synthetic auxin herbicide MCPA tends to antagonise the herbicidal efficacy of the herbicide fenoxaprop, which inhibits ACCase (acetyl coenzyme A carboxylase), in view of the control of grass in cereals. This effect is also observed when different synthetic auxin herbicides, such as dicamba or 2,4-D, are used in combination with another ACCase inhibitor herbicide, pinoxaden.

Antagonism of the herbicidal activity of pinoxaden is also sometimes seen when pinoxaden is mixed with certain herbicidal inhibitors of acetolactate synthase (ALS) such as triasulfuron or tribenuron-methyl (e.g. see results shown hereinafter in Biological Examples 4 and 5).

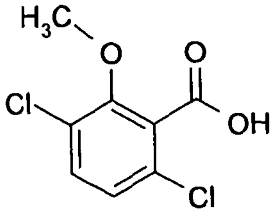
Pinoxaden is a herbicide suitable for use on non-oat cereals such as wheat, barley, rye and/or triticale, especially wheat and/or barley (i.e. is selective for non-oat cereals), and is typically applied post-emergence for control of grassy weeds such as *Alopecurus, Apera, Avena, Lolium, Phalaris* or *Setaria* species, e.g. at application rates of from 30 to 60 g active ingredient / ha (ha = hectare) (these features, e.g. uses or application rates can be used in the present invention). Pinoxaden is typically and preferably used in admixture with cloquintocet-mexyl as a safener. Pinoxaden is disclosed as compound 1.008 in WO 99/47525 A1 (Novartis AG); herbicidal compositions comprising pinoxaden and various co-herbicides are disclosed in WO 01/17351 A1 (Syngenta Participations AG); and a liquid herbicidal composition containing pinoxaden and a built-in phosphate adjuvant such as tris-(2-ethylhexyl) phosphate is disclosed in WO 2008/049618 A2 (Syngenta Participations AG); all of which are incorporated herein by reference. Pinoxaden and its herbicidal uses are disclosed in: M. Muehlebach et al., *Bioorganic & Medicinal Chemistry*, 2009, vol. 17, pp. 4241–4256; M. Muehlebach et al., in "*Pesticide Chemistry. Crop Protection, Public Health, Environmental Safety*", ed. H. Ohkawa et al., 2007, Wiley, Weinheim, pp. 101-110; U. Hofer et al. *Journal of Plant Diseases and Protection*, 2006, Special Issue XX, pp. 989-995; and

"*The Pesticide Manual*", ed. C.D.S. Tomlin, 15th edition, 2009, British Crop Production Council, UK, see entry 687 "pinoxaden" on pp. 911-912; all of which are incorporated herein by reference. Pinoxaden has the following structure:

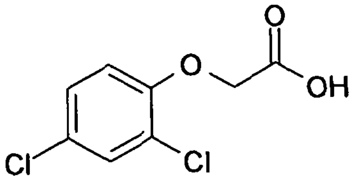


(pinoxaden)

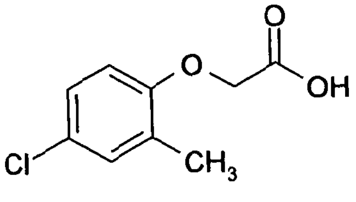
The synthetic auxin herbicides dicamba [3,6-dichloro-2-methoxybenzoic acid], 2,4-D [(2,4-dichlorophenoxy)acetic acid], and MCPA [(4-chloro-2-methylphenoxy)acetic acid], and their herbicidal uses, are disclosed *inter alia* in "*The Pesticide Manual*", ed. C.D.S. To, 15th edition, 2009, British Crop Production Council, UK, see entry 226 "2,4-D" (pp. 294-300), entry 245 "dicamba" (pp. 323-325), and entry 535 "MCPA" (pp. 709-712); all of which are incorporated herein by reference. Dicamba or a salt thereof (e.g. sodium, potassium, or dimethylammonium salt, all of which are commercially available in formulations) is typically used for control of annual and/or perennial broad-leaved weeds, or brush species; e.g. in the following crops: cereals (e.g. wheat, barley, rye or oats, in particular spring or winter wheat, spring barley or spring rye), maize, sorghum, sugar cane, asparagus, perennial seed grasses, or turf; or in pastures, rangeland or non-crop land; e.g. at application rates in crops of from 80 to 400 g or from 100 to 400 g active ingredient / ha, measured as the free acid; or higher rates in pastures; the application rates vary with the specific use; for example, the approved application rate in Canada for the BANVEL (TM) II herbicide (BASF Canada Inc.) containing as active ingredient dicamba as the diglycolamine salt, in wheat, barley, rye or oat crops, is from ca. 110 to ca. 140 g dicamba / ha, measured as the free acid (any of these features e.g. uses or application rates can be used, separately or together, in the present invention). 2,4-D or a salt thereof (e.g. sodium or dimethylammonium salt) is typically used for post-emergence control of annual and/or perennial broad-leaved weeds, e.g. in various crops including cereals, maize, established turf, orchards, sugar cane, rice, etc; e.g. at application rates of from 280 to 2300 g active ingredient / ha, measured as the free acid (these features, e.g. uses or application rates can be used in the present invention). MCPA or a salt thereof (e.g. sodium, potassium, or dimethylammonium salt, all of which are commercially available in formulations) is typically used for post-emergence control of annual and/or perennial broad-leaved weeds; e.g. in the following crops: cereals, herbage seed crops, flax, rice, vines, peas, potatoes, asparagus, grassland, turf, under fruit trees; or on roadside verges or embankments; e.g. at application rates of from 280 to 2250 g active ingredient / ha, measured as the free acid (these features, e.g. uses or application rates can be used in the present invention). The structures of dicamba, 2,4-D, and MCPA are shown below; and are characterised by the presence of a carboxylic acid moiety:



dicamba



2,4-D

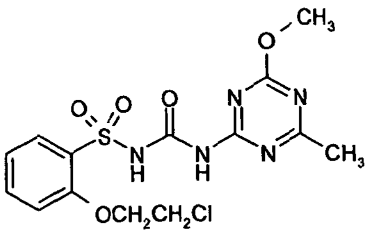


MCPA

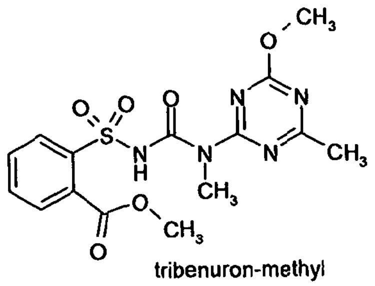
Triasulfuron, tribenuron-methyl, iodosulfuron-methyl (as the sodium salt), mesosulfuron-methyl, and pyroxsulam are disclosed in "*The Pesticide Manual*", ed. C.D.S. Tomlin, 15th edition, 2009, British Crop Production Council, UK, see entry 494 "iodosulfuron-methyl-sodium" (pp. 658-660), entry 550 "mesosulfuron-methyl" (pp. 733-734), entry 753 "pyroxsulam" (pp. 1001-1002), entry 868 "triasulfuron" (pp. 1150-1151), and entry 873 "tribenuron-methyl" (pp. 1156-1158); all of which are incorporated herein by reference.

Triasulfuron is an ALS inhibitor, of the sulfonyl urea structural class, which is typically used pre- or post- emergence for control of broad-leaved weeds, e.g. in cereal crops such as wheat, barley or triticale, e.g. at application rates of from 5 to 10 g active ingredient / ha, measured as the free compound (these features, e.g. uses or application rates can be used in the present invention). Tribenuron-methyl is an ALS inhibitor, of the sulfonyl urea structural class, which is typically used post-emergence for control of broad-leaved weeds, e.g. in cereal crops such as wheat, barley, oats, rye or triticale, e.g. at application rates of from 7.5 to 30 g active ingredient / ha, measured as the free compound (these features, e.g. uses or application rates can be used in the present invention). Iodosulfuron-methyl (usually in the form of the sodium salt) is an ALS inhibitor, of the sulfonyl urea structural class, which is typically used post-emergence for control of grass weeds and/or broad-leaved weeds, e.g. in cereal crops such as winter, spring or durum wheat, triticale, rye or spring barley, e.g. at an application rate of 10 g active ingredient / ha, measured as the free compound (these features, e.g. uses or application rates can be used in the present invention). Typically, iodosulfuron-methyl is used in admixture with mefenpyr-diethyl as a safener. Mesosulfuron-methyl is an ALS inhibitor, of the sulfonyl urea structural class, which is typically used early to mid post-emergence for control of grass weeds and/or (some) broad-leaved weeds, e.g. in cereal crops such as winter, spring or durum wheat, triticale or rye, e.g. at an application rate of 15 g active ingredient / ha, measured as the free compound (these features, e.g. uses or application rates can be used in the present invention). Pyroxsulam is an ALS inhibitor, of the triazolopyrimidine structural class, which is typically used post-emergence for control of annual grasses and/or broad-leaved weeds; e.g. in cereal crops such as spring or winter wheat, winter rye or winter triticale; e.g. at application rates of from 9 to 18.75 g active ingredient / ha, measured as the free compound (these features, e.g. uses or application rates can be used in the present invention). Pyroxsulam is typically used in admixture with cloquintocet-mexyl as a safener.

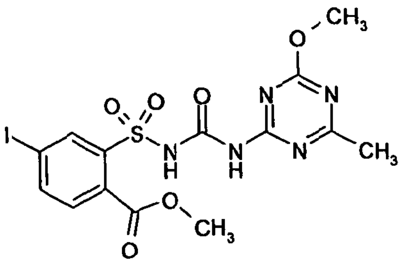
The structures of triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, and pyroxsulam are shown below:



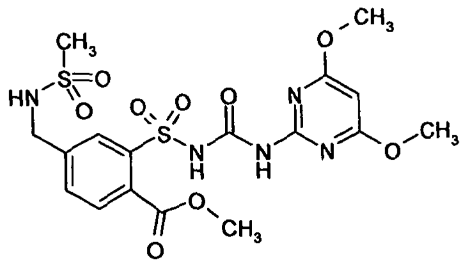
triasulfuron



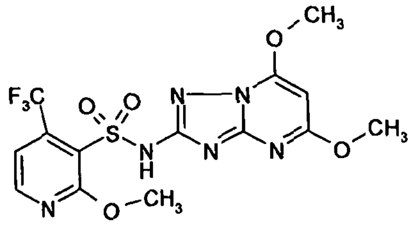
tribenuron-methyl



iodosulfuron-methyl



mesosulfuron-methyl



pyroxsulam

Surprisingly, it has now been found that, in a mixture of a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide with the ACCase inhibitor herbicide pinoxaden, where the mixture is at risk of the pinoxaden-mediated grassy-weed control being antagonised (reduced) by the presence of the synthetic auxin herbicide or ALS inhibitor herbicide, then this antagonism can be reduced, when the synthetic auxin herbicide or ALS inhibitor herbicide is present in form of an aluminium salt. Preferably, this aluminium salt renders the synthetic auxin herbicide or ALS inhibitor herbicide sparingly soluble in water.

Therefore, a first aspect of the present invention provides a herbicidal composition comprising a mixture of (e.g. a herbicidally effective amount of a mixture of):

(a) a first herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the first herbicide is present in the form of an aluminium salt;
wherein the first herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden;

and (b) pinoxaden.

The acidity of the first herbicide, when in a salt-free form, can be as defined by its pK_a value as follows, where the pK_a (also written herein as pKa) is the negative logarithm of the acid dissociation constant K_a. Preferably, the first herbicide, when in a salt-free form, has a pKa of less than 7 (in particular from 0 to less than 7, or from 1 to less than 7); more preferably a pKa of 6 or less (in particular from 0 to 6 or from 1 to 6); still more preferably a pKa of 5.5 or less (in particular from 0 to 5.5 or from 1 to 5.5); yet more preferably a pKa of 5 or less (in particular from 0 to 5 or from 1 to 5). The pKa of the first herbicide, when in a salt-free form, is preferably measured at 15 to 25 °C, more preferably at 20 to 25 °C, for example at 20 °C or at 25 °C.

pKa values of certain acidic ALS inhibitor herbicides encompassed within the invention (when in a salt-free form) are as follows: tribenuron-methyl (pK_a = 4.7), iodosulfuron-methyl-sodium (pK_a = 3.22), mesosulfuron-methyl (pK_a = 4.35), triasulfuron (pK_a = 4.64, measured at 20 °C), sulfosufuron (pK_a = 3.51, measured at 20 °C), flupyrsulfuron-methyl-sodium (pK_a = 4.9), metsulfuron-methyl (pK_a = 3.8, measured at 20 °C), and pyroxsulam (pK_a = 4.67). pKa values of certain acidic synthetic auxin herbicides encompassed within the invention are as follows: dicamba (pK_a = 1.97), MCPA (pK_a = 3.73, measured at 25 °C), and 2,4-D (pK_a = 2.73). Source: e-Pesticide Manual version 5.0; British Crop Production Council, UK, 2008-2010.

Preferably, the synthetic auxin herbicide is defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, stimulates the expression of B-glucuronidase (GUS) in transgenic *Arabidopsis* plantlets line AtEM101 (e.g. as disclosed in Lindsey and Topping, *The Plant Cell*, 1997, vol. 9, pp. 1713-1725) in an assay / test in which:

- seeds of AtEM101 are germinated aseptically on half-strength Murashige and Skoog medium containing a test compound at a range of doses between 0 and 200 uM and assayed for GUS activity at 6 days post-germination; and

- either, for a quantitative GUS assay, protein crude extracts of the plantlets are prepared and a fluorometric assay is used, e.g. as described by Jefferson et al. *EMBO J.*, 1987, vol. 6, pp. 3901-3907;
- or, whole plantlets are transferred to 100 mM sodium phosphate buffer at pH 7.0 containing 10 mM EDTA, 0.1% Triton X-100, 1mM potassium ferricyanide, 1 mM potassium ferrocyanide and 1 mM 5-bromo-4-chloro-3-indolyl β-D-glucuronic acid (X-gluc) and incubated for 12 hours at 37 °C; stained plantlets are then removed and cleared of chlorophyll by soaking in 70% (v/v) ethanol; the amount of overall blue staining is then assessed and compared visually; and

- a synthetic auxin is defined in this assay/test as a test compound which exhibits a dose response of GUS activity or blue staining dependent on the concentration of test compound present during the germination and growth of the AtEM101 Arabidopsis plantlet (and for example can be as depicted in Figure 4A of Lindsey and Topping, *The Plant Cell*, 1997, vol. 9, pp. 1713-1725 and in respect of napthylacetic acid); and

- a synthetic auxin is further defined in this assay/test as a compound that, when assayed / tested under the above conditions, and at a concentration of 50 μM (50 micromolar), results in at least about a doubling (e.g. a doubling or more) of GUS activity or of the amount of blue staining, relative to the amount of GUS activity or blue staining obtained with like AtEM101 plantlets like-grown in the absence of the test compound.

Preferably, an acetolactate synthase (ALS) inhibitor herbicide is defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, inhibits, at a concentration less than 100 μM, the specific activity of acetolactate synthase by more than 90% relative to similar controls run in the absence of the compound; and preferably where the comparative rate measurements are made at or after a reaction time of at least 200 minutes. Preferably, the acetolactate synthase is a non-herbicide-resistant version of ALS. Preferably, the acetolactate synthase has been prepared as described in T. Hawkes et al., in '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136; or more preferably has been prepared according to the Legend to Table 1 on page 119 of said publication.

More preferably, an ALS inhibitor herbicide is defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, inhibits acetolactate synthase according to a assay (test) method comprising the steps of:
- providing an ALS enzyme which has been prepared as described in the Legend to Table 1 on page 119 of T. Hawkes et al., in '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136; and
- assaying (testing) the compound at a range of doses between 0 and 200 µM, in the presence of the ALS enzyme, according to the method described in the legend of Figure 3 on page 124 of T. Hawkes et al. (from '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136); and
- defining the test compound as being an ALS inhibitor if it inhibits, at a concentration less than 100 µM, the specific activity of ALS by more than 90% relative to similar controls run in the absence of the test compound, and where the comparative rate measurements are made at or after a reaction time of at least 200 minutes.

In the invention, the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden. This can be measured using the glasshouse assay for pinoxaden antagonism as described in Assay 3 hereinafter.

Preferably, the first herbicide, in the form of an aluminium salt, is selective on (i.e. suitable for use on) non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley. This can be measured using the glasshouse assay as described in Assay 4 hereinafter ["glasshouse assay for measuring the selectivity on, i.e. suitability for use on, non-oat cereals (e.g. wheat and/or barley) of the first herbicide"].

When the first herbicide is a synthetic auxin herbicide, then preferably it is an aluminium salt of dicamba, 2,4-D or MCPA.

Dicamba is 3,6-dichloro-2-methoxybenzoic acid. 2,4-D is (2,4-dichlorophenoxy)acetic acid]. MCPA is (4-chloro-2-methylphenoxy)acetic acid.

When the first herbicide is an ALS inhibitor herbicide, then preferably it is an aluminium salt of:

- a sulfonyl urea herbicide , preferably triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, sulfosulfuron or flupyrsulfuron-methyl,
- or a triazolopyrimidine herbicide, preferably pyroxsulam.

More preferably, when the first herbicide is an ALS inhibitor herbicide, then it is an aluminium salt of: triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, sulfosulfuron, flupyrsulfuron-methyl, or pyroxsulam.

Still more preferably, when the first herbicide is an ALS inhibitor herbicide, then it is an aluminium salt of: triasulfuron, tribenuron-methyl, or pyroxsulam.

Preferably, the first herbicide is an aluminium salt of: dicamba, 2,4-D, MCPA, triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, sulfosulfuron, flupyrsulfuron-methyl, or pyroxsulam.

More preferably, the first herbicide is an aluminium salt of: dicamba, 2,4-D, MCPA, triasulfuron, tribenuron-methyl, or pyroxsulam.

Still more preferably, the first herbicide is an aluminium salt of: dicamba, MCPA, triasulfuron, or pyroxsulam.

In the composition, the weight ratio of an aluminium salt of dicamba (measured as the free acid) to pinoxaden preferably is 80:1 to 4:3, more preferably is 16:1 to 4:3, or still more preferably is 14:3 to 5:3, or yet more preferably is from 14:3 to 20:9.

In the composition, the weight ratio of an aluminium salt of MCPA (measured as the free acid) to pinoxaden preferably is from 450:1 to 14:3, more preferably from 110:1 to 35:6, or still more preferably is from 110:3 to 35:6.

In the composition, the weight ratio of an aluminium salt of 2,4-D (measured as the free acid) to pinoxaden preferably is from 460:1 to 14:3, or more preferably is from 110:1 to 35:6, or still more preferably is from 100:3 to 20:3.

In the composition, the weight ratio of an aluminium salt of triasulfuron (measured as the free acid) to pinoxaden preferably is from 3:1 to 1:12, or more preferably is from 1:1 to 1:12, or still more preferably is from 1:3 to 1:12.

In the composition, the weight ratio of an aluminium salt of tribenuron-methyl (measured as the free acid) to pinoxaden preferably is from 6:1 to 1:8, or more preferably is from 2:1 to 5:24, or still more preferably is from 1:1 to 1:4.

In the composition, the weight ratio of an aluminium salt of iodosulfuron-methyl (measured as the free acid) to pinoxaden preferably is from 3:1 to 1:12, or more preferably is from 1:1 to 1:12, or still more preferably is from 1:3 to 1:6.

In the composition, the weight ratio of an aluminium salt of mesosulfuron-methyl (measured as the free acid) to pinoxaden preferably is from 4:1 to 1:6, or more preferably is from 4:3 to 1:6, or still more preferably is from 1:2 to 1:4.

In the composition, the weight ratio of an aluminium salt of sulfosulfuron (measured as the free acid) to pinoxaden preferably is from 7:1 to 1:6, or more preferably is from 7:3 to 1:6, or still more preferably is from 7:6 to 1:6.

In the composition, the weight ratio of an aluminium salt of flupyrsulfuron-methyl (measured as the free acid) to pinoxaden preferably is from 3:1 to 1:12, or more preferably is from 1:1 to 1:12, or still more preferably is from 1:3 to 1:6.

In the composition, the weight ratio of an aluminium salt of pyroxsulam (measured as the free acid) to pinoxaden preferably is from 15:4 to 3:20, or more preferably is from 15:12 to 3:20, or still more preferably is from 1:2 to 11:60.

In the herbicidal composition (e.g. liquid or solid composition), it is strongly preferable that at least part of, preferably 50% or more (e.g. 70% or more, e.g. 90% or more, e.g. 95% or more) by weight of, the first herbicide (e.g. a synthetic auxin herbicide or an ALS inhibitor herbicide), which is present in the form of an aluminium salt, is present in the composition in solid form. In particular, the herbicidal composition can be a suspension concentrate composition (e.g. aqueous), a suspoemulsion composition (e.g. aqueous), or a solid composition (e.g. granule or powder composition), in which at least part of, preferably 50% of more (e.g. 70% or more, e.g. 90% or more, e.g. 95% or more) by weight of, the first herbicide is present in the composition in solid form.

Without being bound by theory, the first herbicide being at least partly present in solid form, when it is applied to the foliage e.g. cuticula of a plant e.g. a weed, is thought to be an important factor in the ability of the first herbicide, which is present in the form of an aluminium salt, to mitigate (reduce) the antagonism of the monocotyledonous weed (e.g. grass-weed) herbicidal activity of pinoxaden, wherein such antagonism of pinoxaden might otherwise be caused to an extent by the first herbicide if it were present in a free compound form or in the form of a non-aluminium salt.

Preferably, the first herbicide (e.g. a synthetic auxin herbicide or an ALS inhibitor herbicide), which is present in the form of an aluminium salt, is insoluble in water at 25 °C or has a solubility in water such that 1 litre or more of water is required to dissolve 1 gram of the first herbicide at 25 °C. More preferably, the first herbicide, which is present in the form of an aluminium salt, is insoluble in water at 25 °C or has a solubility in water such that 10 litres or more of water are required to dissolve 1 gram of the first herbicide at 25 °C. Still more preferably, the first herbicide, which is present in the form of an aluminium salt, is insoluble in water at 25 °C or has a solubility in water such that 100 litres or more of water are required to dissolve 1 gram of the first herbicide at 25 °C. Yet more preferably, the first herbicide, which is present in the form of an aluminium salt, is insoluble in water at 25 °C or has a solubility in water such that 1000 litres or more of water are required to dissolve 1 gram of the first herbicide at 25 °C. This insolubility or low solubility in water generally helps to keep 50% of more by weight of the first herbicide in solid form when the herbicidal composition is an aqueous liguid herbicidal composition.

In a preferable embodiment of the first aspect of the present invention, the herbicidal composition of the first aspect of the invention comprises as active ingredient a herbicidally effective amount of a mixture of

a) a synthetic auxin herbicide selected from dicamba, 2,4-D and MCPA, which is present in the form of an aluminium salt, and

b) pinoxaden.

The salts of the synthetic auxin herbicides can be prepared according to the procedure described in US 5,462, 915 or similar methods known in the art. Examples of such salts can be found under CAS 58396-89-7, 58396-88-6 and 89935-92-2.

It is to be understood that the aluminium salts of the first herbicides (acidic synthetic auxin herbicides or acidic ALS inhibitor herbicides), which can be used in the composition according to the present invention, can vary with regard to the content of aluminium in accordance with the valency of the aluminium cation used.

Most typically, the aluminium salt of the first herbicide has a 1 : 1 molar ratio of aluminium : first herbicide. When there is a 1 : 1 molar ratio of aluminium : first herbicide, then preferably the aluminium salt of the first herbicide is a hydroxide salt, usually Al^{3+} [first herbicide$^-$]$(OH^-)_2$. In an alternative embodiment, the aluminium salt of the first herbicide has a 1 : 2 or 1 : 3 molar ratio of aluminium : first herbicide; in which case it can e.g. be Al^{3+} [first herbicide$^-$]$_2(OH^-)$ or Al^{3+} [first herbicide$^-$]$_3$ respectively.

For example, an Al-dicamba salt is usually a 1:1 salt, preferably Al [dicamba]$(OH)_2$ such as Al^{3+}[dicamba$^-$]$(OH^-)_2$ hydrate, e.g. Al^{3+}[dicamba$^-$]$(OH^-)_2{\cdot}5H_2O$ or Al^{3+}[dicamba$^-$]$(OH^-)_2{\cdot}2H_2O$ (e.g. see Salt Examples 1 and 3 hereinafter). Alternatively, an Al-dicamba salt can be a 1:2 salt, preferably Al [dicamba]$_2$(OH) such as Al^{3+}[dicamba$^-$]$_2(OH^-)$ hydrate, e.g. Al^{3+}[dicamba$^-$]$_2(OH^-){\cdot}2H_2O$ (e.g. see Salt Example 7 hereinafter).

An Al-MCPA salt is typically a 1:3 salt (Al [MCPA]$_3$), such as Al^{3+}[MCPA$^-$]$_3$ hydrate, e.g. Al^{3+}[MCPA$^-$]$_3{\cdot}3H_2O$ (see e.g. Salt Example 2 hereinafter).

An Al-triasulfuron salt can be a 1:1 salt, preferably Al [triasulfuron]$(OH)_2$ such as Al^{3+}[triasulfuron$^-$]$(OH^-)_2$ hydrate, e.g. Al^{3+}[triasulfuron$^-$]$(OH^-)_2{\cdot}4H_2O$ (e.g. see Salt Example 4 hereinafter).

An Al-pyroxsulam salt can be a 1:1 salt, preferably Al [pyroxsulam]$(OH)_2$ such as Al^{3+}[pyroxsulam$^-$]$(OH^-)_2$ hydrate.

It is also possible to use these salts of synthetic auxin herbicides or of ALS inhibitor herbicides in microencapsulated form as described in said US 5,462, 915 or, preferably, coated by a carrier material as disclosed in WO01/0841928.

The synthetic auxin and ALS inhibitor herbicides mentioned above are generally known products and commercially available. The ACCase inhibitor herbicide pinoxaden can be used in the composition according to this invention in any available or preparable form.

Preferably in the herbicidal composition according to the invention, (a) is an aluminium salt of dicamba, 2,4-D or MCPA. More preferably, (a) is an aluminium salt of dicamba or MCPA.

Most preferably, (a) is an aluminium salt of dicamba.

In the invention, (b) is pinoxaden.

Preferably, the herbicidal composition according to the invention additionally contain optionally (c) a safener and, optionally, (d) an additional herbicide and, optionally, (e) an oil additive.

Preferably, a safener (c) is present and is selected from cloquintocet-mexyl, fenchlorazole and mefenpyr-diethyl. Preferably, in the composition, the weight ratio of the pinoxaden to the safener is 20:1 to 1:1, e.g. 20:1 to 2:1, e.g. 10:1 to 2:1, e.g. 4:1. Preferably, the safener is cloquintocet-mexyl or mefenpyr-diethyl, more preferably cloquintocet-mexyl.

Preferred additional herbicides (d) are sulfonyl urea herbicides selected from triasulfuron, tribenuron, iodosulfuron, mesosulfuron, sulfosulfuron and flupyrsulfuron, or triazolopyrimidine herbicides selected from pyroxsulam and penoxsulam, or sulphonylamino-carbonyl-triazolinone herbicides selected from flucarbazone-sodium, propoxycarbazone-sodium and thiencarbazone.

In one particular embodiment, (e) is present and is an oil additive selected from an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils, mixtures of such oils and oil derivatives, tris-esters of phosphoric acid with aliphatic or aromatic alcohols and bis-esters of alkyl phosphonic acids with aliphatic or aromatic alcohols.

Further, it has also been found that rather than using herbicide (a) in the form of an aluminium salt, an inorganic salt of aluminium can be added to the spray tank solution of the synthetic auxin herbicide or ALS inhibitor herbicide which is either in the form of the parent acid, or in the form of a different (non-aluminium) salt; and pinoxaden (b) can be incorporated into the formulated composition. Examples of suitable salts include halides, in particular chlorides, sulphates, nitrates and phosphates.

Therefore, a second aspect of this invention provides a herbicidal composition comprising a mixture of (e.g. an herbicidally effective amount of a mixture of):
(a) a non-aluminium herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the non-aluminium herbicide is present in a salt-free form or in the form of a non-aluminium salt;
wherein the non-aluminium herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the non-aluminium herbicide antagonises the herbicidal activity of pinoxaden;
(b) pinoxaden; and
(f) an inorganic salt (e.g. halide, sulphate, nitrate or phosphate) of aluminium.

Preferably, in this second aspect of the invention, the herbicidal composition comprises as active ingredient an herbicidally effective amount of a mixture of:
(a) a synthetic auxin herbicide selected from dicamba, 2,4-D and MCPA,
(b) pinoxaden, and
(f) an inorganic salt (e.g. halide, sulphate, nitrate or phosphate) of aluminium.

It is to be understood that according to this aspect of the invention component (f) can be present in an amount which does not depend on the valency of the synthetic auxin herbicide.

A third aspect of the invention provides a method of reducing the antagonistic effect on the control of weeds (preferably monocotyledonous weeds e.g. grassy weeds) in cereals (preferably non-oat cereals, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley) which is shown by an herbicidal mixture of either a synthetic auxin herbicide with pinoxaden or an ALS inhibitor herbicide with pinoxaden, which comprises applying a herbicidal composition according to the present invention to the plants (i.e. to the weeds and/or to the cereal crops) or to the locus thereof.
A fourth aspect of the invention provides a method of controlling weeds (preferably monocotyledonous weeds e.g. grassy weeds) in cereal crops (preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley) comprising applying a herbicidal composition according to the present invention to the plants (i.e. to the weeds and/or to the cereal crops) or to the locus thereof.

A fifth aspect of the invention provides a method of controlling weeds (preferably monocotyledonous weeds e.g. grassy weeds) in cereal crops (preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley), comprising the steps of:

(i) mixing in a tank a first herbicidal composition and a second herbicidal composition, and optionally a solvent suitable for applying the first and second compositions to plants or to a locus thereof (preferably an aqueous solvent such as water), and optionally a tank-mix adjuvant, to provide a tank-mixed herbicidal composition;

wherein the first herbicidal composition (preferably a suspension concentrate, granule or powder composition) comprises a first herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the first herbicide is present in the form of an aluminium salt;
wherein the first herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden; and

wherein the second herbicidal composition (preferably a liquid composition, e.g. an emulsifiable concentrate composition) comprises pinoxaden; and

(ii) applying the tank-mixed herbicidal composition to the plants (i.e. to the weeds and/or to the cereal crops) or to the locus thereof.

In the fifth aspect of the invention, the first herbicide and/or the pinoxaden can be as defined herein in the first aspect of the invention in its broadest aspect or in any preferred embodiment(s).

In the fifth aspect of the invention, the tank-mixed herbicidal composition can for example be as defined for the herbicidal composition of the first aspect of the present invention in its broadest aspect or in any preferred embodiment(s).

Preferred aspects of the third, fourth and fifth aspects of the invention as as follows.

Preferably, for pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), an application rate of from 5 to 60 g pinoxaden / ha is used, more preferably from 15 to 60 g or from 15 to 45 g or from 30 to 60 g or from 30 to 45 g pinoxaden / ha, still more preferably 30, 40, 45 or 60 g pinoxaden / ha, most preferably 30, 40 or 45 g pinoxaden / ha.

Preferably, for an aluminium salt of dicamba (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, barley and/or rye, e.g. spring or winter wheat, spring barley or spring rye), an application rate of from 80 to 400 g or from 100 to 400 g of dicamba / ha, measured as the free acid, is used. More preferably, from 80 to 240 g or from 100 to 240 g or from 120 to 240 g of dicamba / ha, measured as the free acid (still more preferably from 100 to 140 g, such as 120 g, or 240 g, of dicamba / ha, measured as the free acid) is used.

Preferably, for a mixture of an aluminium salt of dicamba and pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), an application rate of from 80 to 400 g or from 100 to 400 g of dicamba / ha, measured as the free acid, and from 5 to 60 g or from 10 to 60 g pinoxaden / ha, is used. More preferably, from 80 to 240 g or from 100 to 240 g or from 120 to 240 g of dicamba / ha, measured as the free acid (still more preferably from 100 to 140 g, in particular 120 g, or 240 g, of dicamba / ha, measured as the free acid), and from 10 to 60 g or from 15 to 60 g or more preferably from 30 to 60 g or from 30 to 45 g pinoxaden / ha, is used.

Specifically preferred examples of application rates, for a mixture of an aluminium salt of dicamba and pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), are:

- from 100 to 140 g, in particular 120 g, of dicamba / ha, measured as the free acid, and from 30 to 60 g (e.g. 30, 40, 45 or 60 g) or from 30 to 45 g (e.g. 30 or 45 g) pinoxaden / ha; or
- 240 g of dicamba / ha, measured as the free acid, and from 10 to 60 g (e.g. 10, 20, 30, 40, 45 or 60 g) or from 30 to 60 g (e.g. 30, 40, 45 or 60 g) or from 30 to 45 g (e.g. 30, 40 or 45 g) pinoxaden / ha.

Preferably, for an aluminium salt of MCPA (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat and/or barley), an application rate of from 280 to 2250 g of MCPA / ha, measured as the free acid, is used. More preferably, from 350 to 1650 g of MCPA / ha, measured as the free acid, is used. Still more preferably, from 350 to 1100 g of MCPA / ha, measured as the free acid (e.g. from 400 to 900 g, such as 500 g, of MCPA / ha, measured as the free acid) is used.

Preferably, for an aluminium salt of 2,4-D (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat and/or barley), an application rate of from 280 to 2300 g of 2,4-D / ha, measured as the free acid, is used. More preferably, from 350 to 1650 g of 2,4-D / ha, measured as the free acid (e.g. from 400 to 1000 g of 2,4-D / ha, measured as the free acid) is used.

Preferably, for an aluminium salt of triasulfuron (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley and/or triticale), an application rate of from 5 to 15 g (more preferably from 5 to 10 g) of triasulfuron / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of tribenuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale), an application rate of from 7.5 to 30 g (more preferably from 12.5 to 30 g or from 15 to 30 g (e.g. 15, 20 or 30 g), still more preferably from 20 to 30 g) of tribenuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of iodosulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, barley, triticale and/or rye, such as winter, spring or durum wheat, triticale, rye or spring barley), an application rate of from 5 to 15 g (more preferably 10 g) of iodosulfuron-methyl / ha, measured as the free compound, is used. Preferably, iodosulfuron-methyl is used in admixture with a safener such as mefenpyr-diethyl or cloquintocet-mexyl.

Preferably, for an aluminium salt of mesosulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, triticale and/or rye, such as winter, spring or durum wheat, triticale or rye), an application rate of from 10 to 20 g (more preferably 15 g) of mesosulfuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of sulfosulfuron (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat), an application rate of from 10 to 35 g of sulfosulfuron / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of flupyrsulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat), an application rate of from 5 to 15 g (more preferably 10 g) of flupyrsulfuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of pyroxsulam (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, rye and/or triticale, such as spring or winter wheat, winter rye or winter triticale), an application rate of from 9 to 18.75 g (e.g. from 11 to 15 g) of pyroxsulam / ha, measured as the free compound, is used. Preferably, pyroxsulam is used in admixture with a safener, more preferably cloquintocet-mexyl.

A further aspect of the present invention provides an aluminium salt of MCPA, wherein MCPA is (4-chloro-2-methylphenoxy)acetic acid. The Al-MCPA salt is typically a 1:3 salt (Al $[MCPA]_3$), such as $Al^{3+}[MCPA^-]_3$ hydrate, e.g. $Al^{3+}[MCPA^-]_3 \cdot 3H_2O$ (see e.g. Salt Example 2 hereinafter).

A further aspect of the present invention provides an aluminium salt of triasulfuron. The Al-triasulfuron salt can be a 1:1 salt, preferably Al $[triasulfuron](OH)_2$ such as $Al^{3+}[triasulfuron^-](OH^-)_2$ hydrate, e.g. $Al^{3+}[triasulfuron^-](OH^-)_2 \cdot 4H_2O$ (e.g. see Salt Example 4 hereinafter).

A further aspect of the present invention provides an aluminium salt of pyroxsulam. The Al-pyroxsulam salt can be a 1:1 salt, preferably Al $[pyroxsulam](OH)_2$ such as $Al^{3+}[pyroxsulam^-](OH^-)_2$ hydrate.

The herbicidal compositions of the present invention can be prepared in a variety of ways using formulation additives, such as carriers, solvents and surface-active substances. The resulting formulations can be in various physical forms, for example in the form of suspension concentrates, dusting powders, gels, wettable powders, water-dispersible granules, water-dispersible tablets, effervescent compressed tablets, emulsifiable concentrates, microemulsifiable concentrates, oil-in-water emulsions, oil flowables, aqueous dispersions, oily dispersions, suspoemulsions, capsule suspensions, emulsifiable granules, soluble liquids, water-soluble concentrates (with water or a water-miscible organic solvent as carrier), impregnated polymer films or in other forms known, for example, from the Manual on Development and Use of FAO Specifications for Plant Protection Products, 5th Edition, 1999. Such formulations can either be used directly or are diluted prior to use. Diluted formulations can be prepared, for example, with water, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The formulations can be prepared, for example, by mixing the active ingredient with formulation additives in order to obtain compositions in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also be formulated with other additives, for example finely divided solids, mineral oils, vegetable oils, modified vegetable oils, organic solvents, water, surface-active substances or combinations thereof. The active ingredients can also be contained in very fine microcapsules consisting of a polymer. Microcapsules contain the active ingredients in a porous carrier. This enables the active ingredients to be released into their surroundings in controlled amounts (e.g. slow release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by weight of the capsule weight. The active ingredients can be present in the form of a monolithic solid, in the form of fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating membranes comprise, for example, natural and synthetic gums, cellulose, styrene-butadiene copolymers, polyacrylonitrile, polyacrylate, polyester, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art in this connection. Alternatively it is possible for very fine microcapsules to be formed wherein the active ingredient is present in the form of finely divided particles in a solid matrix of a base substance, but in that case the microcapsule is not encapsulated.

The formulation additives suitable for the preparation of the composition according to the invention are generally known *per se*.

As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylenes carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, N,N-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethyl hexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, n-hexane, n-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol (PEG 400), propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, or higher molecular weight alcohols, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, N-methyl-2-pyrrolidone, or the like. Water is generally the carrier of choice for the dilution of the concentrates, e.g. suspension concentrates.

Suitable solid carriers are, for example, talc, kaolin, titanium dioxide, pyrophyllite clay, silica, attapulgite clay, kieselguhr, limestone, calcium carbonate, bentonite, calcium montomorillonite, cottonseed husks, wheatmeal, soybean flour, pumice, wood flour, ground walnut shells, lignin, or similar materials, as described, for example, in CFR 180.1001. (c) & (d).

Suitable surface-active compounds are, depending on the type of the active ingredient to be formulated, non-ionic, cationic and/or anionic surfactants or surfactant mixtures which have good emulsifying, dispersing and wetting properties. The surfactants mentioned below are only to be considered as examples; a large number of further surfactants which are conventionally used in the art of formulation and suitable according to the invention are described in the relevant literature.

Suitable non-ionic surfactants are, especially, polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids or of alkyl phenols which may contain approximately 3 to approximately 30 glycol ether groups and approximately 8 to approximately 20 carbon atoms in the (cyclo)aliphatic hydrocarbon radical or approximately 6 to approximately 18 carbon atoms in the alkyl moiety of the alkyl phenols. Also suitable are water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol or alkyl polypropylene glycol having 1 to approximately 10 carbon atoms in the alkyl chain and approximately 20 to approximately 250 ethylene glycol ether groups and approximately 10 to approximately 100 propylene glycol ether groups. Normally, the abovementioned compounds contain 1 to approximately 5 ethylene glycol units per propylene glycol unit. Examples which may be mentioned are nonylphenoxypolyethoxyethanol, castor oil polyglycol ether, polypropylene glycol/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol or octylphenoxypolyethoxyethanol. Also suitable are fatty acid esters of polyoxyethylene sorbitan, such as polyoxyethylene sorbitan trioleate.

The cationic surfactants are, especially, quaternary ammonium salts which generally have at least one alkyl radical of approximately 8 to approximately 22 C atoms as substituents and as further substituents (unhalogenated or halogenated) lower alkyl or hydroxyalkyl or benzyl radicals. The salts are preferably in the form of halides, methylsulfates or ethylsulfates. Examples are stearyltrimethylammonium chloride and benzylbis(2-chloroethyl)ethylammonium bromide.

Examples of suitable anionic surfactants are water-soluble soaps or water-soluble synthetic surface-active compounds. Examples of suitable soaps are the alkali, alkaline earth or (unsubstituted or substituted) ammonium salts of fatty acids having approximately 10 to approximately 22 C atoms, such as the sodium or potassium salts of oleic or stearic acid, or of natural fatty acid mixtures which are obtainable for example from coconut or tall oil; mention must also be made of the fatty acid methyl taurates. However, synthetic surfactants are used more frequently, in particular fatty sulfonates, fatty sulfates, sulfonated benzimidazole derivatives or alkylaryl sulfonates. As a rule, the fatty sulfonates and fatty sulfates are present as alkali, alkaline earth or (substituted or unsubstituted) ammonium salts and they generally have an alkyl radical of approximately 8 to approximately 22 C atoms, alkyl also to be understood as including the alkyl moiety of acyl radicals; examples which may be mentioned are the sodium or calcium salts of lignosulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and a fatty acid radical of approximately 8 to approximately 22 C atoms. Examples of alkylarylsulfonates are the sodium, calcium or triethanolammonium salts of decylbenzenesulfonic acid, of dibutylnaphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensate.

Also possible are, furthermore, suitable phosphates, such as salts of the phosphoric ester of a p-nonylphenol/(4-14)ethylene oxide adduct, or phospholipids. Further suitable phosphates are tris-esters of phosphoric acid with aliphatic or aromatic alcohols and/or bis-esters of alkyl phosphonic acids with aliphatic or aromatic alcohols, which are a high performance oil-type additive. These tris-esters have been described, for example, in WO0147356, WO0056146, EP-A-0579052 or EP-A-1018299 or are commercially available under their chemical name. Preferred tris-esters of phosphoric acid for use in the new compositions are tris-(2-ethylhexyl) phosphate, tris-n-octyl phosphate and tris-butoxyethyl phosphate, where tris-(2-ethylhexyl) phosphate is most preferred. Suitable bis-ester of alkyl phosphonic acids are bis-(2-ethylhexyl)-(2-ethylhexyl)-phosphonate, bis-(2-ethylhexyl)-(n-octyl)-phosphonate, dibutyl-butyl phosphonate and bis(2-ethylhexyl)-tripropylene-phosphonate, where bis-(2-ethylhexyl)-(n-octyl)-phosphonate is particularly preferred.

The compositions according to the invention can preferably additionally include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive used in the composition according to the invention is generally from 0.01 to 10 %, based on the spray mixture. For example, the oil additive can be added to the spray tank in the desired concentration after the spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil such as MERO®, olive oil or sunflower oil, emulsified vegetable oil, such as AMIGO® (Rhône-Poulenc Canada Inc.), alkyl esters of oils of vegetable origin, for example methyl esters such as methylated rapeseed oil (which is contained in ADIGOR®), or an oil of animal origin, such as fish oil or beef tallow. A preferred additive contains, for example, as active components essentially 80 % by weight alkyl esters of fish oils and 15 % by weight methylated rapeseed oil, and also 5 % by weight of customary emulsifiers and pH modifiers. Especially preferred oil additives comprise alkyl esters of C_8-C_{22} fatty acids, especially the methyl derivatives of C_{12}-C_{18} fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid, being important. Those esters are known as methyl laurate (CAS-111-82-0), methyl palmitate (CAS-112-39-0) and methyl oleate (CAS-112-62-9). A preferred fatty acid methyl ester derivative is Emery® 2230 and 2231 (Cognis GmbH). Those and other oil derivatives are also known from the Compendium of Herbicide Adjuvants, 5th Edition, Southern Illinois University, 2000. Also, alkoxylated fatty acids can be used as additives in the inventive compositions as well as polymethylsiloxane based additives, which have been described in WO08/037373.

The application and action of the oil additives can be further improved by combining them with surface-active substances, such as non-ionic, anionic or cationic surfactants. Examples of such anionic, non-ionic and cationic surfactants are listed on pages 7 and 8 of WO 97/34485. Preferred surface-active substances are anionic surfactants of the dodecylbenzylsulfonate type, especially the calcium salts thereof, and also non-ionic surfactants of the fatty alcohol ethoxylate type. Special preference is given to ethoxylated C_{12}-C_{22} fatty alcohols having a degree of ethoxylation of from 5 to 40. Examples of commercially available surfactants are the Genapol types (Clariant AG). Also preferred are silicone surfactants, especially polyalkyl-oxide-modified heptamethyltrisiloxanes, which are commercially available e.g. as Silwet L-77®, and also perfluorinated surfactants. The concentration of surface-active substances in relation to the total additive is generally from 1 to 30 % by weight. Examples of oil additives that consist of mixtures of oils or mineral oils or derivatives thereof with surfactants are Edenor ME SU®, Turbocharge® (Syngenta AG) and Actipron® (BP Oil UK Limited).

The said surface-active substances may also be used in the formulations alone, that is to say without oil additives.

Furthermore, the addition of an organic solvent to the oil additive/surfactant mixture can contribute to a further enhancement of action. Suitable solvents are, for example, Solvesso® (ESSO) and Aromatic Solvent® (Exxon Corporation).The concentration of such solvents can be from 10 to 80 % by weight of the total weight. Such oil additives, which may be in admixture with solvents, are described, for example, in US-A-4 834 908. A commercially available oil additive disclosed therein is known by the name MERGE® (BASF Corporation). A further oil additive that is preferred according to the invention is SCORE® (Syngenta Crop Protection Canada.)

In addition to the oil additives listed above, in order to enhance the activity of the composition according to the invention it is also possible for formulations of alkylpyrrolidones, (e.g. Agrimax®) to be added to the spray mixture. Formulations of synthetic latices, such as, for example, polyacrylamide, polyvinyl compounds or poly-1-p-menthene (e.g. Bond®, Courier® or Emerald®) can also be used. Solutions that contain propionic acid, for example Eurogkem Pen-e-trate®, can also be mixed into the spray mixture as activity-enhancing agents.

Further additives which can usually be used in pesticidal formulations include crystallisation inhibitors, viscosity-modifying substances, suspending agents, dyes, anti-oxidants, foaming agents, light absorbers, mixing aids, anti-foams, complexing agents, neutralising or pH-modifying substances and buffers, corrosion-inhibitors, fragrances, wetting agents, absorption improvers, micronutrients, plasticisers, glidants, lubricants, dispersants, thickeners, anti-freezes, microbiocides, and also liquid and solid fertilisers.

The herbicidal formulations generally contain from 0.1 to 99 % by weight, especially from 0.1 to 95 % (e.g. from 1 to 95 %, e.g. from 1 to 50 %) by weight, of herbicide (a) and (b), and from 1 to 99.9 % (e.g. 10 to 99.9 % or 50 to 99.9 % or 50 to 99 %) by weight of one or more formulation additives, which preferably includes from 0 to 25 % (e.g. from 1 to 25 %) by weight of a surface-active substance. Whereas commercial products will preferably be formulated as a concentrate (e.g. suspension concentrate) or as a solid composition, the end user will normally employ dilute formulations.

The formulations may also comprise additional active substances, for example plant growth regulators, fungicides or insecticides, and in particular further herbicides or herbicide safeners.

The rate of application of the herbicides (first herbicide (a) in admixture with pinoxaden (b)) may vary within wide limits and depends upon the nature of the soil, the method of application (pre- or post-emergence; seed dressing; application to the seed furrow; no tillage application etc.), the crop plant, the weed or grass to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. The mixture according to the invention (first herbicide (a) together with pinoxaden (b)) for example can be applied at a rate of 1 to 4000 g/ha, especially from 5 to 1000 g/ha.

Preferably, for pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), an application rate of from 5 to 60 g pinoxaden / ha is used, more preferably from 15 to 60 g or from 15 to 45 g or from 30 to 60 g or from 30 to 45 g pinoxaden / ha, still more preferably 30, 40, 45 or 60 g pinoxaden / ha, most preferably 30, 40 or 45 g pinoxaden / ha.

Preferably, for an aluminium salt of dicamba (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, barley and/or rye, e.g. spring or winter wheat, spring barley or spring rye), an application rate of from 80 to 400 g or from 100 to 400 g of dicamba / ha, measured as the free acid, is used. More preferably, from 80 to 240 g or from 100 to 240 g or from 120 to 240 g of dicamba / ha, measured as the free acid (still more preferably from 100 to 140 g, such as 120 g, or 240 g, of dicamba / ha, measured as the free acid) is used.

Preferably, for a mixture of an aluminium salt of dicamba and pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), an application rate of from 80 to 400 g or from 100 to 400 g of dicamba / ha, measured as the free acid, and from 5 to 60 g or from 10 to 60 g pinoxaden / ha, is used. More preferably, from 80 to 240 g or from 100 to 240 g or from 120 to 240 g of dicamba / ha, measured as the free acid (still more preferably from 100 to 140 g, in particular 120 g, or 240 g, of dicamba / ha, measured as the free acid), and from 10 to 60 g or from 15 to 60 g or more preferably from 30 to 60 g or from 30 to 45 g pinoxaden / ha, is used.

Specifically preferred examples of application rates, for a mixture of an aluminium salt of dicamba and pinoxaden (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale, more preferably wheat and/or barley, e.g. spring or winter wheat or spring or winter barley), are:
- from 100 to 140 g, in particular 120 g, of dicamba / ha, measured as the free acid, and from 30 to 60 g (e.g. 30, 40, 45 or 60 g) or from 30 to 45 g (e.g. 30 or 45 g) pinoxaden / ha; or
- 240 g of dicamba / ha, measured as the free acid, and from 10 to 60 g (e.g. 10, 20, 30, 40, 45 or 60 g) or from 30 to 60 g (e.g. 30, 40, 45 or 60 g) or from 30 to 45 g (e.g. 30, 40 or 45 g) pinoxaden / ha.

Preferably, for an aluminium salt of MCPA (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat and/or barley), an application rate of from 280 to 2250 g of MCPA / ha, measured as the free acid, is used. More preferably, from 350 to 1650 g of MCPA / ha, measured as the free acid, is used. Still more preferably, from 350 to 1100 g of MCPA / ha, measured as the free acid (e.g. from 400 to 900 g, such as 500 g, of MCPA / ha, measured as the free acid) is used.

Preferably, for an aluminium salt of 2,4-D (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat and/or barley), an application rate of from 280 to 2300 g of 2,4-D / ha, measured as the free acid, is used. More preferably, from 350 to 1650 g of 2,4-D / ha, measured as the free acid (e.g. from 400 to 1000 g of 2,4-D / ha, measured as the free acid) is used.

Preferably, for an aluminium salt of triasulfuron (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley and/or triticale), an application rate of from 5 to 15 g (more preferably from 5 to 10 g) of triasulfuron / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of tribenuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, such as wheat, barley, rye and/or triticale), an application rate of from 7.5 to 30 g (more preferably from 12.5 to 30 g or from 15 to 30 g (e.g. 15, 20 or 30 g), still more preferably from 20 to 30 g) of tribenuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of iodosulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, barley, triticale and/or rye, such as winter, spring or durum wheat, triticale, rye or spring barley), an application rate of from 5 to 15 g (more preferably 10 g) of iodosulfuron-methyl / ha, measured as the free compound, is used. Preferably, iodosulfuron-methyl is used in admixture with a safener such as mefenpyr-diethyl or cloquintocet-mexyl.

Preferably, for an aluminium salt of mesosulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, triticale and/or rye, such as winter, spring or durum wheat, triticale or rye), an application rate of from 10 to 20 g (more preferably 15 g) of mesosulfuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of sulfosulfuron (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat), an application rate of from 10 to 35 g of sulfosulfuron / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of flupyrsulfuron-methyl (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat), an application rate of from 5 to 15 g (more preferably 10 g) of flupyrsulfuron-methyl / ha, measured as the free compound, is used.

Preferably, for an aluminium salt of pyroxsulam (e.g. on cereal crops, preferably non-oat cereal crops, e.g. wheat, rye and/or triticale, such as spring or winter wheat, winter rye or winter triticale), an application rate of from 9 to 18.75 g (e.g. from 11 to 15 g) of pyroxsulam / ha, measured as the free compound, is used. Preferably, pyroxsulam is used in admixture with a safener, more preferably cloquintocet-mexyl.

Preferred formulations have especially the following compositions:
(% = percent by weight):

<u>Emulsifiable concentrates</u>:	
active ingredient:	1 to 95 %, preferably 60 to 90 %
surface-active agent:	1 to 30 %, preferably 5 to 20 %
liquid carrier:	1 to 80 %, preferably 1 to 35 %
<u>Dusts</u>:	
active ingredient:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %
<u>Suspension concentrates</u>:	
active ingredient:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surface-active agent:	1 to 40 %, preferably 2 to 30 %
<u>Wettable powders</u>:	
active ingredient:	0.5 to 90 %, preferably 1 to 80 %
surface-active agent:	0.5 to 20 %, preferably 1 to 15 %
solid carrier:	5 to 95 %, preferably 15 to 90 %
<u>Granules</u>:	
active ingredient:	0.1 to 30 %, preferably 0.1 to 15 %
solid carrier:	99.5 to 70 %, preferably 97 to 85 %,

where the term "active ingredient" refers to the mixture of herbicide a) with herbicide b).

The following Examples further illustrate, but do not limit, the invention.

F1. Emulsifiable concentrates	a)	b)	c)	d)
active ingredient	5 %	10 %	25 %	50 %
calcium dodecylbenzene-sulfonate	6 %	8 %	6 %	8 %
castor oil polyglycol ether (36 mol of ethylene oxide)	4 %	-	4 %	4 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	4 %	-	2 %
NMP	-	-	10 %	20 %
arom. hydrocarbon mixture C_9-C_{12}	85 %	78 %	55 %	16 %

Emulsions of any desired concentration can be prepared from such concentrates by dilution with water.

F2. Solutions	a)	b)	c)	d)
active ingredient	5 %	10 %	50 %	90 %
1-methoxy-3-(3-methoxy-propoxy)-propane	-	20 %	20 %	-
polyethylene glycol MW 400	20 %	10 %	-	-
NMP	-	-	30 %	10 %
arom. hydrocarbon mixture C_9-C_{12}	75 %	60 %	-	-

The solutions are suitable for application in the form of microdrops.

F3. Wettable powders	a)	b)	c)	d)
active ingredient	5 %	25 %	50 %	80 %
sodium lignosulfona	4 %	-	3 %	-
sodium lauryl sulfate	2 %	3 %	-	4 %
sodium diisobutylnaphthalene-sulfonate	-	6 %	5 %	6 %
octylphenol polyglycol ether (7-8 mol of ethylene oxide)	-	1 %	2 %	-
highly disperse silicic acid	1 %	3 %	5 %	10 %
kaolin	88 %	62 %	35 %	-

The active ingredient is thoroughly mixed with the additives and the mixture is thoroughly ground in a suitable mill, yielding wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granules	a)	b)	c)
active ingredient	0.1 %	5 %	15 %
highly disperse silicic acid	0.9 %	2 %	2 %
inorg. carrier (diameter 0.1 - 1 mm) e.g. $CaCO_3$ or SiO_2	99.0 %	93 %	83 %

The active ingredient is dissolved in methylene chloride, the solution is sprayed onto the carrier and the solvent is subsequently evaporated off *in vacuo*.

F5. Coated granules	a)	b)	c)
active ingredient	0.1 %	5 %	15 %
polyethylene glycol MW 200	1.0 %	2 %	3 %
highly disperse silicic acid	0.9 %	1 %	2 %
inorg. carrier (diameter 0.1 - 1 mm) e.g. $CaCO_3$ or SiO_2	98.0 %	92 %	80 %

The finely ground active ingredient is applied uniformly, in a mixer, to the carrier moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

F6. Extruder granules	a)	b)	c)	d)
active ingredient	0.1 %	3 %	5 %	15 %
sodium lignosulfonate	1.5 %	2 %	3 %	4 %
carboxymethylcellulose	1.4 %	2 %	2 %	2 %
kaolin	97.0 %	93 %	90 %	79 %

The active ingredient is mixed and ground with the additives and the mixture is moistened with water. The resulting mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)	c)
active ingredient	0.1 %	1 %	5 %
talcum	39.9 %	49 %	35 %
kaolin	60.0 %	50 %	60 %

Ready-to-use dusts are obtained by mixing the active ingredient with the carriers and grinding the mixture in a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
active ingredient	3 %	10 %	25 %	50 %
ethylene glycol	5 %	5 %	5 %	5 %
nonylphenol polyglycol ether (15 mol of ethylene oxide)	-	1 %	2 %	-
sodium lignosulfonate	3 %	3 %	4 %	5 %

carboxymethylcellulose	1 %	1 %	1 %	1 %
37 % aqueous formaldehyde solution	0.2 %	0.2 %	0.2 %	0.2 %
silicone oil emulsion	0.8 %	0.8 %	0.8 %	0.8 %
water	87 %	79 %	62 %	38 %

The finely ground active ingredient is intimately mixed with the additives, yielding a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

The term "active ingredient" in the examples mentioned above refers to the mixture of herbicide a) with herbicide b).

Crops of useful plants in which the compositions according to the invention can be used include especially cereals, cotton, soybeans, sugar beet, sugar cane, plantation crops, rape, maize and/or rice, and/or for non-selective weed control. In a particular embodiment, the herbicidal composition of the invention is for use on cereal crops; preferably non-oat cereal crops; more preferably wheat, barley, rye and/or triticale; most preferably wheat (e.g. winter wheat, spring wheat or durum wheat) and/or barley (e.g. winter or spring barley). The term "crops" is to be understood as also including crops that have been rendered tolerant to herbicides or classes of herbicides (for example ALS, GS, EPSPS, PPO, ACCase and HPPD inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant e.g. to imidazolinones, such as imazamox, by conventional methods of breeding is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®.

The weeds to be controlled may be monocotyledonous weeds (e.g. grassy weeds) and/or dicotyledonous weeds; such as, for example, Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and/or Veronica.

Preferably, the weeds to be controlled comprise *Avena*, *Lolium*, *Alopecurus*, and/or *Setaria* species, such as, in particular, *Avena fatua*, *Lolium multiflorum*, *Lolium rigidum*, *Lolium perenne*, *Alopecurus myosuroides*, *Setaria viridis* and/or *Setaria lutescens*. More preferably the weeds comprise *Avena*, *Lolium*, and/or *Alopecurus* species. Most preferably, the weeds comprise *Avena fatua*.

Crops are also to be understood as being those which have been rendered resistant to harmful insects by genetic engineering methods, for example Bt maize (resistant to European corn borer), Bt cotton (resistant to cotton boll weevil) and also Bt potatoes (resistant to Colorado beetle). Examples of Bt maize are the Bt-176 maize hybrids of NK® (Syngenta Seeds). The Bt toxin is a protein that is formed naturally by *Bacillus thuringiensis* soil bacteria. Examples of toxins and transgenic plants able to synthesise such toxins are described in EP-A-451 878, EP-A-374 753, WO 93/07278, WO 95/34656, WO 03/052073 and EP-A-427 529. Examples of transgenic plants that contain one or more genes which code for an insecticidal resistance and express one or more toxins are KnockOut® (maize), Yield Gard® (maize), NuCOTIN33B® (cotton), Bollgard® (cotton), NewLeaf® (potatoes), NatureGard® and Protexcta®. Plant crops and their seed material can be resistant to herbicides and at the same time also to insect feeding ("stacked" transgenic events). Seed can, for example, have the ability to express an insecticidally active Cry3 protein and at the same time be glyphosate-tolerant. The term "crops" is to be understood as also including crops obtained as a result of conventional methods of breeding or genetic engineering which contain so-called output traits (e.g. improved flavour, storage stability and nutritional content).

Areas under cultivation are to be understood as including land where the crop plants are already growing as well as land intended for the cultivation of those crop plants.

The rates of application of the herbicide mixture are generally from 0.001 to 2 kg/ha, but preferably from 0.005 to 1 kg/ha.

The ratio by weight of herbicide a) and b) in the composition according to the invention is preferably from 1 : 100 to 100 : 1, in particular 1:20 to 20:1.

The rate of application of safener in relation to herbicide depends largely on the method of application. In the case of field treatment, which is effected either using a tank mixture comprising a combination of safener and herbicide mixture or by separate application of safener and herbicide mixture, the ratio of herbicides to safener is generally from 100:1 to 1:10, preferably from 20:1 to 1:1. In the case of field treatment, from 0.001 to 1.0 kg of safener/ha, preferably from 0.001 to 0.25 kg of safener/ha, is generally applied.

In the composition according to the invention, the amounts of oil additive employed are generally from 0.01 to 2 %, based on the spray mixture. The oil additive can, for example, be added to the spray tank in the desired concentration after the spray mixture has been prepared.

EXAMPLES

SALT AND COMPOSITION EXAMPLES - Preparations used in Biological Examples 1, 2, 3, 4 and 5

All formulations (compositions) are quoted as "acid equivalent" (AE) of dicamba, MCPA, triasulfuron and so on. For example, MCPA-potassium SL050 represents 50 g/L MCPA acid equivalent (present as the potassium salt) in water. Generally speaking, the salts of the synthetic auxin herbicides can be prepared according to the procedure described in US 5,462, 915 or similar methods. Furthermore, the specific details of the preparations involved in Biological Examples 1, 2, 3, 4 and 5 are given below.

Composition Example 1 - Preparation of dicamba-aluminium SC070 composition, for use in glasshouse studies of Biological Example 1

(a) Preparation of aluminium salt of dicamba (1 : 1 molar ratio) (referenced as "Salt Example 1")

Dicamba acid (22.1 grams, 0.1 mole) was dissolved in 20 ml water with enough KOH (as 45% w/w solution, i.e. the KOH present is 45% of the total weight of [KOH+water] present) to ensure complete dissolution. Aluminium trichloride hexahydrate (12.1 g, 0.05 mole) was dissolved in 25 ml water and added drop-wise to the dicamba solution while stirring. The resulting slurry was brought to pH 7 by adding more KOH (as 45% w/w solution) and was heated to 80°C for 1.5 hours, before filtering and drying the filtered product. Yield: 19.7 grams. Composition of dried product (by elemental analysis, 59.3% dicamba content): $Al^{3+}[dicamba^-](OH^-)_2{\cdot}5H_2O$.

(b) Preparation of SC070 suspension concentrate composition of aluminium-dicamba

An SC070 composition (SC = suspension concentrate) was prepared by bead-milling aluminium dicamba (2.6 grams, $Al^{3+}[dicamba^-](OH^-)_2{\cdot}5H_2O$, prepared as described in preparation step (a), Salt Example 1 above) to an average particle size of less than 5 μm, with a dispersant Atlox® 4913 (1 gram, hence 0.3 grams of actual dispersant) and silicone antifoam SAG® 1572 (0.1 grams) as formulants. The mixture was diluted with de-ionised water to the desired strength to prepare the suspension concentrate. The formulants are defined below.

Atlox™ 4913 (available from Croda; http://www.croda.com) is as follows: Chemical description: acrylic copolymer solution; Product description: Atlox 4913 is a 30% aqueous polymeric surfactant, e.g. suitable for use as a dispersant in suspension concentrate, suspoemulsion or seed coating formulations.

SAG® 1572 Antifoam (available from Momentive ; http://ww2.momentive.com) is a silicone antifoam emulsion, e.g. suitable for water-based Ag formulations or related surfactant concentrates.

Composition Example 2 - Dicamba-aluminium SC050 suspension concentrate composition (as polymer coated particles by coacervation technique), for use in glasshouse studies of Biological Example 1

An SC050 composition was prepared by bead-milling aluminium dicamba (2.6 grams, $Al^{3+}[dicamba^-](OH^-)_2 \cdot 5H_2O$, prepared as described in Salt Example 1 above) to an average particle size of less than 5 μm, with a dispersant Morwet ® D425 (0.3 grams) and a silicone antifoam SAG® 1572 (0.1 grams) as formulants. The mixture was diluted with water (7 grams) to give 13% w/w aluminium dicamba. For the coacervation, 1.5 weight equivalents of Cymel® 385 resin (specifically, 3.15 grams) and 1.6 grams of Atlox® 4913 were added, then the pH was decreased to 5 using citric acid and the mixture was stirred at 50°C for 2.5 hours. Coacervated aluminium dicamba particles of 10 μm average particle size were obtained in this manner. The composition was diluted with de-ionised water to obtain the SC050 composition for glasshouse testing. The formulants are as defined above and below.

Morwet ® D425 (available from Akzo Nobel; *www.akzonobel.com*) is a naphthalene-based dispersant suitable for preparing agrochemical suspension concentrate formulations. Cymel® 385 resin (available from Cymel ; *www.cytec.com)* is a highly alkylated melamine resin described fully at Cytec's website: http://www.cytec.com/liquids/Downloads/CymelResins.pdf

Composition Example 3 - MCPA-aluminium SC100 composition, for use in glasshouse studies of Biological Example 2

(a) Preparation of aluminium salt of MCPA (1 : 3 molar ratio) (referenced as "Salt Example 2")

MCPA acid (21.1 g, 0.1 mole) was dissolved in 100 ml water with enough KOH (as 45% w/w solution) to ensure complete dissolution. Aluminium trichloride hexahydrate (12.1 g, 0.05 mole) was dissolved in 25 ml water and half was added drop-wise to the MCPA solution while stirring, then 50 ml water was added before the remainder of the aluminium trichloride hexahydrate was added. The resulting slurry was stirred at room temperature for 1.5 hours before filtering and drying the filtered product. Composition of dried product (by elemental analysis, 89.4% MCPA acid content): $Al^{3+}[MCPA^-]_3{\cdot}3H_2O$.

(b) Preparation of SC100 composition of aluminium-MCPA

A "millbase" was prepared by bead-milling the pre-isolated aluminium MCPA (2 grams, $Al^{3+}[MCPA^-]_3{\cdot}3H_2O$, prepared as described in step (a), Salt Example 2, above) to an average particle size of less than 5 μm, with a dispersant (0.30 grams of Morwet® D425), a silicone antifoam (0.04 grams, SAG® 1572) and 7.68 grams of de-ionised water. For the final formulation, 5.6 grams of this "millbase" was diluted with 1 gram of Atlox® 4913 and 3.83 grams of water to the desired strength as 10 milliliters of the required SC100 MCPA acid equivalent composition.

Reference Composition Example 4 - MCPA potassium SL050 composition

MCPA acid (10.5 g, 0.05 mole) was added to 30 ml water with 1.2 molar equivalents of KOH (85%) and stirred until all solid had dissolved, before diluting with water to the desired concentration.

Reference Composition Example 5 - Sodium dicamba (BANVEL SGF(E) ™) composition

Finally, regarding formulations used in Biological Examples 1 and 2, Banvel® SGF(E) is a commercially available 240 g/L acid equivalent (AE) dicamba formulation presented as a sodium salt.

Composition Example 6 - Dicamba-aluminium SC100 composition, for use in field trial of Biological Example 3

(a) Preparation of aluminium salt of dicamba (1 : 1 molar ratio) (referenced as "Salt Example 3")

Dicamba acid active ingredient of 88% purity (specifically, 25.2 grams of powder, hence 0.1 moles acid equivalent of dicamba) was mixed with 40 ml of water and additionally with 42.3

grams equivalent to 0.34 moles of KOH as a 45% w/w solution to give complete dissolution of the pesticide powder. Aluminium trichloride hexahydrate (27.4 g, 0.113 moles) was dissolved in 40 ml water and added to the dicamba solution whilst stirring. The resulting slurry was mixed at room temperature for 2 hours before filtering, water washing and drying the resultant filtered reaction product. The composition of the dried product (by elemental analysis, 69.4% dicamba content) was determined to be: $Al^{3+}[dicamba^-](OH^-)_2 \cdot 2H_2O$.

(b) Preparation of SC100 composition of aluminium dicamba

A SC100 composition was prepared by bead-milling aluminium-dicamba (14 grams, $Al^{3+}[dicamba^-](OH^-)_2 \cdot 2H_2O$, prepared as described in step (a), Salt Example 3, above) to an average particle size of less than 5 µm, with a dispersant Morwet ® D425 (2.5 grams) and silicone antifoam SAG® 1572 (0.5 grams) as formulants, and diluting with deionised water (to a total of 72 grams) to the desired strength. Thereafter, Atlox® 4913 (2.5 grams) was added with mixing as a further dispersant to ensure physical stability of the SC100 composition during the shipping and handling operations involved in the field trial. This yields the required specification SC100 Al-dicamba-based fluid for the field trial disclosed in Biological Example 3 hereinafter. Inerts / formulants are as follows:

Morwet ® D425 (available from Akzo Nobel; *www.akzonobel.com*) is a naphthalene-based dispersant powder eg suitable for use in preparing agrochemical suspension concentrate formulations.

Atlox™ 4913 (dispersant sold by Croda; http://www.croda.com): Chemical description: acrylic copolymer solution. Product description: Atlox 4913 is a 30% aqueous solution of polymeric surfactant eg suitable for use as a dispersant in suspension concentrate, suspoemulsion or seed coating formulations.

SAG® 1572 Antifoam (available from Momentive; http://ww2.momentive.com) is a silicone antifoam emulsion, e.g. suitable for water-based Ag formulations or related surfactant concentrates.

Reference Composition Example 7

Finally, regards formulations used in Biological Example 3 (field trial of aluminium dicamba), Banvel® 4S is a commercially available 480 g/L acid equivalent (AE) dicamba formulation presented as a dimethylammonium (DMA) salt.

Salt Example 4 - Preparation of aluminium salt of triasulfuron (1 : 1 molar ratio), for use in glasshouse trial of Biological Example 4

A slurry of triasulfuron active ingredient of 96.5% purity (10.0 grams, 0.024 mole) in 100 grams of water was mixed with enough KOH (as a 10% w/w aqueous solution) to obtain a pH between 7 and 8. Aluminium trichloride hexahydrate (6.1 grams, 0.025 mole) was added to the triasulfuron slurry in small portions over a period of 35 minutes while stirring and maintaining the pH between 7 and 8 by adding more KOH solution as necessary. The resulting slurry was stirred at room temperature for 2 hours before filtering and drying the filtered product in a vacuum oven. The composition of dried product (by elemental analysis, 75.1% triasulfuron content) was determined to be: $Al^{3+}[triasulfuron^{-}](OH^{-})_2{\cdot}4H_2O$.

Composition Example 8 - Preparation of SC100 composition of aluminium-triasulfuron, for use in glasshouse trial of Biological Example 4

A millbase was prepared by bead-milling aluminium-triasulfuron (3.0 grams, $Al^{3+}[triasulfuron^{-}](OH^{-})_2{\cdot}4H_2O$, prepared as described in Salt Example 4 above) to an average particle size of less than 5 μm, with a dispersant Atlox® 4913 (1 gram, hence 0.3 grams of actual dispersant), silicone antifoam SAG® 1572 (0.1 grams) and 6.0 grams of de-ionised water. For the final formulation, 3.7 grams of this millbase was diluted with 0.6 grams of Atlox® 4913 and 5.7 grams of water to the desired strength as 10 milliliters of the required SC100 triasulfuron acid equivalent composition.

Salt Example 5 – Potential preparation of aluminium salt of pyroxsulam

A slurry of pyroxsulam active ingredient of 98.9% purity (10.0 grams, 0.023 mole) in 90 ml of water was mixed with enough KOH (as a 10% w/w aqueous solution) to obtain a pH between 7 and 8. Aluminium trichloride hexahydrate (5.6 grams, 0.023 mole) was added to the pyroxsulam slurry in small portions over a period of 30 minutes while stirring and maintaining the pH between 7 and 8 by adding more KOH solution as necessary. The resulting slurry was stirred at room temperature for 2 hours before filtering and drying the filtered product in a vacuum oven. At the time of filing, the analysis of this product was incomplete, such that the presence of an aluminium salt of pyroxsulam has not yet been confirmed.

Salt Example 6 - Preparation of aluminium salts of other herbicidal active ingredients

The method, disclosed in Salt Examples 4 and 5 hereinabove for preparing aluminium-triasulfuron and aluminium-pyroxsulam, is applied to prepare aluminium salts of other acidic herbicidal active ingredients e.g. an ALS inhibitor herbicide, e.g. a sulfonyl urea herbicide, such as, in particular, tribenuron-methyl, iodosulfuron-methyl or mesosulfuron-methyl. This method would be roughly as follows:

A slurry of active ingredient [e.g. an ALS inhibitor herbicide, e.g. a sulfonyl urea herbicide, e.g. tribenuron-methyl, iodosulfuron-methyl or mesosulfuron-methyl] (0.023 to 0.025 moles, 1 mole equivalent) in 90 to 100 ml of water is mixed with enough KOH (as a 10% w/w aqueous solution) to obtain a pH between 7 and 8. Aluminium trichloride hexahydrate (5.6 to 6.1 grams, 0.023 to 0.025 moles, 1 mole equivalent) is added to the slurry in small portions over a period of 30-35 minutes while stirring and maintaining the pH between 7 and 8 by adding more KOH solution as necessary. The resulting slurry is stirred at room temperature for 2 hours before filtering and drying the filtered product in a vacuum oven.

If a base-addition salt (e.g. alkali metal, alkaline earth metal, ammonium or tetraC_1-$_4$alkylammonium salt) of the active ingredient, e.g. ALS inhibitor herbicide such as sulfonyl urea herbicide, in particular iodosulfuron-methyl-sodium (i.e. sodium salt of iodosulfuron-methyl), is used as the starting material, the method will have to be modified accordingly. In one optional embodiment, the above-described experimental of Salt Example 6 is varied by first converting the base-addition salt of the active ingredient (e.g. ALS inhibitor) to the free, acidic, non-salt form of the first herbicide, for example converting iodosulfuron-methyl-sodium to iodosulfuron-methyl. In a second alternative embodiment, the above-described experimental of Salt Example 6 is varied by adding less KOH to the slurry of the active ingredient (e.g. ALS inhibitor) in the first step of the experimental, but still sufficient KOH to obtain a pH between 7 and 8, before addition of the aluminium trichloride hexahydrate.

Salt Example 7 - Preparation of 1 : 2 molar ratio aluminium salt of dicamba

Dicamba acid active ingredient of 88% purity (specifically, 13.8 grams of powder, hence 0.055 moles acid equivalent of dicamba) was mixed well with 25 grams of water and furthermore 19.3 millilitres (ml) of KOH as a 45% w/w aqueous solution were added to give complete dissolution of the pesticidal powder. Aluminium trichloride hexahydrate (12.1 g, 0.05 moles) was dissolved in 25 grams of deionised water and then added to the already prepared dicamba solution whilst stirring over a period of 10 minutes. The resulting slurry was mixed at 60°C for 2 hours taking care to avoid any water losses. After allowing the glass reaction container to cool back to room temperature, the resultant reaction product material was filtered, water washed and dried at 80°C in a vacuum oven for 8 hours. The composition of the dried product (by elemental analysis, 84.6% dicamba content) was determined to be: $Al^{3+}[dicamba^-]_2(OH^-)\cdot 2H_2O$.

Reference Composition Example 9 - Other compositions used in glasshouse tests

Other chemical materials used in the various glasshouse evaluations are as follows:

Logran® 20WG – supplied as standard commercial product – contains 20% w/w of triasulfuron.

Express® 75WG – supplied as standard commercial product – contains 75% w/w of tribenuron-methyl.

Axial® 100EC – supplied as standard commercial product – contains 100g/L of pinoxaden.

BIOLOGICAL EXAMPLES

Method used in the glasshouse studies for Biological Examples 1, 2, 4 and 5

Viable seeds of the target species are sown in individual clumps (10-20 seeds, depending upon species) at a 2cm depth, into 50cm x 15cm biodegradable troughs containing a non-sterilised, standard clay loam soil.

The following species are used:

- TRZAS - Winter Wheat 'Hereward' – a standard European wheat variety included to verify that the wheat-selectivity of the pinoxaden has not been compromised.
- AVEFA – *Avena fatua*; 'wild-oat' in British English
- LOLMU – *Lolium multiflorum*; 'Italian ryegrass' in British English
- ALOMY – *Alopecurus myosuroides*; 'blackgrass' in British English
- SETVI - *Setaria viridis*; ‚giant foxtail' in British English
- GALAP – *Galium aparine*; 'goosegrass' in British English (a broad-leaved (dicotyledonous) weed species used in the sulfonyl urea assessments only for Examples 4 and 5)

The troughs are watered appropriately and are not supplied with additional nutrients throughout the course of the test. Plants are grown on for approximately 16 days prior to application until they reach a growth stage of 2-3 leaves or early onset of tillering (Zadoks 13-21) to give a standard Post-emergence application timing. Applications are made using a conventional research cabinet sprayer, 8002E flat fan nozzles, 2 bar of pressure and an application volume of 200l/ha (tap water); two replicates are used.

The graminicides used are standard commericial formulations applied with recommended tank-mix adjuvants. For example, pinoxaden is applied as AXIAL ™ EC100, a formulation containing 100 g / L pinoxaden and 25 g / L cloquintocet-mexyl as a safener; it is tank-mixed with the adjuvant ADIGOR ™ (containing methylated rapeseed oil, available from Syngenta) at 0.5% by volume of the spray solution.

Formulations of the test "first herbicide" (synthetic auxin herbicide or ALS inhibitor herbicide) used are applied at fixed, 'acid equivalent' (AE) rates that would be appropriate for commericial levels of weed control, irrespective of formulation type. For example, dicamba is applied at 240g AE / ha, MCPA and 2,4-D at 500g AE / ha.

Crop injury is recorded at both 7 and 14-16 days after application; weed efficacy is only recorded at 14-16 days after application. A visual, 0-100% assessment scale is used, where 0% = no visible effects and 100% = complete plant destruction.

BIOLOGICAL EXAMPLE 1 – glasshouse test – pinoxaden + dicamba salt(s)

A glasshouse evaluation was made to quantify any antagonistic effects on the grass species AVEFA, LOLMU and ALOMY.

The following treatments were applied as stated in Table 1A and Table 1B:

Columns 1A, 2A, 3A :

Axial 100EC (pinoxaden) composition, mixed with Banvel® SGF(E) (that is, 240SL as Na salt of dicamba) – in detail, the latter is 240 g/L acid equivalent of dicamba delivered as a sodium salt aqueous solution (Reference Composition Example 5) (see Table 1A).

Columns 1B, 2B, 3B (according to invention) :

Axial 100EC (pinoxaden) composition, mixed with dicamba-aluminium SC070 composition The latter is 70 g/L acid equivalent of dicamba delivered as an aluminium salt suspension (Composition Example 1) (see Table 1A).

Columns 1C, 2C, 3C (according to invention):

Axial 100EC (pinoxaden) composition, mixed with dicamba-aluminium SC050 composition (as polymer coated particles)

The latter is 50 g/L acid equivalent of dicamba delivered as an aluminium salt suspension, whereby the particles are coated in a polymer layer (Composition Example 2) (see Table 1A).

Columns 1D, 2D, 3D :

In addition, an Axial ™ (pinoxaden) / Adigor ™ (adjuvant) spray was applied to each of the three weed species for comparison (see Table 1B).

Table 1A contains an evaluation of a range of formulations of dicamba in combination with pinoxaden to quantify any antagonistic effects.

Table 1A

% WEED CONTROL from mixing AXIAL with three different dicamba formulations (three weed species averaged across 2 replicates)

Column	1A	1B	1C	2A	2B	2C	3A	3B	3C
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and	and	and	and	and	and
Herbicide (ii)	Na-dicamba	Al-dicamba	Al-dicamba (coated)	Na-dicamba	Al-dicamba	Al-dicamba (coated)	Na-dicamba	Al-dicamba	Al-dicamba (coated)
Rates (i)/(ii) g/ha									
5 / 240	13	58	53	70	68	58	0	30	38
10 / 240	55	75	68	73	80	78	23	45	73
20 / 240	73	75	83	85	88	85	68	75	73
40 / 240	80	90	85	95	97	100	80	88	83
Weed species	AVEFA	AVEFA	AVEFA	LOLMU	LOLMU	LOLMU	ALOMY	ALOMY	ALOMY

Table 1B

% WEED CONTROL from AXIAL alone (three weed species averaged across 2 replicates)

Column	1D	2D	3D
Herbicide (i) – pinoxaden only	AXIAL	AXIAL	AXIAL
Rates (a) in g/ha			
5	63	83	15
10	78	83	53
20	78	90	70
40	93	99	80
Weed species	AVEFA	LOLMU	ALOMY

It can be observed that, in this glasshouse test, the percentage weed control for AVEFA is less or substantially less for the treatments in column 1A (pinoxaden +Na-dicamba) as compared to those treatments in column 1B (pinoxaden +Al-dicamba) and column 1C (pinoxaden + coated Al-dicamba), at the application rates of 5, 10 and 40 g pinoxaden / ha and 240 g AE dicamba / ha. It can also be observed that, in this glasshouse test, the percentage weed control for ALOMY is substantially less for the treatments in column 3A (pinoxaden +Na-dicamba) as compared to those treatments in column 3B (pinoxaden +Al-dicamba) and column 3C (pinoxaden + coated Al-dicamba), at the application rates of 5 and 10 g pinoxaden / ha and 240 g AE dicamba / ha. It can also be observed that, in this glasshouse test, the percentage weed control for ALOMY appears to be slightly less for the treatments in column 3A (pinoxaden +Na-dicamba) as compared to those treatments in column 3B (pinoxaden +Al-dicamba) and column 3C (pinoxaden + coated Al-dicamba), at the application rates of 20 and 40 g pinoxaden / ha and 240 g AE dicamba / ha.

In summary for this Biological Example 1, in these glasshouse tests, antagonism of pinoxaden herbicidal activity in grass species weed control appears to be reduced by replacing the sodium salt of dicamba with the aluminium salt of dicamba (for both coated and uncoated examples), with regard to the two weeds species AVEFA and ALOMY, for the tested application rates of 5 and 10 g (and, for AVEFA, 40 g) pinoxaden / ha and 240 g AE dicamba / ha.

For the treatments of aluminium-dicamba and aluminium-dicamba (coated) there was no herbicide damage (zero%) observed for TRZAS - Winter Wheat 'Hereward', at the tested application rates of 5, 10, 20 and 40 g pinoxaden / ha and 240 g AE dicamba / ha..

For the sodium-dicamba treatment using Banvel® SGF(E), there was a small amount of damage to TRZAS (wheat), but this was not considered significant, as shown below:

pinoxaden g/ha and dicamba g/ha	Control of TRZAS (%)
5 / 240	0
10 / 240	5
20 / 240	15
40 / 240	10

BIOLOGICAL EXAMPLE 2 – glasshouse test – pinoxaden + MCPA salt(s)

An evaluation was made to quantify any antagonistic effects on the grass species AVEFA, LOLMU, SETVI and ALOMY.

The following treatments were applied as stated in Table 2:

Columns 4A, 5A, 6A and 7A :

Axial 100EC (pinoxaden) composition, mixed with MCPA-Potassium SL050 composition The latter is 50 g/L acid equivalent of MCPA delivered as a potassium salt aqueous solution (Reference Composition Example 4) (see Table 2A).

Columns 4B, 5B, 6B and 7B :

Axial 100EC (pinoxaden) composition, mixed with MCPA-aluminium SC100 composition The latter is 100 g/L acid equivalent of MCPA delivered as an aluminium salt suspension (Composition Example 3) (see Table 2A).

Columns 4C, 5C, 6C and 7C :

Axial 100EC (pinoxaden) composition alone (without any MCPA applied) – see Table 2B

Table 2A contains an evaluation of a range of formulations of MCPA in combination with pinoxaden to quantify any antagonistic effects.

Table 2A

% WEED CONTROL from mixing AXIAL with two different MCPA formulations (four weed species averaged across 2 replicates)

Column	4A	4B	5A	5B	6A	6B	7A	7B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and	and	and	and	and
Herbicide (ii)	K-MCPA	Al-MCPA	K-MCPA	Al-MCPA	K-MCPA	Al-MCPA	K-MCPA	Al-MCPA
Rates (i) / (ii) g/ha 5 / 500	0	45	10	27.5	22.5	62.5	5	60
10 / 500	2.5	67.5	10	47.5	75	82.5	45	72.5
20 / 500	37.5	85	40	72.5	92.5	97.5	77.5	89.5
40 / 500	85	95	70	82.5	100	100	96.5	100
Weed species	AVEFA	AVEFA	ALOMY	ALOMY	SETVI	SETVI	LOLMU	LOLMU

Table 2B

% WEED CONTROL from AXIAL alone (four weed species averaged across 2 replicates)

Column	4C	5C	6C	7C
Herbicide (i) – pinoxaden only	AXIAL	AXIAL	AXIAL	AXIAL
Rates of (i) in g/ha				
5	58	18	73	73
10	85	43	85	95
20	94	73	99	100
40	99	93	100	100
Weed species	AVEFA	ALOMY	SETVI	LOLMU

It can be observed that the percentage weed control for AVEFA is substantially less for the treatments in column 4A (pinoxaden +K-MCPA) as compared to those treatments in column 4B (pinoxaden +Al-MCPA), at the application rates of 5, 10, 20 and 40 g pinoxaden / ha and 500 g AE MCPA / ha. It can also be observed that the percentage weed control for ALOMY, SETVI and LOLMU are substantially less for the treatments in column 5A, 6A and 7A (pinoxaden +K-MCPA) as compared to those treatments in columns 5B, 6B and 7B (pinoxaden +Al-MCPA) respectively, at the application rates of 5, 10 and 20 (and, for ALOMY, 40) g pinoxaden / ha and 500 g AE MCPA / ha.

In summary for this Biological Example 2, antagonism of pinoxaden herbicidal activity in grass species weed control appears to be substantially reduced by replacing the potassium salt of MCPA with the aluminium salt of MCPA for the four weeds species AVEFA, SETVI, ALOMY and LOLMU, for most or all of the application rates tested.

For all the treatments in Biological Example 2, there was no herbicide damage (zero%) observed for TRZAS - Winter Wheat 'Hereward', at the application rates tested of 5, 10, 20 and 40 g pinoxaden / ha and 500 g AE MCPA / ha.

BIOLOGICAL EXAMPLE 3 – field trials data – pinoxaden + dicamba salt(s)

All formulations are quoted as "acid equivalent" (AE) of dicamba. For example, dicamba-aluminium SC100 suspension concentrate composition represents 100 g / L dicamba acid equivalent (as the aluminium (Al) salt) in water. Generally speaking, the salts of the synthetic auxin herbicides can be prepared according to the procedure described in US 5,462, 915 or similar methods.

The specific herbicidal compositions used in Biological Example 3 are disclosed hereinabove in:
- Composition Example 6 (aluminium dicamba SC 100 composition), and
- Reference Composition Example 7 (Banvel® 4S composition containing dicamba dimethylammonium (DMA) salt.

Method used in the field trial studies

All field trial studies involving aluminium dicamba were conducted globally following recommendations of the Syngenta 'Manual for Field Trials in Crop Protection, 4th edition, 2004', which is a revised and updated version of a publicly available booklet (W. Püntener, "Manual for field trials in plant protection", 2nd edn, 1981, Documenta Ciba-Geigy, Basel, Switzerland, 205 pp.). Field trial methodology to assess weed control efficacy against target grasses and crop tolerance in wheat was carried out according to Syngenta internal principles of good field science, following or adapted from regulatory recommendations such as EPPO or FAO guidelines.

The following species were used:

- Winter Wheat 'Canciller', 'Manager', 'Caphorn', 'Apache', 'Enesco', 'Cezanne'– some standard European wheat varieties to verify that the wheat-selectivity of the selective herbicide pinoxaden has not been compromised.
- AVEFA – *Avena fatua*; 'wild-oat' in British English, was present in two trials
- LOLMU – *Lolium multiflorum*; 'Italian ryegrass' in British English, was present in two trials
- ALOMY – *Alopecurus myosuroides*; 'blackgrass' in British English, was present in two trials

Formulations were applied on winter wheat and grass weeds which had reach the tillering growth stage (Zadoks 21-25) to give the standard post-emergence application timing. Applications were made using a conventional field research sprayer, 2 bar of pressure and an application volume in range of 200-400 L / ha (with tap water); three replicates were used. For example, pinoxaden was applied as commercially-available AXIAL® EC50, an emulsifiable concentrate formulation containing *inter alia* 50 g / L pinoxaden, 25 g / L cloquintocet-mexyl as a safener, a "built-in" adjuvant which is tris-(2-ethylhexyl) phosphate, one or more organic solvents including tetrahydrofurfuryl alcohol, and emulsifier(s); as disclosed in WO 2008/049618 (see in particular Example 1, Composition B on pages 7-9 of WO 2008/049618, incorporated herein by reference).

Formulations of the dicotyledonous-weed herbicide used (here, dicamba) are applied at fixed, 'acid equivalent' (AE) rates that would be appropriate for commericial levels of weed control, irrespective of formulation type. In this example, dicamba (as acid equivalent) is applied at 120g AE dicamba / ha in this set of field trials, which is a or the field application rate approved for dicamba in the European Union.

Crop injury is recorded at both 10-15 and 21-28 days after application. A visual, 0-100% assessment scale is used, where 0% = no visible effects and 100% = complete plant destruction. Weed efficacy is recorded at 10-15 days and 21-28 days after application and at full ear emergence of the grass weeds. A visual assessment of percentage of control versus the untreated population of the weed was made to quantify any antagonistic effects on the grass species AVEFA, LOLMU and ALOMY.

The following treatments were applied as stated in Table 3:

Columns 1A, 2A, 3A :

Axial 50EC (pinoxaden) emulsifiable concentrate composition, mixed with Banvel® 4S (that is, 480SL as dimethylammonium (DMA) salt of dicamba; Reference Composition Example 7). In detail, the latter contains 480 g/L acid equivalent of dicamba delivered as a DMA salt aqueous solution.

Columns 1B, 2B, 3B (according to invention):

Axial 50EC (pinoxaden) emulsifiable concentrate composition, mixed with dicamba-aluminium SC100 suspension concentrate composition (Composition Example 6).

The latter composition contains 100 g/L acid equivalent (AE) of dicamba delivered as an aluminium salt suspension.

Columns 1C, 2C, 3C:

Axial 50EC (pinoxaden) emulsifiable concentrate composition alone as a comparison.

Table 3 contains an evaluation of a range of formulations of dicamba in combination with pinoxaden to quantify any antagonistic effects.

Table 3

% WEED CONTROL of three grass species from mixing AXIAL with Al-dicamba SC100 formulation (averaged across 2 field trials per weed species, reference HPXD01S 4-2010UN)

Column	1A	1B	1C	2A	2B	2C	3A	3B	3C
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
And	and	and	-	and	and	-	and	and	-
Herbicide (ii)	DMA-dicamba (BANVEL)	Al-dicamba 100SC	-	DMA-dicamba (BANVEL)	Al-dicamba 100SC	-	DMA-dicamba (BANVEL)	Al-dicamba 100SC	-
Rates (i) / (ii) in g/ha									
30 / 120	64	69	84	ND	ND	ND	ND	ND	ND
45 / 120	73	82	86	95	96	95	71	78	73
60 / 120	ND	ND	ND	98	98	99	95	97	97
Weed species	AVEFA	AVEFA	AVEFA	ALOMY	ALOMY	ALOMY	LOLMU	LOLMU	LOLMU

Key - ND means "spraying not done at this rate"

It can be observed that the percentage weed control for AVEFA is substantially less for the treatments in column 1A (pinoxaden +DMA-dicamba) as compared to those treatments in column 1B (pinoxaden +Al-dicamba) and column 1C (pinoxaden alone), at the tested application rates of 30 and 45 g pinoxaden / ha and 120 g AE dicamba / ha. For LOLMU, at application rates of 45 g pinoxaden / ha and 120 g AE dicamba / ha, Al-dicamba + pinoxaden appears to show a numerically higher control (78%, column 3B) compared with DMA-dicamba + pinoxaden (71%, column 3A). It can also be observed that the percentage weed control for ALOMY is not different for the treatments in column 2A as compared to those treatments in columns 2B and 2C. In these trials on ALOMY, and possibly also on LOLIUM, antagonism by the DMA salt of dicamba of the herbicidal activity of pinoxaden had apparently not occurred, at the tested application rates.

In summary for this Biological Example 3, antagonism of pinoxaden herbicidal activity in grass species weed control is substantially reduced by replacing the DMA salt of dicamba with the aluminium salt of dicamba, with regard to the weed species AVEFA (*Avena fatua*).

Finally, for the treatments of Al-Dicamba/AXIAL, there was not any herbicide damage (zero%) observed for the Winter Wheat (any variety), at the tested application rates of 30, 45 and 60 g pinoxaden / ha and 120 g AE dicamba / ha. For the DMA-dicamba treatment using Banvel® 4S/AXIAL and the AXIAL alone treatment, again there was not any damage recorded to Winter Wheat (any variety), at the tested application rates of 30, 45 and 60 g pinoxaden / ha and 120 g AE dicamba / ha.

Biological Example 4 – glasshouse test of pinoxaden + triasulfuron or triasulfuron-aluminium

A further glasshouse evaluation was made to quantify any antagonistic effects on the grass species AVEFA, LOLMU, SETVI, ALOMY and GALAP of the pesticide triasulfuron and the aluminium salt thereof.

An additional weed to previous examples is used to measure control of a representative broad-leaf: GALAP – *Galium aparine*; 'goosegrass' a broad-leaved (dicotyledonous) weed species

There were no treatments applied to TRZAS - Winter Wheat 'Hereward' in this glasshouse screen.

The following treatments were applied as stated in Table 4:

Columns 1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A, 9A and 10A : see Table 4a, 4b, 4c and 4d Axial 100EC (pinoxaden) composition, mixed with triasulfuron as Logran 20WG composition. The latter is 200g/kg of triasulfuron delivered as a water-dispersible granule.

Columns 1B, 2B, 3B, 4B, 5B, 6B, 7B, 8B, 9B and 10B : see Table 4a, 4b, 4c and 4d Axial 100EC (pinoxaden) composition, mixed with triasulfuron-aluminium SC100 composition (Composition Example 8). The latter is 100 g/L equivalent of triasulfuron as an aluminium salt suspension concentrate.

Columns 11, 12, 13, 14 and 15 :
Axial 100EC (pinoxaden) composition alone (without any triasulfuron applied) – see Table 4e.

Columns 16, 17, 18, 19 and 20 :
Logran 20WG (triasulfuron) composition alone (without any pinoxaden applied) – see Table 4f

Tables 4a to 4f contain an evaluation of two different formulations of triasulfuron in combination with Axial (pinoxaden) and Adigor (as adjuvant) to quantify any antagonistic effects.

Tables 4a to 4d show % WEED CONTROL of three grass species from mixing AXIAL with Al-triasulfuron SC100 formulation as compared to mixing AXIAL with LOGRAN 20WG (averaged across 2 replicates for 5 weed species)

Table 4a

Column	1A	1B	2A	2B	3A	3B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and	and	and
Herbicide (ii)	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC
Rates (i) / (ii) g/ha						
15 / 5	20	45	50	28	83	85
30 / 5	68	78	55	53	94	99
45 / 5	90	95	60	65	100	100
Weed species	AVEFA	AVEFA	ALOMY	ALOMY	SETVI	SETVI

Table 4b

Column	4A	4B	5A	5B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and
Herbicide (ii)	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC
Rates (i) / (ii) g/ha				
15 / 5	78	80	87	87
30 / 5	87	85	95	94
45 / 5	96	99	97	87
Weed species	LOLMU	LOLMU	GALAP	GALAP

Table 4c

Column	6A	6B	7A	7B	8A	8B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and	and	and
Herbicide (ii)	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC
Rates (i) / (ii) g/ha						
15 / 15	15	40	50	63	93	85
30 / 15	80	90	65	50	95	100
45 / 15	93	91	73	48	99	100
Weed species	AVEFA	AVEFA	ALOMY	ALOMY	SETVI	SETVI

Table 4d

Column	9A	9B	10A	10B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL
and	and	and	and	and
Herbicide (ii)	Logran 20WG	Al-triasulfuron as 100SC	Logran 20WG	Al-triasulfuron as 100SC
Rates (i) / (ii) g/ha				
15 / 15	73	83	99	90
30 / 15	93	93	90	95
45 / 15	97	95	92	NP
Weed species	LOLMU	LOLMU	GALAP	GALAP

Key - NP means that “the assessment was not possible at this rate” – the weeds failed to emerge from the soil

Table 4e

% WEED CONTROL from AXIAL alone (five weed species averaged across 2 replicates)

Column	11	12	13	14	15
Herbicide (i) – pinoxaden only	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
Rates of (i) in g/ha					
15	50	23	93	75	0
30	85	78	100	93	0
45	93	80	100	99	0
Weed species	AVEFA	ALOMY	SETVI	LOLMU	GALAP

Table 4f

% WEED CONTROL from LOGRAN20WG alone (five weed species averaged across 2 replicates)

Column	16	17	18	19	20
Herbicide (ii) – triasulfuron only	LOGRAN 20WG	LOGRAN 20WG	LOGRAN 20WG	LOGRAN 20WG	LOGRAN 20WG
Rates of (ii) in g/ha					
5	0	30	0	20	92
15	0	45	0	38	94
Weed species	AVEFA	ALOMY	SETVI	LOLMU	GALAP

It can be observed in Tables 4a and 4c that the percentage weed control for the AVEFA species appears to be less for the treatments in column 1A and 6A as compared to those treatments in column 1B and 6B respectively, at the application rates of 15 or 30 g/ha of pinoxaden and at 5 or 15 g AE triasulfuron / ha.

In summary for this Biological Example 4, antagonism of pinoxaden herbicidal activity in grass species weed control appears to be reduced by replacing the LOGRAN 20WG triasulfuron commercial product with the aluminium salt of triasulfuron for the AVEFA weed species.

Biological Example 5 – glasshouse test of pinoxaden + tribenuron-methyl

A glasshouse evaluation was also made to quantify any antagonistic effects on the grass species AVEFA, LOLMU, SETVI, ALOMY and GALAP of the pesticide tribenuron-methyl (as Express 75WG) in combination with Axial ™ (pinoxaden).

An additional weed to previous examples is used to measure control of a representative broad-leaf: GALAP – *Galium aparine*; 'goosegrass' a broad-leaved (dicotyledonous) weed species

There were no treatments applied to TRZAS - Winter Wheat 'Hereward' in this glasshouse screen.

The following treatments were applied as stated in Tables 5a, 5b and 5c:

Columns 1A, 2A, 3A, 4A and 5A: see Tables 5a and 5b
Axial 100EC with tribenuron-methyl (as Express 75WG)
The latter is 750g/kg of tribenuron-methyl delivered as a water-dispersible granule

Columns 1B, 2B, 3B, 4B and 5B: see Tables 5a and 5b
Axial 100EC applied alone
The latter is 100 g/L equivalent of pinoxaden as an emulsifiable concentrate (EC)

Columns 6, 7, 8, 9 and 10 : see Table 5c
Express 75WG alone (without any pinoxaden applied)

Tables 5a, 5b and 5c

Tables 5a and 5b contain an evaluation of AXIAL applied with EXPRESS 75WG in order to quantify any antagonistic effects.
Tables 5a and 5b show % WEED CONTROL of three grass species from mixing AXIAL with EXPRESS (tribenuron) 75WG formulation as compared to AXIAL alone (averaged across 2 replicates for 5 weed species)

Table 5a

Column	1A	1B	2A	2B	3A	3B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL	AXIAL
and	and		and		and	
Herbicide (ii) tribenuron-methyl	Express 75WG		Express 75WG		Express 75WG	
Rates (i) / (ii) g/ha						
15 / 15	33	50	28	23	68	93
30 / 15	78	85	40	78	83	100
45 / 15	90	93	33	80	89	100
Weed species	AVEFA	AVEFA	ALOMY	ALOMY	SETVI	SETVI

Table 5b

Column	4A	4B	5A	5B
Herbicide (i) pinoxaden	AXIAL	AXIAL	AXIAL	AXIAL
and	and		and	
Herbicide (ii) tribenuron-methyl	Express 75WG		Express 75WG	
Rates (i) / (ii) g/ha				
15 / 15	88	75	97	0
30 / 15	89	93	93	0
45 / 15	90	99	95	0
Weed species	LOLMU	LOLMU	GALAP	GALAP

Table 5c

% WEED CONTROL from EXPRESS 75WG alone (data for five weed species averaged across 2 replicates)

Column	6	7	8	9	10
Herbicide (i) – tribenuron-methyl only	EXPRESS 75WG	EXPRESS 75WG	EXPRESS 75WG	EXPRESS 75WG	EXPRESS 75WG
Rate of (i) in g/ha 15	0	25	0	25	95
Weed species	AVEFA	ALOMY	SETVI	LOLMU	GALAP

It can be observed in Table 5a that the percentage weed control for AVEFA and SETVI appears to be reduced at all measured application rates when EXPRESS 75WG (containing tribenuron-methyl as active ingredient) is sprayed together with AXIAL (pinoxaden) as compared to the weed control achieved for AXIAL alone, as shown and to the extent shown in the above tables.

In summary for this glasshouse Biological Example 5, antagonism of pinoxaden herbicidal activity in grass species weed control is demonstrated for AVEFA and SETVI when EXPRESS 75WG (containing tribenuron-methyl as active ingredient) is applied together with AXIAL (containing pinoxaden).

ASSAYS

Assay 1 - Synthetic auxin herbicide assay

In a preferred embodiment of the invention, the definition of and/or an assay or test for a synthetic auxin herbicide is as follows.

A synthetic auxin herbicide can be defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, stimulates the expression of B-glucuronidase (GUS) in transgenic *Arabidopsis* plantlets line AtEM101 (as disclosed in Lindsey and Topping, *The Plant Cell*, 1997, vol. 9, pp. 1713-1725). For the test, seeds of AtEM101 are germinated aseptically on half-strength Murashige and Skoog medium containing a test compound at a range of doses between 0 and 200 uM and assayed for GUS activity at 6 days post-germination. For quantitative GUS assays, protein crude extracts of the plantlets are prepared and a fluorometric assay is used as described by Jefferson et al. *EMBO J.*, 1987, vol. 6, pp. 3901-3907. Alternatively, whole plantlets are transferred to 100 mM sodium phosphate buffer at pH 7.0 containing 10 mM EDTA, 0.1% Triton X-100, 1mM potassium ferricyanide, 1 mM potassium ferrocyanide and 1 mM 5-bromo-4-chloro-3-indolyl β-D-glucuronic acid (X-gluc) and incubated for 12 h at 37 °C. Stained plantlets are then removed and cleared of chlorophyll by soaking in 70% (v/v) ethanol. The amount of overall blue staining is then assessed and compared visually. A synthetic auxin is defined in this assay/test as a test compound which exhibits a dose response of blue staining or GUS activity dependent on the concentration of test compound present during the germination and growth of the AtEM101 Arabidopsis plantlet, and can for example be as depicted in Figure 4A of Lindsey and Topping, *The Plant Cell*, 1997, vol. 9, pp. 1713-1725 and in respect of napthylacetic acid. A synthetic auxin is further defined in this assay/test as a compound that, when assayed / tested under the above conditions, and at a concentration of 50 μM (50 micromolar) results in at least about a doubling of GUS activity or of the amount of blue staining relative to the amount of GUS activity or blue staining obtained with like AtEM101 plantlets like-grown in the absence of the test compound.

Assay 2 - Acetolactate synthase (ALS) inhibition assay

In a preferred embodiment of the invention, the definition of and/or an assay or test for an ALS inhibitor herbicide is as follows.

An ALS inhibitor herbicide can be defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, inhibits acetolactate synthase according to the following method. ALS enzyme is prepared as described in the Legend to table 1. on page 119 of T. Hawkes et al., in '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136. ALS inhibitor herbicides is defined, in this assay / test, as a compound that, when assayed / tested at a range of doses between 0 and 200 μM, and according to the method described in the legend of Figure 3 on page 124 of T. Hawkes et al. (from '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136), inhibits, at a concentration less than 100 μM, the specific activity of ALS by more than 90% relative to like controls run absent of the test compound, and where the comparative rate measurements are made at or after a reaction time of at least 200 minutes.

Assay 3 - Glasshouse assay for pinoxaden antagonism

A suitable glasshouse assay / test, to determine whether or not the "first herbicide", when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden, is as follows.

Viable seeds of the target species are sown in individual clumps (10-20 seeds, depending upon species) at a 2cm depth, into 50cm x 15cm biodegradable troughs containing a non-sterilised, standard clay loam soil.

The following species are used:

- AVEFA – *Avena fatua*; 'wild-oat' in British English
- LOLMU – *Lolium multiflorum*; 'Italian ryegrass' in British English
- ALOMY – *Alopecurus myosuroides*; 'blackgrass' in British English
- SETVI - *Setaria viridis*; 'giant foxtail' in British English
- (Optional): TRZAS - Winter Wheat 'Hereward' – a standard European wheat variety, optionally included to verify that the wheat-selectivity of the pinoxaden has not been compromised.

The troughs are watered appropriately and are not supplied with additional nutrients throughout the course of the test. Plants are grown on for approximately 16 days prior to application until they reach a growth stage of 2-3 leaves or early onset of tillering (Zadoks 13-21) to give the standard post-emergence application timing. Applications are made using a (e.g. conventional) research cabinet sprayer (e.g.: 8002E flat fan nozzles, 2 bar of pressure) and an application volume of 200 L / ha (tap water); usually, two replicates are used. The pinoxaden is typically used in a commercial formulation applied with recommended tank-mix adjuvants. Preferably, pinoxaden is applied as AXIAL ™ EC100, a formulation containing 100 g / L pinoxaden and 25 g / L cloquintocet-mexyl safener; it is tank mixed with the adjuvant ADIGOR ™ (containing methylated rapeseed oil, available from Syngenta) at 0.5% by volume of the spray solution.

Crop injury (e.g. to wheat) is recorded at both 7 and 14-16 days after application; weed efficacy is only recorded at 14-16 days after application. A visual, 0-100% assessment scale is used, where 0% = no visible effects and 100% = complete plant destruction.

Application rates to be used in the glasshouse pinoxaden antagonism assay

Formulations used for the other herbicide (the "first herbicide"), which is being tested for whether or not it antagonises the herbicidal activity of pinoxaden, are applied at fixed, 'acid equivalent' (AE) application rates suitable for commercial in-field levels of weed control, irrespective of formulation type; most preferably using application rates suitable for use on cereal crops (preferably non-oat cereal crops, e.g. wheat and/or barley). For example, dicamba can be applied at ca. 240g / ha (or alternatively at from 100 to 140, e.g. ca. 120, g / ha), measured as the free acid; MCPA and/or 2,4-D can be applied at ca. 500g / ha, measured as the free acid.

For a "first herbicide" active ingredient being assayed / tested, application rates should be X or 2X where X = recommended field application rate as disclosed for that herbicide in *"The Pesticide Manual"*, 15th Edition, 2009, British Crop Production Council, UK, or future editions thereof. Alternatively, application rates may be identified from journal, book and/or patent publications for the specific active ingredient under test. Where no such published information is available, a dose response designed to cover the full range of activities predicted for that herbicide class should be applied; typically for ALS inhibitor (e.g. sulfonyl urea) class herbicides: 5, 25, 150 g active ingredient / ha; e.g. for other classes (e.g.

synthetic auxins): 10, 50, 250, 1250 g active ingredient / ha, all measured as the free compound (acid equivalent).

All application rates for the "first herbicide" should be applied in all combinations with each of the tested pinoxaden application rates, which are typically: 5, 10, 20 and 40 g pinoxaden / ha (which e.g. were the rates used with dicamba and MCPA in Biological Examples 1 and 2); or 15, 30 and 45 g pinoxaden / ha (which e.g. were the rates used with triasulfuron in Biological Example 3).

Where the potentially-antagonizing "first herbicide" also exhibits graminicide (grass-weed-herbicidal) activity (e.g. iodosulfuron-methyl or mesosulfuron-methyl), a dose response of the potentially-antagonizing "first herbicide" should be applied as a solo application, as well as all application rate combinations of pinoxaden plus the potentially-antagonizing "first herbicide".

Antagonism of pinoxaden may then be determined by the application of Colby's formula:
(Observed 1 + Observed 2) – ((Observed 1 x Observed 2) / 100),
to calculate the expected weed control values for mixtures; where Observed 1 is the weed efficacy value recorded for the pinoxaden alone and Observed 2 is the weed efficacy value recorded for the potentially-antagonizing "first herbicide" alone at a given application rate. Where observed values are smaller than the calculated expected value, antagonism is deemed to have occurred.

Assay 4 - Glasshouse assay for measuring the selectivity on, i.e. suitability for use on, non-oat cereals (e.g. wheat and/or barley) of the first herbicide

A suitable glasshouse assay / test, to determine / measure whether or not the "first herbicide", in the form of an aluminium salt, is selective on (i.e. suitable for use on) non-oat cereals such as wheat, barley, rye and/or triticale, is as follows.

Viable seeds of the target species are sown in individual clumps (10-20 seeds, depending upon species) at a 2cm depth, into 50cm x 15cm biodegradable troughs (or pots of equivalent depth) containing a non-sterilised, standard clay loam soil.

One of the following species are used, to test the selectivity on (suitability for) one crop:

- TRZAS (Wheat) - Winter Wheat 'Hereward' – a standard European wheat variety;

- (Optional): A typical European or North American variety of winter or spring barley;
- (Optional): A typical European or North American variety of rye;
- (Optional): A typical European or North American variety of triticale.

The troughs (or pots) are watered appropriately and are not supplied with additional nutrients throughout the course of the test. Plants are grown on for approximately 16 days prior to application until they reach a growth stage of 2-3 leaves or early onset of tillering (Zadoks 13-21) to give the standard post-emergence application timing. Applications of the first herbicide (in the form of an aluminium salt) are made using a (e.g. conventional) research cabinet sprayer (e.g.: 8002E flat fan nozzles, 2 bar of pressure) and an application volume of 200 L / ha (tap water); usually, two replicates are used.

Non-oat cereal crop injury (e.g. to wheat) is recorded at both 7 days and 14-16 days after application. A visual, 0-100% assessment scale is used, where 0% = no visible effects and 100% = complete plant destruction.

Formulations used for the "first herbicide" are applied at fixed, 'acid equivalent' (AE) application rates (i.e. rates measured as the free compound) which are suitable for commercial in-field levels of weed control, irrespective of formulation type; most preferably using application rates suitable for use on non-oat cereal crops such as wheat, barley, rye and/or triticale. For example, dicamba can be applied at ca. 240g / ha measured as the free acid (or alternatively at from 100 to 140 g / ha, e.g. ca. 120 g / ha, measured as the free acid); MCPA and/or 2,4-D can be applied at ca. 500g / ha measured as the free acid; triasulfuron can be applied at from 5 to 15 g / ha measured as the free acid, and pyroxsulam can be applied at from 9 to 18.75 g / ha measured as the free acid.

For a "first herbicide" active ingredient being assayed / tested, application rates should be X or 2X where X = recommended field application rate as disclosed for that herbicide in *"The Pesticide Manual"*, 15th Edition, 2009, British Crop Production Council, UK, or future editions thereof. Alternatively, application rates may be identified from journal, book and/or patent publications for the specific active ingredient under test. Where no such published information is available, a dose response designed to cover a reasonable range of activities predicted for that herbicide class should be applied (but, in this Assay 4, without using very high application rates); therefore, for ALS inhibitor (e.g. sulfonyl urea) class herbicides: 5, 15, 40 g active ingredient / ha, measured as the free compound / free acid; e.g. for other classes (e.g. for synthetic auxin herbicides): 20, 100, 300 g active ingredient / ha, all measured as the free compound / free acid (acid equivalent).

The glasshouse tests are preferably also done in the absence, and in the presence, of a safener suitable for use with non-oat cereals such as wheat, preferably using a weight ratio of the first herbicide (measured as the free acid) to the safener of 20:1 to 1:1, e.g. 10:1 to 2:1. If used, the suitable safener to be used in the test is cloquintocet-mexyl or mefenpyr-diethyl.

The first herbicide, in the form of an aluminium salt, is determined in this Assay 4 to be selective for (i.e. suitable for use on) the non-oat cereal tested (e.g. wheat) if either or both of criteria (a) or (b) are fulfilled:

Criterion (a): The above-mentioned glasshouse assay(s)/test(s) show a level of damage (phytotoxicity) to the crop tested (e.g. wheat) of 30% or less (preferably 20% or less) as measured by visual assessment at 14-16 days after application of the first herbicide, in the absence of a safener suitable for use with non-oat cereals, and at all application rates of the first herbicide which have been tested in the present assay (see above criteria for which application rates to be tested).

Criterion (b): The above-mentioned glasshouse assay(s)/test(s) show a level of damage (phytotoxicity) to the crop tested (e.g. wheat) of 30% or less (preferably 20% or less) as measured by visual assessment at 14-16 days after application of the first herbicide, in the presence of a safener being cloquintocet-mexyl or mefenpyr-diethyl, and using a weight ratio of the first herbicide (measured as the free acid) to the safener of 20:1 to 1:1 or preferably 10:1 to 2:1, and at all application rates of the first herbicide which have been tested in the present assay (see above criteria for which application rates to be tested).

CLAIMS

1. A herbicidal composition comprising a mixture of:

(a) a first herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the first herbicide is present in the form of an aluminium salt;
wherein the first herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden;

and (b) pinoxaden.

2. A herbicidal composition as claimed in claim 1, wherein the first herbicide, when in a salt-free form, has a pKa of less than 7, measured at 20 to 25 °C.

3. A herbicidal composition as claimed in claim 2, wherein the first herbicide, when in a salt-free form, has a pKa of from 0 to 5.5, measured at 20 to 25 °C.

4. A herbicidal composition as claimed in claim 1, 2 or 3, wherein the synthetic auxin herbicide is defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, stimulates the expression of B-glucuronidase (GUS) in transgenic *Arabidopsis* plantlets line AtEM101 in an assay in which:

- seeds of AtEM101 are germinated aseptically on half-strength Murashige and Skoog medium containing a test compound at a range of doses between 0 and 200 uM and assayed for GUS activity at 6 days post-germination; and

- either, for a quantitative GUS assay, protein crude extracts of the plantlets are prepared and a fluorometric assay is used;
- or, whole plantlets are transferred to 100 mM sodium phosphate buffer at pH 7.0 containing 10 mM EDTA, 0.1% Triton X-100, 1mM potassium ferricyanide, 1 mM potassium ferrocyanide and 1 mM 5-bromo-4-chloro-3-indolyl β-D-glucuronic acid (X-gluc) and incubated for 12 hours at 37 °C; stained plantlets are then removed and cleared of

chlorophyll by soaking in 70% (v/v) ethanol; the amount of overall blue staining is then assessed and compared visually; and

- a synthetic auxin is defined in this assay as a test compound which exhibits a dose response of GUS activity or blue staining dependent on the concentration of test compound present during the germination and growth of the AtEM101 Arabidopsis plantlet; and

- a synthetic auxin is further defined in this assay as a compound that, when assayed under the above conditions, and at a concentration of 50 μM (50 micromolar), results in at least about a doubling of GUS activity or of the amount of blue staining, relative to the amount of GUS activity or blue staining obtained with like AtEM101 plantlets like-grown in the absence of the test compound.

5. A herbicidal composition as claimed in claim 1, 2, 3 or 4, wherein an acetolactate synthase (ALS) inhibitor herbicide is defined as a compound that is a herbicide and that, either itself or after the removal of any procide groups present thereon, inhibits, at a concentration less than 100 μM, the specific activity of acetolactate synthase by more than 90% relative to similar controls run in the absence of the compound, wherein the comparative rate measurements are made at or after a reaction time of at least 200 minutes;

and wherein the acetolactate synthase has been prepared as described in T. Hawkes et al., in '*Herbicides and Plant Metabolism*': ed. A.D. Dodge, Society for Experimental Biology Seminar Series 38, Cambridge University Press, Unitied Kingdom, 1989, pp. 113-136.

6. A herbicidal composition as claimed in any one of the preceding claims, wherein the first herbicide, in the form of an aluminium salt, is selective on, i.e. is suitable for use on, wheat and/or barley.

7. A herbicidal composition as claimed in any one of the preceding claims, wherein the first herbicide is an aluminium salt of: dicamba, 2,4-D, MCPA, triasulfuron, tribenuron-methyl, iodosulfuron-methyl, mesosulfuron-methyl, sulfosulfuron, flupyrsulfuron-methyl, or pyroxsulam.

8. A herbicidal composition as claimed in claim 7, wherein:
the weight ratio of an aluminium salt of dicamba (measured as the free acid) to pinoxaden is 16:1 to 4:3;

the weight ratio of an aluminium salt of MCPA (measured as the free acid) to pinoxaden is from 110:1 to 35:6;

the weight ratio of an aluminium salt of 2,4-D (measured as the free acid) to pinoxaden is from 110:1 to 35:6;

the weight ratio of an aluminium salt of triasulfuron (measured as the free acid) to pinoxaden is from 1:1 to 1:12;

the weight ratio of an aluminium salt of tribenuron-methyl (measured as the free acid) to pinoxaden is from 2:1 to 5:24;

the weight ratio of an aluminium salt of iodosulfuron-methyl (measured as the free acid) to pinoxaden is from 1:1 to 1:12;

the weight ratio of an aluminium salt of mesosulfuron-methyl (measured as the free acid) to pinoxaden is from 4:3 to 1:6; and

the weight ratio of an aluminium salt of sulfosulfuron (measured as the free acid) to pinoxaden is from 7:3 to 1:6;

the weight ratio of an aluminium salt of flupyrsulfuron-methyl (measured as the free acid) to pinoxaden is from 1:1 to 1:12; and

the weight ratio of an aluminium salt of pyroxsulam (measured as the free acid) to pinoxaden is from 15:12 to 3:20.

9. A herbicidal composition as claimed in claim 7 or 8, wherein the first herbicide is an aluminium salt of: dicamba, MCPA, triasulfuron, or pyroxsulam.

10. A herbicidal composition as claimed in claim 9, wherein:

the weight ratio of an aluminium salt of dicamba (measured as the free acid) to pinoxaden is 14:3 to 5:3;

the weight ratio of an aluminium salt of MCPA (measured as the free acid) to pinoxaden is from 110:3 to 35:6;

the weight ratio of an aluminium salt of triasulfuron (measured as the free acid) to pinoxaden is from 1:3 to 1:12; and

the weight ratio of an aluminium salt of pyroxsulam (measured as the free acid) to pinoxaden is from 1:2 to 11:60.

11. A herbicidal composition as claimed in claim 9 or 10, wherein the first herbicide is a 1:1 salt of aluminium dicamba, Al $[MCPA]_3$, a 1:1 salt of aluminium triasulfuron, or a 1:1 salt of aluminium pyroxsulam.

12. A herbicidal composition as claimed in any one of the preceding claims, wherein 50% or more by weight of the first herbicide, which is present in the form of an aluminium salt, is present in the composition in solid form.

13. A herbicidal composition as claimed in any one of the preceding claims, comprising as active ingredient an herbicidally effective amount of a mixture of
(a) a synthetic auxin herbicide selected from dicamba, 2,4-D and MCPA, which is present in the form of an aluminium salt, and
(b) pinoxaden.

14. A herbicidal composition as claimed in claim 13, wherein (a) is the aluminium salt of dicamba or MCPA.

15. A herbicidal composition as claimed in claim 13, wherein (a) is the aluminium salt of dicamba.

16. A herbicidal composition as claimed in any one of the preceding claims, comprising optionally (c) a safener and, optionally, (d) an additional herbicide and, optionally, (e) an oil additive.

17. A herbicidal composition as claimed in claim 16, wherein (c) is present and is a safener selected from cloquintocet-mexyl, fenchlorazole and mefenpyr-diethyl.

18. A herbicidal composition as claimed in claim 16 or 17, wherein (d) is present and is a sulfonyl urea herbicide selected from triasulfuron, tribenuron, iodosulfuron, mesosulfuron, sulfosulfuron and flupyrsulfuron, or a triazolopyrimidine herbicide selected from pyroxsulam and penoxsulam, or a sulphonylamino-carbonyl-triazolinone herbicide selected from flucarbazone-sodium, propoxycarbazone-sodium and thiencarbazone.

19. A herbicidal composition as claimed in claim 16, 17 or 18, wherein (e) is present and is an oil additive selected from an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils, mixtures of such oils and oil derivatives, tris-esters of phosphoric acid with aliphatic or aromatic alcohols and bis-esters of alkyl phosphonic acids with aliphatic or aromatic alcohols.

20. A herbicidal composition comprising a mixture of:
(a) a non-aluminium herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the non-aluminium herbicide is present in a salt-free form or in the form of a non-aluminium salt;
wherein the non-aluminium herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the non-aluminium herbicide antagonises the herbicidal activity of pinoxaden;
(b) pinoxaden; and
(f) an inorganic salt of aluminium.

21. A herbicidal composition as claimed in claim 20, comprising as active ingredient an herbicidally effective amount of a mixture of
(a) a synthetic auxin herbicide selected from dicamba, 2,4-D and MCPA,
(b) pinoxaden, and
(f) an inorganic salt of aluminium.

22. A method of reducing the antagonistic effect on the control of monocotyledonous weeds in non-oat cereals which is shown by a herbicidal mixture of either a synthetic auxin herbicide with pinoxaden or an ALS inhibitor herbicide with pinoxaden, which comprises applying a herbicidal composition as defined in any one of claims 1 to 21 to the plants or to the locus thereof.

23. A method of controlling weeds in non-oat cereal crops comprising applying a herbicidal composition as defined in any one of claims 1 to 21 to the plants or to the locus thereof.

24. A method of controlling weeds in non-oat cereal crops, comprising the steps of:

(i) mixing in a tank a first herbicidal composition and a second herbicidal composition, and optionally a solvent suitable for applying the first and second compositions to plants or to a locus thereof, and optionally a tank-mix adjuvant, to provide a tank-mixed herbicidal composition;

wherein the first herbicidal composition comprises a first herbicide being a synthetic auxin herbicide or an acetolactate synthase (ALS) inhibitor herbicide;
wherein the first herbicide is present in the form of an aluminium salt;

wherein the first herbicide is sufficiently acidic, when in a salt-free form, to allow the formation of an aluminium salt thereof; and
wherein the first herbicide, when in a salt-free form or when in a non-aluminium salt form, antagonises the herbicidal activity of pinoxaden; and

wherein the second herbicidal composition comprises pinoxaden; and

(ii) applying the tank-mixed herbicidal composition to the plants or to the locus thereof.

25. A method as claimed in claim 22, 23 or 24, wherein the first herbicide is as defined in any one of claims 2 to 12.

26. A method as claimed in claim 22, 23, 24 or 25, wherein the pinoxaden is applied at an application rate of from 15 to 60 g pinoxaden / ha.

27. A method as claimed in claim 22, 23, 24, 25 or 26, wherein the pinoxaden is applied at an application rate of from 30 to 45 g pinoxaden / ha.

28. A method as claimed in claim 22, 23, 24, 25, 26 or 27, wherein the first herbicide or the synthetic auxin herbicide, as appropriate, is an aluminium salt of dicamba, and the aluminium salt of dicamba is applied at an application rate of from 80 to 240 g of dicamba / ha, measured as the free acid.

29. A method as claimed in 22, 23, 24 or 25, wherein
the first herbicide or the synthetic auxin herbicide, as appropriate, is an aluminium salt of dicamba;
the aluminium salt of dicamba is applied at an application rate of from 100 to 140 g of dicamba / ha, measured as the free acid; and
the pinoxaden is applied at an application rate of from 30 to 60 g pinoxaden / ha.

30. A method as claimed in claim 22, 23, 24 or 25, wherein
the first herbicide or the synthetic auxin herbicide, as appropriate, is an aluminium salt of dicamba;
the aluminium salt of dicamba is applied at an application rate of from 100 to 140 g of dicamba / ha, measured as the free acid; and
the pinoxaden is applied at an application rate of from 30 to 45 g pinoxaden / ha.

31. A method as claimed in any one of claims 22 to 30, wherein the weeds comprise *Avena*, *Lolium*, and/or *Alopecurus* species.

32. A method as claimed in claim 31, wherein the weeds comprise *Avena fatua*.

33. A method as claimed in any one of claims 22 to 32, wherein the non-oat cereals or non-oat cereal crops are wheat, barley, rye and/or triticale.

34. An aluminium salt of pyroxsulam.

35. An aluminium salt as claimed in claim 34, which is Al [pyroxsulam]$(OH)_2$.

36. An aluminium salt of triasulfuron.

37. An aluminium salt as claimed in claim 36, which is Al [triasulfuron]$(OH)_2$.

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000292

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N43/90 A01N37/40 A01N39/04 A01N47/36
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/120554 A1 (SYNGENTA PARTICIPATIONS AG [CH]; RAMACHANDRAN RAVI [CA]; SHULKIN ANNA) 16 November 2006 (2006-11-16) page 2, line 25 - page 3, line 27 page 7, line 29 - page 8, line 13 page 15, lines 7-18 claims 12,23,29,43 -----	1-33
A	WO 2004/080171 A2 (BASF AG [DE]; WITSCHEL MATTHIAS [DE]; ZAGAR CYRILL [DE]; LANDES ANDREA) 23 September 2004 (2004-09-23) abstract page 6, lines 5-7 page 6, line 40 - page 7, line 1 claim 1 -----	1-37
A	EP 0 304 282 A1 (DU PONT [US]) 22 February 1989 (1989-02-22) page 14: compound 5claims 13,14 -----	34-37

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 6 July 2011	Date of mailing of the international search report 22/07/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Götz, Gerhard

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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