

Description

The invention relates to concentrated aqueous emulsion compositions of N-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine, (pendimethalin) and methods for their preparation. Pendimethalin emulsifiable compositions are known from Chemical Abstract, vol. 97, (1982), p.203, abstract no. 105609m and EP-A-0 006 348.

SUMMARY OF THE INVENTION

The invention is herbicidal concentrated oil in water emulsion compositions comprising on a weight basis about 5% to 40% pendimethalin;

5% to 40% of a water immiscible solvent;

10 0.5% to 5.0% of an alkylphenol polyethylene oxide condensate and

0.5% to 5.0% of an ethylene oxide/propylene oxide block copolymer as emulsifying agents;

0% to 5.0% of an anionic dispersant; and sufficient water to total 100%.

Surprisingly it has been found that the compositions of this invention provide physically and chemically stable concentrated oil in water emulsions of pendimethalin which remain homogeneous and free flowing for extended periods of time and also retain their physical stability through repeated freezing and thawing cycles without settling, separating, coalescing, or precipitating insoluble solids, and which do not require the presence of inorganic salts in the aqueous phase. Uniquely, it has been found that the addition of inorganic salts to the aqueous phase is detrimental to the formation and stability of concentrated aqueous emulsion compositions of the present invention containing pendimethalin.

20 The compositions of this invention comprise a continuous aqueous phase having dispersed therein an organic water immiscible solvent containing pendimethalin; having an average droplet size of less than 5 microns and preferably less than 2 microns; and the emulsifiers and dispersants described above.

A preferred group of ethylene oxide/propylene oxide block copolymers for use in the compositions of this invention are butyl-omega-hydroxypoly(oxypropylene block polymer with poly(oxyethylene) having an average molecular weight in a range of 2,400 to 3,500, with alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymers having an HLB of 12 and a viscosity at 25 ° C of 2,000 CPS, (TOXIMUL® 8320, Stepan Chemical Co) being a most preferred member of this class of emulsifiers.

Preferred alkylphenol polyethylene oxide condensates for use in the compositions of the invention are the nonylphenol ethoxylates, with nonylphenol ethoxylate (9 to 10 mols of ethylene oxide) (FLO MO® 9N, DeSoto, Inc. Sellers Chemical Div.) being a most preferred member of this class of emulsifiers.

Preferred dispersing agents include the free acids of alkylphenol polyethylene oxide condensate phosphate esters, and dialkylphenol polyethylene oxide condensate phosphate esters, and the alkali metal salts especially the sodium salts of fatty acid taurides or fatty acid alkyltaurides. Examples of such fatty acids, which are frequently used in the form of mixtures, are straight-chain or branched saturated or mono- or polyunsaturated aliphatic carboxylic acids having about 10 to 20 carbon atoms, such as lauric acid, palmitic acid, stearic acid, myristic acid and especially oleic acid. The alkyl radical in fatty acid alkyltaurides is a lower alkyl radical with up to 4 C atoms, especially the methyl radical. Sodium N-methyl-N-oleoyltaurate (IGEPON® T77, GAF Corporation), nonylphenol ethoxylate phosphate ester (6 mols EO) (FLO MO® 6NP, DeSoto, Inc.), dinonylphenol ethoxylate phosphate ester (14 mols EO) (FLO MO® 14 DNP, DeSoto, Inc.), being most preferred dispersing agents from these classes of compounds.

It is of course recognized that although it is not required in order to obtain stable compositions, that the concentrated emulsion compositions of the present invention may also optionally contain minor quantities (i.e., up to 10%) of adjuvants commonly employed in agricultural emulsion formulations such as antifoaming agents, biocides, antifreezing agents, rheological control agents, coloring agents and the like, in order to accommodate cultural agricultural practices and preferences and climatic variations.

Organic solvents suitable for use as the organic phase in the compositions of this invention include hydrocarbon, aromatic hydrocarbon, chlorinated hydrocarbon and chlorinated aromatic hydrocarbon solvents and mixtures thereof; such as toluene, xylenes, polynuclear aromatic hydrocarbons such as naphthalenes and alkylnaphthalenes and mixtures thereof, many of which are available from the fractionation of crude oil and in general have distillation ranges in the temperature range of about 118 to 305 ° C and are commercially available under a variety of tradenames; mono or polychloroalkanes such as dichloroethane, and mono or polychlorobenzene and toluenes.

The compositions of the invention may readily be prepared by high shear mixing in a temperature range of about 20 ° C to 75 ° C of a mixture comprising the organic phase containing pendimethalin which may also contain a portion or all of the emulsifying agent(s) with an aqueous phase which may also contain the dispersing agent, and/or a portion or all of the emulsifying sufficient period of time to obtain an emulsion having an average droplet size of 5 microns or less and preferably less than 2 microns.

In accordance with the above procedure, compositions of the invention may be prepared by

A. Preparing an organic phase by

1. adding the desired quantity of pendimethalin to a sufficient quantity of the organic solvent;
2. if desired, adding a portion or all of the emulsifying agent(s);
3. agitating until all the solids dissolve;
4. optionally clarifying the organic phase by filtration.

B. Preparing an aqueous phase by adding if desired the dispersing agent and a portion or all of the emulsifying agent(s).

C. Preparing the concentrated emulsion by combining the aqueous phase and the organic phase and subjecting the mixture to high shear mixing and continue mixing until a homogeneous emulsion having the desired droplet size is obtained, and package the product.

In general, the above procedure has been found suitable for the preparation of the stable concentrated emulsions of this invention both by adding the aqueous phase to the organic phase or by adding the organic phase to the aqueous phase and has also yielded equally good results when the emulsifying agents reside in either the organic phase or the aqueous phase.

The present invention is further illustrated by the following non-limiting examples.

EXAMPLES 1-5**Preparation of concentrated aqueous emulsion of pendimethalin**

An aqueous solution of the emulsifying agents and dispersing agents, listed in Table I below, at 60°C is combined with a solution of pendimethalin in the water immiscible solvents listed in Table I below.

The resulting mixture is subjected to high shear mixing for 10 minutes at 60°C and the mixing continued thereafter until the emulsion has cooled to 20°C, after which the composition is collected.

Utilizing the above procedure yields the stable concentrated aqueous emulsions listed in Table II below.

TABLE I**1. Emulsifying and Dispersing Agent**

- a. nonylphenol ethoxylate (9 to 10 mols of ethylene oxide)
- b. alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymer, HLB 12, viscosity @ 25°C: 2000 CPS
- c. sodium N-methyl-N-oleoyltaurate
- d. dinonylphenol ethoxylate phosphate ester (14 mols EO)
- e. nonylphenol ethoxylate phosphate ester (6 mols EO)

2. Organic Solvent

- a. monochlorobenzene
- b. aromatic hydrocarbon mixture (C₈ to C₉ aromatics, distillation range 155-173°C; AROMATIC® 100, Exxon)

3. Water

TABLE II

	Pendimethalin % w/w	Organic solvent/ % w/w	% Emulsifying and dispersing agent/ % w/w		Water
1	34.9	2a/30.0	1a/2.0	1b/2.0	29.1
2	25.0	2a/29.9	1a/2.0	1b/2.1	38.9
3	20.0	2a/30.0	1a/2.0	1b/2.0	44.0
4	30.0	2b/29.9	1a/2.0	1b/2.2	34.0
5	30.1	2b/30.0	1a/2.0	1b/2.0	33.9

EXAMPLE 6

Attempt to prepare a concentrated aqueous emulsion containing pendimethalin with sodium chloride in the aqueous phase

An aqueous phase comprising on a weight basis 5.4% of sodium chloride, 2.0% sodium N-methyl-N-oleoyltaurate, and 35.4% of water is combined with an organic phase comprising on a weight basis 2.0% of nonylphenol ethoxylate (9-10 mols of ethylene oxide), 2.0% of alpha-butyl-omega-hydroxy-ethyleneoxide propylene oxide block copolymer having an HLB of 12 and viscosity @ 25°C of 2000 CPS; 23.5% of pendimethalin and 30.0% monochlorobenzene and the resulting mixture is subjected to high shear mixing for 15 minutes. Upon completion of the mixing, the mixture separates immediately upon standing indicating that no emulsion is formed.

Claims

1. Herbicidal concentrated oil in water emulsion compositions characterized by on a weight basis about 5% to 40% pendimethalin;
5% to 40% of a water immiscible solvent;
0.5% to 5.0% of an alkylphenol polyethylene oxide condensate;
0.5% to 5.0% of an ethylene oxide/propylene oxide block copolymer;
0% to 5.0% of an anionic dispersant; and
sufficient water to total 100%.
2. A composition according to claim 1
wherein the alkylphenol polyethylene oxide condensate is a nonylphenol ethoxylate with 9 to 10 mols of ethylene oxide;
the ethylene oxide/propylene oxide block copolymer is a butyl-omega-hydroxypoly(oxypropylene) block copolymer with poly(oxyethylene) having a molecular weight in a range of 2,400 to 3,500;
the anionic dispersing agent is an alkali metal salt of fatty acid tauride or fatty acid alkyltauride or a free acid of an alkylphenol ethoxylate phosphate ester or a dialkylphenol ethoxylate phosphate ester.
3. A composition according to claim 2 wherein the dispersed organic phase has an average droplet size of less than 2 microns.
4. A composition according to claim 3 wherein the organic solvent is chlorobenzene, xylene or an aromatic hydrocarbon mixture having a distillation range in a temperature range of 118°C to 305°C.
5. A composition according to claim 4 wherein the surfactants are
alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymer having an HLB of 12 and a viscosity at 25°C of 2,000 CPS,
nonylphenol ethoxylate (9 to 10 mols of ethylene oxide), and the dispersing agent is
sodium N-methyl-N-oleoyltaurate or
nonylphenol ethoxylate phosphate ester (6 mols EO), or
dinonylphenol ethoxylate phosphate ester (14 mols EO).
6. A composition according to claim 5 characterized by on a weight basis
20% to 35% pendimethalin;
25% to 35% water immiscible solvent;
1.5% to 2.5% alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymer having an HLB of 12 and a viscosity at 25°C of 2,000 CPS;
1.5% to 2.5% nonylphenol ethoxylate (9 to 10 mols of ethylene oxide);
1.5% to 2.5% dispersing agent; and a sufficient amount of water to total 100%.
7. A method for preparing herbicidal concentrated oil in water emulsion compositions characterized by on a weight basis combining 0.5% to 5.0% of an alkylphenol polyethylene oxide condensate, 0.5% to 5.0% of an ethylene oxide/propylene oxide block copolymer and 0% to 5.0% of an anionic dispersant to form a solution of the emulsifying and dispersing agents; mixing said solution with 5% to 40% pendimethalin in 5% to 40% water immiscible solvent; high shear mixing said mixture at 60°C; cooling

**EXAMPLE 6**

Attempt to prepare a concentrated aqueous emulsion containing pendimethalin with sodium chloride in the aqueous phase

An aqueous phase comprising on a weight basis 5.4% of sodium chloride, 2.0% sodium N-methyl-N-oleoyltaurate, and 35.4% of water is combined with an organic phase comprising on a weight basis 2.0% of nonylphenol ethoxylate (9-10 mols of ethylene oxide), 2.0% of alpha-butyl-omega-hydroxy-ethyleneoxide propylene oxide block copolymer having an HLB of 12 and viscosity @ 25°C of 2000 CPS; 23.5% of pendimethalin, and 30.0% monochlorobenzene and the resulting mixture is subjected to high shear mixing for 15 minutes. Upon completion of the mixing, the mixture separates immediately upon standing indicating that no emulsion is formed.

Claims

1. Herbicidal concentrated oil in water emulsion compositions characterized by on a weight basis about 5% to 40% pendimethalin;
5% to 40% of a water immiscible solvent;
0.5% to 5.0% of an alkylphenol polyethylene oxide condensate;
0.5% to 5.0% of an ethylene oxide/propylene oxide block copolymer;
0% to 5.0% of an anionic dispersant; and
sufficient water to total 100%.
2. A composition according to claim 1
wherein the alkylphenol polyethylene oxide condensate is a nonylphenol ethoxylate with 9 to 10 mols of ethylene oxide;
the ethylene oxide/propylene oxide block copolymer is a butyl-omega-hydroxypoly(oxypropylene) block copolymer with poly(oxyethylene) having a molecular weight in a range of 2,400 to 3,500;
the anionic dispersing agent is an alkali metal salt of fatty acid tauride or fatty acid alkyltauride or a free acid of an alkylphenol ethoxylate phosphate ester or a dialkylphenol ethoxylate phosphate ester.
3. A composition according to claim 2 wherein the dispersed organic phase has an average droplet size of less than 2 microns.
4. A composition according to claim 3 wherein the organic solvent is chlorobenzene, xylene or an aromatic hydrocarbon mixture having a distillation range in a temperature range of 118°C to 305°C.
5. A composition according to claim 4 wherein the surfactants are
alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymer having an HLB of 12 and a viscosity at 25°C of 2,000 CPS,
nonylphenol ethoxylate (9 to 10 mols of ethylene oxide), and the dispersing agent is
sodium N-methyl-N-oleoyltaurate or
nonylphenol ethoxylate phosphate ester (6 mols EO), or
dinonylphenol ethoxylate phosphate ester (14 mols EO).
6. A composition according to claim 5 characterized by on a weight basis
20% to 35% pendimethalin;
25% to 35% water immiscible solvent;
1.5% to 2.5% alpha-butyl-omega-hydroxy-ethylene oxide propylene oxide block copolymer having an HLB of 12 and a viscosity at 25°C of 2,000 CPS;
1.5% to 2.5% nonylphenol ethoxylate (9 to 10 mols of ethylene oxide);
1.5% to 2.5% dispersing agent; and a sufficient amount of water to total 100%.
7. A method for preparing herbicidal concentrated oil in water emulsion compositions characterized by on a weight basis combining 0.5% to 5.0% of an alkylphenol polyethylene oxide condensate, 0.5% to 5.0% of an ethylene oxide/propylene oxide block copolymer and 0% to 5.0% of an anionic dispersant to form a solution of the emulsifying and dispersing agents; mixing said solution with 5% to 40% pendimethalin in 5% to 40% water immiscible solvent; high shear mixing said mixture at 60°C; cooling



said high shear mixture to 20°C and collecting the concentrated oil in water emulsion.

Patentansprüche

- 5 1. Herbizide konzentrierte Öl-in-Wasser-Emulsionszusammensetzungen, gekennzeichnet durch ungefähr
5% bis 40% Pendimethalin;
5% bis 40% eines mit Wasser nicht mischbaren Lösungsmittels;
0,5% bis 5,0% eines Alkylphenolpolyethylenoxid-Kondensats;
0,5% bis 5,0% eines Ethylenoxid/Propylenoxid-Block-Copolymers;
10 0% bis 5,0% eines anionischen Dispergiemittels; und ausreichend Wasser auf insgesamt 100%
auf Gewichtsbasis.
- 15 2. Zusammensetzung nach Anspruch 1,
worin das Alkylphenolpolyethylenoxid-Kondensat ein Nonylphenolethoxylat mit 9 bis 10 Mol Ethylenoxid
ist; das Ethylenoxid/Propylenoxid-Block-Copolymer ein Butyl-omega-hydroxypoly(oxypropylen)-Block-
Copolymer mit Poly(oxyethylen), das ein Molekulargewicht im Bereich von 2400 bis 3500 aufweist, ist;
das anionische Dispergiemittel ein Alkalimetallsalz von Fettsäuretaurid oder Fettsäurealkyltaurid oder
eine freie Säure eines Alkylphenolethoxylatphosphatesters oder eines Dialkylphenolethoxylatphosphate-
20 sters ist.
3. Zusammensetzung nach Anspruch 2, worin die dispergierte organische Phase eine durchschnittliche
Tröpfchengröße von weniger als 2 µm aufweist.
- 25 4. Zusammensetzung nach Anspruch 3, worin das organische Lösungsmittel Chlorbenzol, Xylol oder eine
aromatische Kohlenwasserstoffmischung mit einem Destillationsbereich in einem Temperaturbereich
von 118°C bis 305°C ist.
- 30 5. Zusammensetzung nach Anspruch 4, worin die Tenside alpha-Butyl-omega-hydroxy-ethylenoxid-
propylenoxid-Block-Copolymer mit einem HLB von 12 und einer Viskosität bei 25°C von 2000 CPS,
Nonylphenolethoxylat (9 bis 10 Mol Ethylenoxid) sind und das Dispergiemittel
Natrium-N-methyl-N-oleoyltaurat oder Nonylphenolethoxylatphosphatester (6 Mol EO) oder Dinonylphe-
nolethoxylatphosphatester (14 Mol EO) ist.
- 35 6. Zusammensetzung nach Anspruch 5, gekennzeichnet durch 20% bis 35% Pendimethalin;
25% bis 35% mit Wasser nicht mischbares Lösungsmittel; 1,5% bis 2,5% alpha-Butyl-omega-hydroxy-
ethylenoxid-propylenoxid-Block-Copolymer mit einem HBL von 12 und einer Viskosität bei 25°C von
2000 CPS;
1,5% bis 2,5% Nonylethoxylat (9 bis 10 Mol Ethylenoxid); 1,5% bis 2,5% Dispergiemittel; und einer
40 ausreichenden Menge Wasser auf insgesamt 100% auf Gewichtsbasis.
- 45 7. Verfahren zur Herstellung herbizider konzentrierter Öl-in-Wasser-Emulsionszusammensetzungen, ge-
kennzeichnet durch das Zusammengeben von, auf Gewichtsbasis, 0,5% bis 5,0% eines
Alkylphenolpolyethylenoxid-Kondensats, 0,5% bis 5,0% eines Ethylenoxid/Propylenoxid-Block-Copoly-
mers und 0% bis 5,0% eines anionischen Dispergiemittels, um eine Lösung der emulgierenden und
dispergierenden Mittel zu bilden; das Mischen der Lösung mit 5% bis 40% Pendimethalin in 5% bis
40% mit Wasser nicht mischbarem Lösungsmittel; das Hochscher-Mischen der Mischung bei 60°C;
das Abkühlen der Hochscher-Mischung auf 20°C und das Sammeln der konzentrierten Öl-in-Wasser-
Emulsion.

50 Revendications

1. Compositions herbicides concentrées sous forme d'émulsion huile dans l'eau, caractérisées par
environ, sur base pondérale,
55 5 % à 40 % de pendiméthaline ;
5 % à 40 % d'un solvant non miscible à l'eau ;
0,5 % à 5,0 % d'un produit de condensation de poly(oxyde d'éthylène) sur un alkylphénol ;
0,5 % à 5,0 % d'un copolymère séquencé oxyde d'éthylène/oxyde de propylène ;
0 % à 5,0 % d'un dispersant anionique ; et



une quantité d'eau suffisante pour faire un total de 100 %.

2. Composition selon la revendication 1, dans laquelle
le produit de condensation de poly(oxyde d'éthylène) sur un alkylphénol est un éthoxylat de nonylphénol ayant 9 à 10 moles d'oxyde d'éthylène ;
le copolymère séquencé oxyde d'éthylène/oxyde de propylène est un copolymère séquencé butyl-oméga-hydroxy-poly(oxypropylène)-poly(oxyéthylène) ayant un poids moléculaire compris dans l'intervalle de 2400 à 3500 ;
l'agent dispersant anionique est un sel de métal alcalin de tauride d'acide gras ou d'alkyltauride d'acide gras ou un acide libre d'un ester phosphorique d'éthoxylat d'alkylphénol ou d'un ester phosphorique d'éthoxylat de dialkylphénol.
3. Composition selon la revendication 2, dans laquelle la phase organique dispersée a une taille moyenne de gouttelettes inférieure à 2 micromètres.
4. Composition selon la revendication 3, dans laquelle le solvant organique est le chlorobenzène, le xylène ou un mélange d'hydrocarbures aromatiques ayant un intervalle de distillation compris dans l'intervalle de température de 118 °C à 305 °C.
5. Composition selon la revendication 4, dans laquelle les agents tensio-actifs sont
un copolymère séquencé alpha-butyl-oméga-hydroxy-(oxyde d'éthylène)-(oxyde de propylène) ayant un RHL de 12 et une viscosité à 25 °C de 2000 cPo,
un éthoxylat de nonylphénol (9 à 10 moles d'oxyde d'éthylène),
et l'agent dispersant est
le N-méthyl-N-oléoyltaurate de sodium, ou
un ester phosphorique d'éthoxylat de nonylphénol (6 moles de OE), ou
un ester phosphorique d'éthoxylat de dinonylphénol (14 moles de OE).
6. Composition selon la revendication 5, caractérisée par, sur base pondérale,
20 % à 35 % de pendiméthaline ;
25 % à 35 % de solvant non miscible à l'eau ;
1,5 % à 2,5 % de copolymère séquencé alpha-butyl-oméga-hydroxy-(oxyde d'éthylène)-(oxyde de propylène) ayant un RHL de 12 et une viscosité à 25 °C de 2000 cPo ;
1,5 % à 2,5 % d'éthoxylat de nonylphénol (9 à 10 moles d'oxyde d'éthylène) ;
1,5 % à 2,5 % d'agent dispersant ; et
une quantité d'eau suffisante pour faire un total de 100 %.
7. Procédé pour préparer des compositions herbicides concentrées sous forme d'émulsion huile dans l'eau, caractérisé en ce qu'on combine, sur base pondérale, 0,5 % à 5,0 % d'un produit de condensation de poly(oxyde d'éthylène) sur un alkylphénol, 0,5 % à 5,0 % d'un copolymère séquencé oxyde d'éthylène/oxyde de propylène et 0 % à 5,0 % d'un dispersant anionique pour former une solution des agents émulsionnants et dispersants; on mélange ladite solution avec 5 % à 40 % de pendiméthaline dans 5 % à 40 % d'un solvant non miscible à l'eau ; on mélange ledit mélange sous fort cisaillement à 60 °C ; on refroidit ledit mélange sous fort cisaillement jusqu'à 20 °C ; et l'on recueille l'émulsion concentrée huile dans l'eau.