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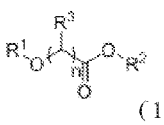
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(54) Title: SOLVENTS FOR AGRICULTURAL APPLICATIONS AND PESTICIDE FORMULATIONS



(1)

(57) Abstract: Solvents for pesticides and pesticide formulations are provided, said solvents comprise an ether ester of Formula (1): wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6.

SOLVENTS FOR AGRICULTURAL APPLICATIONS AND PESTICIDE FORMULATIONS

Field

The present invention relates to solvents for agricultural applications (e.g., pesticides) and to pesticide formulations.

Introduction

Aromatic solvents, such as xylene, have been regularly utilized in agricultural applications. Xylene is commonly used as it provides several advantages, such as dissolving a variety of active ingredients and being easily emulsified in water on dilution. However, there are number of disadvantages to xylene's use as a solvent such as flammability, combustibility, and toxicity. Thus, there is a need for solvent alternatives to xylene for use in agricultural applications.

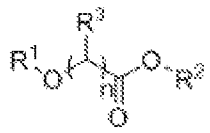
A variety of alternatives to xylene have been considered such as aromatic fluids produced from petroleum-based raw materials such as naphtha solvents composed of C_9-C_{13} aromatics. However, such solvents still have issues such as low flash point and high toxicity.

It would be desirable to have new solvents for agricultural applications having good dissolution properties while also having an improved environmental/health/safety profile.

Summary

The present invention provides solvents for pesticides that, in some embodiments, have a dissolving ability comparable to that of xylene while also being more environmentally friendly.

In one aspect, the present invention provides a solvent for pesticides that comprises an ether ester of Formula 1:



(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6. In some embodiments, R^1 and R^2 are ethyl groups, R^3 is hydrogen, and n is 2.

In another aspect, the present invention provides a pesticide formulation that comprises the ether ester of Formula 1 and a pesticide.

These and other embodiments are described in more detail in the Detailed Description.

Detailed Description

As used herein, "a," "an," "the," "at least one," and "one or more" are used interchangeably. Thus, for example, an aqueous composition that includes particles of "a" hydrophobic polymer can be interpreted to mean that the composition includes particles of "one or more" hydrophobic polymers.

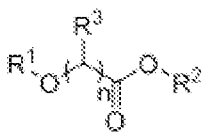
The numerical ranges disclosed herein include all values from, and including, the lower and upper value. For ranges containing explicit values (e.g., 1 to 7), any subrange between any two explicit values is included (e.g., 1 to 2; 2 to 6; 5 to 7; 3 to 7; 5 to 6; etc.).

The terms "comprising," "including," "having," and their derivatives, are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is specifically disclosed. In order to avoid any doubt, all compositions claimed through use of the term "comprising" may include any additional additive, adjuvant, or compound, whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step, or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step, or procedure not specifically delineated or listed. The term "or," unless stated otherwise, refers to the listed members individually as well as in any combination. Use of the singular includes use of the plural and vice versa.

Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight and all test methods are current as of the filing date of this disclosure.

"Solvent" and like terms mean a substance that is capable of dissolving another substance (i.e., a solute) to form an essentially uniformly dispersed mixture (i.e., solution) at the molecular or ionic size level.

Embodiments of the present invention relate to solvents for pesticides. In some embodiments, a solvent for pesticides comprises an ether ester of Formula 1:



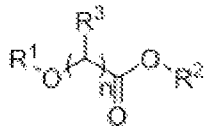
(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6. In some embodiments, R^1 and R^2 are ethyl groups, R^3 is hydrogen, and n is 2.

Embodiments of the present invention also relate to pesticide formulations. In some embodiments, a pesticide formulation comprises a pesticide and a solvent according to any of the embodiments disclosed herein. In some embodiments, the solvent comprises 1 to 90 weight percent of the formulation and the pesticide comprises 10 to 99 weight percent of the formulation. The solvent, in some embodiments, comprises 2 to 70 weight percent of the formulation, and the pesticide comprises 30 to 98 weight percent of the formulation. In some embodiments, the pesticide comprises one or more of chlopyrifos, tebuconazole, difenoconazole, triazolone, quizalofop-p-ethyl, myclobutanil, pyraclostrobin, bifenthrin, buprofezin, and beta-cypermethrin.

Solvents for Pesticides

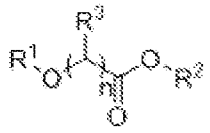
Solvents for pesticides according to some embodiments of the present invention comprise an ether ester of Formula 1:



(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6. In some embodiments, R^1 and R^2 are ethyl groups, R^3 is hydrogen, and n is 2.

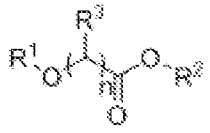
Solvents for pesticides according to some embodiments of the present invention consist of an ether ester of Formula 1:



(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6. In some embodiments, R^1 and R^2 are ethyl groups, R^3 is hydrogen, and n is 2.

Solvents for pesticides according to some embodiments of the present invention consist essentially of an ether ester of Formula 1:



(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6. In some embodiments, R^1 and R^2 are ethyl groups, R^3 is hydrogen, and n is 2.

In one embodiment the ether ester is ethyl-3-ethoxy propionate and are commercially available from The Dow Chemical Company as UCAR™ Ester EEP.

Solvents for pesticides of the present invention can comprise, consist of, or consist essentially of two or more ether esters of Formula 1. "Two or more ether esters of Formula 1" means that the solvent comprises at least two distinct ether esters of Formula 1 (e.g., a first ether ester in which R^1 and R^2 methyl and a second ether ester in which R^1 and R^2 are ethyl; or a first ether ester in which n is 2 and a second ether ester in which n is 3 and all other substituents or components of the two ether esters are the same; etc. The ether esters can differ from one another in more than one substituent or component, and the solvent can comprise any number of different ether esters of Formula 1.

In some embodiments, solvents of the present invention comprise or consist essentially of at least 95 percent by weight of ether esters of Formula 1. Solvents of the present invention, in other embodiments, comprise or consist essentially of at least 95 weight percent, or at least 97 weight percent, or at least 98 weight percent or at least 99 weight percent, or at least 99.9 weight percent of ether esters of Formula 1.

In some embodiments, solvents of the present invention comprise or consist essentially of at least 95 percent by weight ethyl-3-ethoxy propionate. Solvents of the present invention, in other embodiments, comprise or consist essentially of at least 95 weight percent, or at least 97 weight percent, or at least 98 weight percent or at least 99 weight percent, or at least 99.9 weight percent of ethyl-3-ethoxy propionate.

Pesticide Formulations

Pesticide formulations according to the present invention comprise a pesticide and a solvent according to any of the embodiments of solvents for pesticides disclosed herein. These pesticides include, but are not limited to, chlopyrifos, tebuconazole, difenoconazole, triazolone, quizalofop-p-ethyl, myclobutanil, pyraclostrobin, bifenthrin, buprofezin, and beta-cypermethrin.

In some embodiments, a pesticide formulation comprises 1 to 90 weight of a solvent according to any of the solvents for pesticides disclosed herein and 10 to 99 weight percent of the pesticide, each based on the total weight of the formulation. In some embodiments, a pesticide formulation comprises 2 to 70 weight of the solvent and 30 to 98 weight percent of the pesticide, each based on the total weight of the formulation.

In some embodiments, a pesticide formulation consists of 1 to 90 weight of a solvent according to any of the solvents for pesticides disclosed herein and 10 to 99 weight percent of the pesticide, each based on the total weight of the formulation. In some embodiments, a pesticide formulation consists of 2 to 70 weight of the solvent and 30 to 98 weight percent of the pesticide, each based on the total weight of the formulation.

In some embodiments, a pesticide formulation consists essentially of 1 to 90 weight of a solvent according to any of the solvents for pesticides disclosed herein and 10 to 99 weight percent of the pesticide, each based on the total weight of the formulation. In some embodiments, a pesticide formulation consists essentially of 2 to 70 weight of the solvent and 30 to 98 weight percent of the pesticide, each based on the total weight of the formulation.

Optional materials that are not essential to the operability of, but can be included in, the pesticide formulations of this invention include, but are not limited to, _ antioxidants, colorants, water scavengers, stabilizers, and the like. These materials do not have any material impact on the efficacy of the pesticide formulation. These optional materials are used in known amounts, e.g., 0.10 to 5, or 4, or 3, or 2, or 1, weight percent based on the weight of the solvent, and they are used in known ways.

Pesticide formulations can be prepared using techniques known to those of skill in the art. For example, the active ingredient (pesticide) can be dissolved in a solvent, and then emulsifiers or other conventional additives can be added.

Some embodiments of the invention will now be described in detail in the following Examples.

Examples

The following examples are given to illustrate the invention and should not be construed as limiting its scope. All parts and percentages are by weight unless otherwise indicated.

The following solvents in Table 1 are evaluated for performance as a solvent for pesticides:

Table 1

Solvent	Chemical
Comparative Solvent A	xylene
Comparative Solvent B	Solvesso 150
Inventive Solvent 1	ethyl 3-ethoxypropionate

The xylene is from Sinopharm, Co., China. Solvesso 150 is an aromatic solvent (CAS No. 64742-94-5) from ExxonMobil Chemical Co. The ethyl 3-ethoxypropionate is UCAR™ Ester EEP available from The Dow Chemical Company. The solubility of various pesticides in these solvents are evaluated. The pesticides are shown in Table 2:

Table 2

Components	Supplier
Chlopyrifos	Zhongye Chemical Co. (China)
Tebuconazole	Liannong Chemical Co. (China)
Difenoconazole	Suli Chemical Co. (China)
Triazolone	Qizhou Chemical Co. (China)
Quizalofop-p-ethyl	Jingbo Chemical Co. (China)
Myclobutanil	Shengya Chemical Co. (China)
Pyraclostrobin	Shentai Chemical Co. (China)
Bifenthrin	Lier Chemical Co. (China)
Buprofezin	Anbang Chemical Co. (China)
Beta-cypermethrin	Tianyuan Bio-chemical Co. (China)

Each pesticide powder is added by solvent in 2% stepwise increments to the final pesticide concentration. Each pesticide reaches a concentration where the pesticide powder is not dissolved by the solvent. The concentration just prior to the concentration where the pesticide powder is not dissolved is shown in Table 3. Thus, the data in Table 3 reflects a solubility that is no more than 2% lower than the actual solubility.

Table 3

Active Ingredients	Comparative Solvent A (weight %)	Comparative Solvent B (weight %)	Inventive Solvent 1 (weight %)
Chlopyrifos	70	54	63
Tebuconazole	4.0	2.0	16
Difenoconazole	34	19	33
Triazolone	23	12	32
Quizalofop-p-ethyl	32	23	22
Myclobutanil	27	23	39
Pyraclostrobin	42	31	47

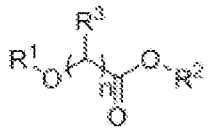
Active Ingredients	Comparative Solvent A (weight %)	Comparative Solvent B (weight %)	Inventive Solvent 1 (weight %)
Bifenthrin	45	44	43
Buprofezin	10	16	18
Beta-cypermethrin	32	34	43

In comparing the dissolving ability of Comparative Solvent A and Inventive Solvent 1, Comparative Solvent A has a stronger dissolving ability than Inventive Solvent 1 for some active ingredients (e.g., chlopyrifos, quizalofop-p-ethyl and bifenthrin). However, for the rest of evaluated active ingredients, Inventive Solvent 1 exhibits better solubility than Comparative Solvent A. Overall, Inventive Solvent 1 is believed to exhibit comparable dissolving performance relative to Comparative Solvent A with respect to the various pesticides evaluated. While exhibiting comparable dissolving performance, Inventive Solvent 1 is also advantageously believed to be more environmentally friendly than Comparative Solvent A.

In comparing the dissolving ability of Comparative Solvent B and Inventive Solvent 1, the two solvents have comparable dissolving ability as to three of the evaluated active ingredients (buprofezin, bifenthrin and quizalofop-p-ethyl). For the other active ingredients, Inventive Solvent 1 provides much better solubility performance than Comparative Solvent B. Thus, Inventive Solvent 1 has a stronger dissolving ability for these active ingredients than Comparative Solvent B. While exhibiting generally stronger dissolving performance, Inventive Solvent 1 is also advantageously believed to be more environmentally friendly than Comparative Solvent B.

WE CLAIM:

1. A solvent for pesticides comprising an ether ester of Formula 1:



(Formula 1)

wherein R^1 and R^2 are each independently one of an alkyl group having 1 to 4 carbon atoms or an aryl group, wherein R^3 is hydrogen, methyl, or ethyl, and wherein n is 1 to 6.

2. The solvent of claim 1, wherein R^1 and R^2 are ethyl groups, R^3 is hydrogen, and wherein n is 2.

3. The solvent of claim 1 or claim 2, wherein the solvent comprises two or more ether esters of Formula 1.

4. A pesticide formulation comprising:
the solvent of any of claims 1 to 3; and
a pesticide.

5. The pesticide formulation of claim 4, wherein the solvent comprises 1 to 90 weight percent of the formulation and wherein the pesticide comprises 10 to 99 weight percent of the formulation.

6. The pesticide formulation of claim 4 or claim 5, wherein the pesticide comprises one or more of chlopyrifos, tebuconazole, difenoconazole, triazolone, quizalofop-p-ethyl, myclobutanil, pyraclostrobin, bifenthrin, buprofezin, and beta-cypermethrin.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/109246

A. CLASSIFICATION OF SUBJECT MATTER

C07C 69/708(2006.01)i; C07C 69/76(2006.01)i; A01N 25/02(2006.01)i

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)

C07C; 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 practicable, search terms used)

WPI,EPODOC,CNPAT,CNKI,REGISTRY(STN),CAPLUS(STN):solvent,pesticide,formulation,herbicide,emulsion,formul?, emuls?,solubility,ether,methoxy,ethoxy,propoxy,butoxy,ester,acetate,propionate,carboxylate,763-69-9,5349-56-4,618890-93-0

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 20030109415 A1 (WALTER KUHN ET AL) 12 June 2003 (2003-06-12) description, page 1, paragraphs [0010]-[0011]	1
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☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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	Date of mailing of the international search report
20 July 2018	**09 August 2018**

Name and mailing address of the ISA/CN	Authorized officer
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Facsimile No. **(86-10)62019451**	Telephone No. **86-(10)-53962324**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/109246

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2017/109246

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