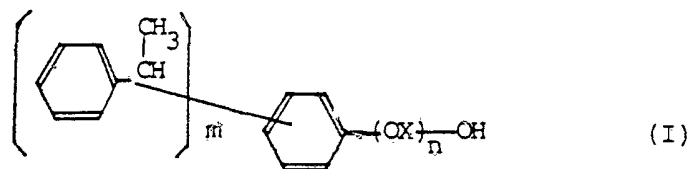


(12) PATENT ABRIDGMENT (11) Document No. AU-B-35202/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 617809

- (54) Title
SURFACE ACTIVE AGENTS BASED ON POLY (1-PHENYL ETHYL) PHENOLS
- International Patent Classification(s)
(51)⁴ **C08G 065/34 A01N 025/30 C08G 065/08**
- (21) Application No. : **35202/89** (22) Application Date : **25.05.89**
- (30) Priority Data
- (31) Number (32) Date (33) Country
20777 /88 27.05.88 IT ITALY
- (43) Publication Date : **30.11.89**
- (44) Publication Date of Accepted Application : **05.12.91**
- (71) Applicant(s)
GERONAZZO S.P.A.
- (72) Inventor(s)
ANTONIO MARCHETTO; ANGHELITO MASCHERONI; GEORGES RUFFO
- (74) Attorney or Agent
SHELSTON WATERS , 55 Clarence Street, SYDNEY NSW 2000
- (56) Prior Art Documents
AU 33954/89 A01N B01F
US 4564632
US 4315832

(57) Claim

1. Surface active agent characterised by comprising at least one poly-oxyethylenated and -oxypropylenated poly (1-phenyl ethyl) phenol of following formula (I)



wherein:

- . m is 2 or 3
- . $(OX)_n$ represents a statistic succession of recurrent oxyethylenated units and recurrent oxypropylenated units
- . n being such that the total number of recurrent oxyalkylenated units of the radical $(OX)_n$ is between 16 and 35, with a ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units of between 75/25 and 90/10.

617809

AUSTRALIA

PATENTS ACT 1990

C O M P L E T E S P E C I F I C A T I O N

FOR A STANDARD PATENT

O R I G I N A L

Name of Applicant: GERONAZZO S.p.A.

Actual Inventors: ANTONIO MARCHETTO, ANGHELITO MASCHERONI and
GEORGES RUFFO

Address for Service: SHELSTON WATERS
55 Clarence Street
SYDNEY NSW 2000

Invention Title: "SURFACE ACTIVE AGENTS BASED ON POLY (1-PHENYL
ETHYL) PHENOLS"

The following statement is a full description of this invention,
including the best method of performing it known to me/us:-



DESCRIPTION

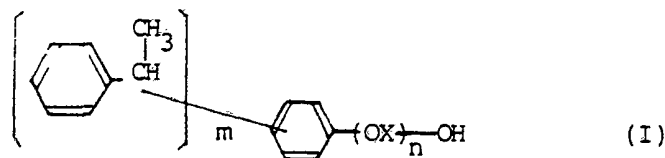
The present invention concerns a surface active substance based on poly (1-phenyl ethyl) phenols which contain recurrent statistically distributed polyoxyethylenated and polyoxypropylenated units, the process for the preparation thereof and the use thereof for producing emulsifiable concentrated solutions of active materials which are then diluted to obtain emulsions which are ready for use.

It is known that it is possible to prepare biocidal compositions which can be dispersed in water by means of surface active agents of the polyoxyethylenated tri (1-phenyl ethyl) phenol type or which bear recurrent polyoxyethylenated and polyoxypropylenated units which are distributed in accordance with a given sequence (Japanese patent application published under the No 25526/1975).

The main disadvantage of that type of surface active agent is that the degree of solubility thereof in the organic solvents used in the phytosanitary field is inadequate.

The applicants found a surface active agent which is soluble in that type of solvents.

The surface active agent which is the subject-matter of the present invention comprises at least one poly-oxyethylenated and -oxypropylenated poly (1-phenyl ethyl) phenol of following formula (I):



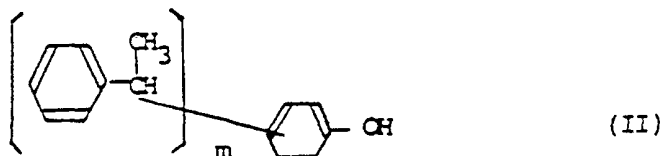
wherein:

- . m is 2 or 3
- . (OX)_n represents a statistic succession of recurrent oxyethylenated

units and recurrent oxypropylenated units

. n being such that the total number of recurrent oxyalkylenated units of the radical $(OX)_n$ is between about 16 and about 35 and preferably between 20 and 30, with a ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units which is between about 75/25 and 90/10 and preferably between 80/20 and 90/10.

The surface active agent which is the subject-matter of the invention can be produced by means of the action of at least one poly (1-phenyl ethyl) phenol of formula (II):



and a mixture of monoethylene glycol and monopropylene glycol in accordance with a monoethylene glycol/monopropylene glycol ratio corresponding to the desired ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units.

That operation is preferably carried out for a period of time of the order of between 20 minutes and 40 minutes, at a temperature of 140 to 180°C, in the presence of 0.5 to 1.5% by weight with respect to the finished product of an alkaline base, for example soda, as a catalyst. The product of formula II and the whole of the monoalkylene glycols equivalent to a product of formula $H-(OX)_n-OH$ are used in stoichiometric amounts or amounts which are close to stoichiometry.

The present invention also concerns concentrated emulsifiable solutions which are produced by means of the formulation of active materials which are soluble in organic solvents by means of the surface active agent according to the invention.

The following may be mentioned as active materials which can form



emulsifiable concentrated solutions: insecticides, acaricides, fungicides and various associations thereof, herbicides, nematocides, molluscicides, substances with an attraction effect, repellent substances and rodenticides.

5 As examples of insecticides which are suitable in accordance with the present invention, mention may be made of those which belong to the following families:

- organo-halogenated or chlorinated substances;
- carbinols;
- 10 - organo-phosphorated substances;
- sulphones and sulphonates;
- carbamates;
- benzoyl ureas; and
- synthetic pyrethrinoids.

15 Fungicides which may be used in the present invention may be selected from the following:

- carbamates;
- derivatives of benzene;
- derivatives of phenol;
- 20 - quinones;
- dicarboximides;
- amines and amides;
- diazines;
- sulphamides and sulphur-bearing derivatives;
- 25 - guanidines;
- heterocyclic compounds;
- metallic monoethyl phosphites; and
- organo-stannic substances.

As chemical substances which have herbicidal properties, mention may
30 be made of those which are included in the following families of chemical products:

Phenolic compounds;

- carbamates;
- substituted ureas;
- diazines;
- 5 - triazines;
- amides;
- quaternary ammonium compounds;
- benzonitriles;
- toluidines; and
- 10 - triazoles and other substances.

The emulsifiable concentrated solutions favourably comprise:

- at least one active material
- an organic solvent for said active material
- the surface active agent of the present invention, possibly with
- 15 the addition of one or more anionic, cationic, non-ionic or amphoteric surface active agents which are usual in this type of use
- an optional wetting agent
- optionally a stabilizing agent and
- various coadjuvant substances.

- 20 The organic solvents which can be used are those which are normally used in this type of formulation. By way of example, mention may be made of aromatic hydrocarbons, cyclohexanone, methylhexahydronaphthalene, tetrahydronaphthalene, dimethylsulphoxide, dimethylformamide, dibutylphthalate, isophorone, N-methylpyrrolidone, butyrolactone
- 25 Said solvent may possibly be eliminated if the active material used is liquid at a temperature of between -20 and 50°C.

The surface active agent of the present invention also has a wetting capability; accordingly the presence of a wetting agent is not indispensable; if however the presence of such a wetting agent is

30 desired, it may be selected from the following:

- soaps of alkali metals such as sodium or potassium salts of C_8-C_{24} saturated or unsaturated fatty acids, sodium N-lauryl sarcosinate, sodium N-acylsarcosinate,

- alkaline sulphonates such as alkylsulphonates of the sodium
5 diethylhexylsulphosuccinate type; alkylbenzenesulphonates of the type nonyl- or dodecyl-benzenesulphonates of sodium, diethynolamine, triethynolamine or N-methylcyclohexylamine; alkaline alkyl-naphthalene sulphonates; and alkaline N-alkyltaurates; and

- sulphates and sulphur-bearing products such as alkaline
10 alkylsulphates of the sodium laurylsulphate type; polyoxyethylenated and sulphated fatty alcohols; and polyoxyethylenated and sulphated alkylphenols.

Among the optional stabilizing agents that may be used, mention may be made of organic acids selected from optionally halogenated aliphatic
15 monocarboxylic acids (formic, monochloroacetic, propionic, citric and tartaric acids ...), hydroxycarboxylic acids which are aliphatic (glycolic...) or aromatic (benzoic, phthalic...) and which are optionally substituted (dichlorobenzoic, dimethoxybenzoic, hydroxybenzoic, dihydroxybenzoic, nitrobenzoic, nitroisophthalic...), and sulphonic acids (methane-
20 sulphononic, benzenesulphonic, p-toluenesulphonic...).

The term various coadjuvant substances means the other ingredients or additives which are usual in the formulation of agricultural products, in particular penetration agents, corrosion inhibitors, adhesives ...

The proportions by weight of the different constituents of the
25 emulsifiable concentrated solutions are generally as follows:

- 0.1 to 90 parts by weight of active material
- from 0.5 to 25 parts by weight of surface active agent of the invention
- from 0 to 25 parts of wetting agent
- 30 - and an amount to make up 100 parts of organic solvent.

The emulsifiable concentrated solutions may be obtained in known manner, for example by mixing the different constituents and subjecting them to agitation until homogenized.

It is then only necessary to dilute them with a given amount of water
5 to produce emulsions which are ready for use.

The emulsifiable concentrated solutions have the following properties:

- good stability in respect of storage, and
 - good stability throughout the period of use, once diluted in water
- 10 at the dosage for use.

The following examples are given by way of example and are not to be considered as limiting the scope and spirit of the invention.

EXAMPLE 1

Preparation of the surface active compositions of the invention

15 Introduced into a reaction vessel are tristyrylphenol and soda (1% by weight with respect to the finished product), and then monoethyleneglycol and monopropyleneglycol are introduced at the same time.

The reaction is performed at 160°C for 30 minutes.

The relative quantities of monoethyleneglycol and monopropyleneglycol
20 correspond to the ratios OE/OP set forth in Table I.

The tristyrylphenol and the monoalkyleneglycols are used in stoichiometric amounts.

OE indicates a recurrent ethylene oxide unit (or ethoxylated unit)

OP indicates a recurrent propylene oxide unit (or propoxylated unit).

25 EXAMPLES 2 to 8

1 g of surface active agent (SAA) prepared in accordance with Example 1, the characteristics of which are set forth in Table I, is introduced into 20 cm³ of xylene or SHELLSOL which is marketed by SHELL.

The mixture is agitated for 5 minutes, using a magnetic agitator.

The appearance of the solution obtained is checked after a residence time of 72 hours at 0°C (CIPAC MT 39.1 method).

It is found that all the solutions are clear.

5 EXAMPLES 9 to 13

The checks in respect of solubility which are described in Examples 2 to 8 are repeated, with the surface active agent of the invention being replaced by one of the following products:

- (Example 9) SOPROPHOR CY/8, ethoxylated tri (1-phenyl ethyl) phenol which bears 20 moles of ethylene oxide, marketed by RHONE-POULENC

- (Example 10) tri (1-phenyl ethyl) phenol which bears a propoxylated sequence $(OP)_{n1}$ and an ethoxylated sequence $(OE)_{n2}$ in a terminal position, that is to say a product whose group $(OX)_{n1}OH$ is $(OP)_{n1}(OE)_{n2}OH$, with a number of recurrent OE+OP units of 25 and an OE/OP ratio of 90/10;

- (Example 11) tri (1-phenyl ethyl) phenol bearing a sequence $(OP)_{n1}$ and a sequence $(OE)_{n2}$ in a terminal position, with a number of recurrent OE/OP units of 34 and an OE/OP ratio of 90/10;

- (Example 12) tri (1-phenyl ethyl) phenol which bears a sequence $(OE)_{n1}$ and a sequence $(OP)_{n2}$ in a terminal position, that is to say a product in which the group $(OX)_{n1}OH$ is $(OE)_{n1}(OP)_{n2}OH$, with a number of recurrent OE+OP units of 25 and an OE/OP ratio of 90/10;

- (Example 13) tri (1-phenyl ethyl) phenol bearing a sequence $(OE)_{n1}$ and a sequence $(OP)_{n2}$ in a terminal position, with a number of 25 recurrent OE+OP units of 34 and an OE/OP ratio of 90/10.

The results of the checking tests appear in Table II (CIPAC MT 39.1 method).

It is found that none of the solutions is clear and that a certain number thereof contain sediments.

COMPARATIVE EXAMPLES 14 to 16

A surface active agent is prepared, the characteristics of which are set forth in Table I, in accordance with the mode of preparation used in Example 1.

5 Stability of the emulsifiable concentrates

Emulsifiable concentrates are prepared, starting from different active materials, using the following procedure:

The active material is dissolved in xylene and then a surface active agent (SAA) is added, which constitutes the subject of one of Examples 2 to 16, and calcium dodecylbenzenesulphonate (CaDDBS) is added. The amounts of constituents used depend on the active material used:

15	- diazinone	60 parts by weight
	SAA	2.6 " " "
	CaDDBS	2.4 " " "
	xylene	35 " " "
20	- lindane	20 parts by weight
	SAAA	3.1 " " "
	CaDDBS	1.9 " " "
	xylene	75 " " "
25	- malathion	50 parts by weight
	SAA	3.4 " " "
	CaDDBS	2.6 " " "
	xylene	45 " " "
	- trifluralin	25 parts by weight
	SAA	2.3 " " "
	CaDDBS	2.7 " " "
	xylene	70 " " "

The mixture obtained is subjected to agitation until homogenized; that thus gives emulsifiable concentrated liquid compositions.

The stability of the emulsions in water which are prepared starting from those compositions is measured using the CIPAC MT 36.1 method in standardized waters A (20 ppm hardness), D (342 ppm hardness) and C (500 ppm hardness) after 60 minutes or 120 minutes.

5 The results of that test are set forth in Tables III and IV.

It is found that it is impossible to prepare emulsifiable concentrates using the products of Examples 14 to 16.

TABLE I

EXAMPLE	OE + OP	OE/OP	APPEARANCE OF THE SOLUTION Pure SAA in	
			xylene	SHELLSOL
2	16	90/10	clear	clear
3	20	90/10	"	"
4	25	90/10	"	"
5	34	90/10	"	"
6	25	84/16	"	"
7	20	80/20	"	"
8	25	80/20	"	"
14	16	50/50	"	"
15	25	50/50	"	"
16	34	50/50	"	"

TABLE II

EXAMPLE	OE + OP	OE/OP	APPEARANCE OF THE SOLUTION Pure SAA in	
			xylene	SHELLSOL
9	20 OE	100/0	0.5% *	0.5% *
10	25-OP+OE	90/10	5% *	15% *
11	34-OP+OE	90/10	2% *	48% *
12	25-OE+OP	90/10	cloudy	5% *
13	34-OE+OP	90/10	cloudy	35% *

* : amounts of sedimented substances

TABLE III

ACTIVE MATERIAL		DIAZINONE			LINDANE			MALATHION			TRIFLURALIN		
Product of Example	Time after dilution	Stability of the emulsion - cream in ml -											
		A	D	C	A	D	C	A	D	C	A	D	C
2	60	0	0	0	0	0	0	0	0.1	0.2	0.5	0	0
	120	0.5	0	0	0	0	0	2.5	1	0.5	2	0	0
3	60	1	0	0	0	0	0	0.6	0	0	0.5	0	0
	120	2	0	0	0	0	0	1	0	0	1	0	0
4	60	0	0	0	0	0	0	0	0	0	1.5	0	0
	120	0.5	0	0	0	0	0	0.7	0	0	2	0.05	0.05
5	60	0	0	0	0	0	0	0	0	0	2	0.5	0.05
	120	0.5	0	0	0	0	0	1.2	0.1	0.05	2.5	1	1
6	60	0.2	0	0	0	0	0	0.5	0	0	0	0	0
	120	0.5	0	0	0.5	0	0	1	0	0	1	0	0.5
7	60	-	-	-	0	0	0	0.6	0	0	1	0	0
	120	-	-	-	0	0	0	1.1	0	0	2	0	0
8	60	0	0	0	0	0	0	0.4	0	0	0	0	0
	120	0.5	0	0	0	0	0	0.8	0	0	0.5	0	1

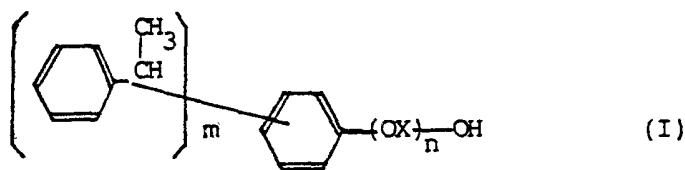
45 5 89 3500

TABLE IV

ACTIVE MATERIAL		DIAZINONE			LINDANE			MALATHION			TRIFLURALIN		
Product of Example	Time after dilution	Stability of the emulsion - cream in ml -											
		A	D	C	A	D	C	A	D	C			
		A	D	C	A	D	C	A	D	C	A	D	C
9	60	0.2	0	0	0	0	0	0.4	0	0	0.5	0	0
	120	0.5	0	0	0	0	0	0.8	0	0	1.5	0.1	0
10	60	1	0	0	0	0	0	0.4	0	0	0.5	0	0
	120	2	0	0	0	0	0	0.8	0	0	1.5	0.1	0
11	60	1	0	0	0	0	0	1	0	2	0.5	0	0
	120	2	0	0	0.5	0	0.5	2	0.1	5	1.5	0	1.2
12	60	1	0	0	0	0	0	0	0.05	5	2	0.5	0.5
	120	2	0	0.2	0.5	0.5	0.5	0.1	5	6	3	1	1
13	60	1	0	0	0	0	0	2	0.6	0.3	1.5	0.5	5
	120	2	0	0.5	0	0	0	3.5	1.2	0.7	2	1	6
14	60	negative			negative			negative			negative		
	120												
15	60	negative			negative			negative			negative		
	120												
16	60	negative			negative			negative			negative		
	120												

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. Surface active agent characterised by comprising at least one poly-oxyethylenated and -oxypropylenated poly (1-phenyl ethyl) phenol of following formula (I)

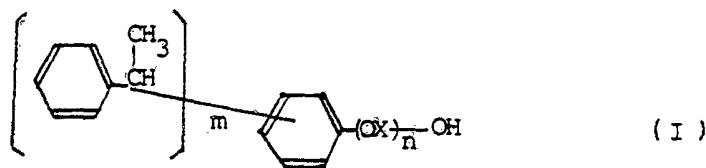


wherein:

- . m is 2 or 3
- . $(\text{OX})_n$ represents a statistic succession of recurrent oxyethylenated units and recurrent oxypropylenated units
- . n being such that the total number of recurrent oxyalkylenated units of the radical $(\text{OX})_n$ is between 16 and 35, with a ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units of between 75/25 and 90/10.

2. A surface active agent according to claim 1 characterised in that the ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units is between 80/20 and 90/10.

3. A process for the preparation of a surface active agent of the following formula:

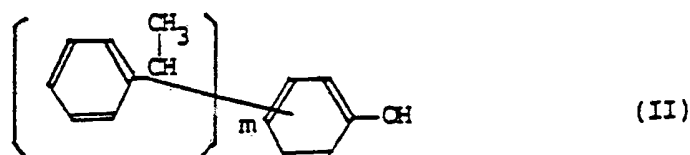


wherein:

- . m is 2 or 3
- . $(\text{OX})_n$ represents a statistic succession of recurrent oxyethylenated

units and recurrent oxypropylenated units

. n being such that the total number of recurrent oxyalkylenated units of the radical $(OX)_n$ is between about 16 and about 35, with a ratio between the number of recurrent oxyethylenated units and the number of recurrent oxypropylenated units of between 75/25 and 90/10, by means of the action of at least one poly (1-phenyl ethyl) phenol of formula (II):



and a mixture of monoethyleneglycol and monopropyleneglycol in the presence of an alkaline base as a catalyst and in accordance with a monoethyleneglycol/monopropyleneglycol molar ratio of between 75/20 and 90/10, with a molar ratio between the product of formula II and the equivalent $H-(OX)_n-OH$ which is close to the stoichiometric ratio.

4. A process according to claim 3 characterised in that the molar ratio between monoethyleneglycol and monopropyleneglycol is between 80/20 and 90/10.

5. A process according to claim 3 or claim 4 characterised in that the condensation operation is carried out at a temperature of the order of magnitude of 140 to 180°C.

6. Use of the surface active agent according to claim 1 or claim 2 for producing emulsifiable concentrated solutions of phytosanitary active materials.

7. Emulsifiable concentrated solutions of phytosanitary active materials comprising:

- 0.1 to 90 parts by weight of phytosanitary active material
- 0.5 to 25 parts by weight of a surface active agent according to claim 1 or claim 2
- 0 to 25 parts of a wetting agent, and
- an amount to make up 100 parts of organic



GERONAZZO S.p.A.

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

A 5x5 grid of dots. The dots are arranged in a cross shape, with a horizontal row of 5 dots and a vertical column of 5 dots. The intersection of the row and column is a single dot, resulting in a total of 9 dots.

MTS