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PLANT PROTECTION SUSPO EMULSIONS

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(71) Applicant(s)
RHONE-POULENC CHIMIE

(72) Inventor(s)
JEAN-FRANCOIS FIARD

(74) Attorney or Agent
SHELSTON WATERS , 55 Clarence Street, SYDNEY NSW 2000

(57) Claim

1. Aqueous suspo emulsion of solid plant protection active substance which has a melting point higher than or equal to 45°C and is essentially insoluble in water, characterised in that it comprises at least sucroglycerides, the said active substance and either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester, and water.

2. Suspo emulsion of plant protection active substance according to claim 1, characterised in that the said suspo emulsion is obtained by mixing:

- an aqueous emulsion comprising at least sucroglycerides,
- with an aqueous suspension of the said active substance, comprising at least either a nonionic and/or anionic surfactant or a surfactant system

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comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester.

52. Use of the suspo emulsions according to any one of claims 1 to 51, if appropriate after dilution with water, for the treatment and the protection of plants.

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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

Name of Applicant: RHONE-POULENC CHIMIE

Actual Inventor: Jean-François Fiard

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

Invention Title: "PLANT PROTECTION SUSPO EMULSIONS"

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

PLANT PROTECTION SUSPO EMULSIONS

The present invention relates to new plant protection suspo emulsions.

The plant protection active substances, such as insecticides, germicides, herbicides, fungicides, acaricides, nematicides, molluscicides, rodenticides, attractants, repellants and combinations of several of these compounds, are generally insoluble in water.

They may usually be used in the form of solutions in organic solvents, these solutions then being emulsified in water, during their use.

The use of solvents, such as xylenes or kerosene, presents obvious environmental pollution problems.

Another mode of preparation of the compositions of active substances consists of fluid aqueous dispersions, commonly termed "flowable", which are diluted during their application.

These aqueous dispersions contain one or more surfactants.

The increasingly serious account which is taken of the various environmental pollution problems leads to the search for increasingly less toxic plant protection compositions.

The present invention contributes to this development by the use of a surfactant system consisting at least in part of non-toxic, non-irritant and biodegradable compounds.

The emulsifying and dispersing character of the sucroglycerides is known for the preparation of aqueous dispersed systems of fatty substances.

The sucroglycerides are mixtures of products, obtained by transesterification of natural or synthetic triglycerides with sucrose. These mixtures contain monoglycerides, diglycerides, small amounts of triglycerides which have not been transesterified, and monoesters and diesters of sucrose.

Patent EP-A-0,091,331, which describes a process for the preparation of fluid sucroglycerides, also indicates that the said sucroglycerides have surfactant properties which may be utilised, in particular, for the preparation of emulsions of essential oils or of skimmed milk to which fat is reintroduced. The sucroglycerides may also be combined with lecithins and fluid oils.

Swiss Patent 423,442 describes a process for the preparation of emulsions of oils or of solid fatty matter in water, using sucroglycerides and a lecithin as emulsifier system.

The present invention consists in utilising this emulsifying and/or dispersing power of the sucroglycerides in order to obtain suspo emulsions of plant protection active substances, as well as the capacity of the sucroglycerides for modifying the bioavailability of the active substances.

More precisely, the invention consists of an

aqueous suspo emulsion of solid plant protection active substance which has a melting point higher than or equal to 45°C and is essentially insoluble in water, characterised in that it comprises at least sucroglycerides, the said active substance and either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester, and water.

The suspo emulsion according to the invention may be obtained by mixing the various constituent compounds.

However, in order better to adjust the desired properties, that is to say, in particular, the size of the particles in emulsion and the size of the particles in suspension, the suspo emulsion will preferably be prepared from an aqueous suspension of the active substance and an aqueous emulsion based on sucroglycerides.

Preferably, the invention therefore consists of a suspo emulsion of solid plant protection active substance which has a melting point higher than or equal to 45°C and is essentially insoluble in water, characterised in that the said suspo emulsion is obtained by mixing:

- an aqueous emulsion comprising at least sucroglycerides,

- with an aqueous suspension of the said active substance, comprising either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester.

The aqueous suspension, which serves to prepare the suspo emulsion of the invention, preferably also contains a wetting agent in its surfactant system, although the alkoxylated triglycerides may also play this role, in particular for the suspensions having the lowest concentration of active substance.

The aqueous emulsion used in the present invention therefore contains at least water and sucroglycerides.

As indicated above, the sucroglycerides originate from the transesterification of triglycerides by sucrose.

In the present text, the term "sucroglycerides" will be used in the plural in order to indicate that they do not consist of a single chemical compound.

The triglycerides used are generally the triglycerides of saturated or unsaturated aliphatic acids having at least 4 carbon atoms. Preferably the acids from which the triglycerides are derived have 10 to 20 carbon atoms.

The preparation of the sucroglycerides can be carried out using synthetic triglycerides, obtained by reaction of glycerol and fatty acids, as the starting material. However, it is more valuable from the economic standpoint to make use of natural triglycerides. These natural triglycerides are mixtures of triglycerides.

Examples which may be mentioned of such natural triglycerides are lard, suet, groundnut oil, butter oil, cottonseed oil, linseed oil, olive oil, palm oil, grapeseed oil, fish oil, soya oil, castor oil, colza oil, copra oil and coconut oil.

In the present invention, the sucroglycerides used originate from palm oil, lard, copra oil, suet, colza oil and castor oil.

They are either in liquid form, such as the sucroglycerides from colza oil or castor oil, or in the form of pastes of higher or lower consistency, differing, in particular, in respect of their melting point:

- lard sucroglycerides: 47 to 50°C
- suet sucroglycerides: 50 to 55°C
- palm oil sucroglycerides: 55 to 58°C
- copra oil sucroglycerides: 60 to 62°C.

A method for the preparation of sucroglycerides is described in Patent FR-A-2 463 512.

Several different sucroglycerides may be used in the aqueous emulsion in order, in particular, to use

their different specific properties.

The aqueous emulsion of sucroglycerides which participates in the composition of the suspo emulsion may also comprise a phospholipid, in combination with the sucroglycerides.

The following may be mentioned amongst the phospholipids used with the sucroglycerides within the framework of the invention: crude lecithins of vegetable or animal origin, such as soya lecithin, egg yolk lecithin and any lecithin fraction.

This emulsion may also comprise other compounds, such as alkoxylated triglycerides, alkoxylated fatty acids, sorbitan esters and alkoxylated sorbitan esters, which are more particularly chosen from ethoxylated triglycerides, ethoxylated fatty acids, sorbitan esters and ethoxylated sorbitan esters.

The ethoxylated triglycerides may be ethoxylated triglycerides of vegetable or animal origin (such as lard, suet, groundnut oil, butter oil, cottonseed oil, linseed oil, olive oil, palm oil, grapeseed oil, fish oil, soya oil, castor oil, colza oil, copra oil and coconut oil).

The ethoxylated fatty acids are esters of ethoxylated fatty acids (such as, for example, oleic acid or stearic acid).

The sorbitan esters are cyclised sorbitol esters of C_{10} to C_{20} fatty acids, such as lauric acid,

stearic acid or oleic acid. These sorbitan esters may also be ethoxylated.

In the present invention the term ethoxylated triglyceride relates both to the products obtained by ethoxylation of a triglyceride by ethylene oxide and to those obtained by transesterification of a triglyceride by a polyethylene glycol.

Likewise, the term ethoxylated fatty acid includes both the products obtained by ethoxylation of a fatty acid by ethylene oxide and those obtained by esterification of a fatty acid by a polyethylene glycol.

The aqueous emulsion, which participates in the composition of the suspo emulsions of the invention, generally comprises, by weight relative to the total volume of the emulsion:

- from 0.1% to 60% of sucroglycerides,
- from 0 % to 50% of phospholipid,
- from 0 % to 20% of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester,
- and water to make up to 100%.

Preferably, the composition in weight by volume of the aqueous emulsion is as follows:

- from 3% to 50% of sucroglycerides,
- from 0% to 40% of phospholipid,
- from 0% to 15% of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester

and/or alkoxylated sorbitan ester,

- and water to make up to 100%.

The aqueous emulsions used to prepare the suspo emulsions of the invention have a very good physico-chemical stability and a good compatibility with a large number of suspensions of active substances.

The aqueous emulsion of sucroglycerides may be prepared by simple mixing of the various constituents, using any known techniques.

Preferably, in order to obtain particle sizes of the order of a few micrometres, the micronisation of the emulsion will be carried out using a colloid mill or a high-speed turbine stirrer.

The plant protection active substance used in the present invention is substantially insoluble in water, which signifies that its solubility in water at 20°C is less than 5 g/litre.

It is obvious that the active substances used must be stable with respect to water.

Mixtures of such active substances may be used without departing from the scope of the invention.

The following may be mentioned as non-limiting examples of active substances which may be used in the suspo emulsions of the invention:

- deltamethrin,
- propham,
- tetramethrin,

- furalaxyl,
- heptachlor,
- propanil,
- oxadiazon,
- triflumizole,
- dimethamethrin,
- atrazine,
- diuron,
- neburon,
- linuron,
- isoproturon,
- simazine,
- amethryne,
- phenmidipham,
- pendimethalin.

The sucroglycerides which may participate in the composition of the surfactant system of the suspensions of active substance have been defined above for the aqueous emulsions.

In some cases it may be advantageous to combine a phospholipid, as defined above, with the sucroglycerides, without the presence of such a compound constituting a critical element of the suspension of active substance.

In the surfactant system based on sucroglycerides, which is used in the suspension, the ratio by weight of phospholipid/sucroglycerides is generally from 0 to 3.

The surfactant system based on sucroglycerides, which may be used to prepare the suspension of active substance, also contains at least one alkoxylated triglyceride and/or one alkoxylated fatty acid and/or one sorbitan ester and/or one alkoxylated sorbitan ester. These are more particularly the ethoxylated triglycerides, ethoxylated fatty acids, sorbitan esters and ethoxylated sorbitan esters which have been described above.

The alkoxylated triglycerides and/or the alkoxylated fatty acids and/or the sorbitan esters and/or the alkoxylated sorbitan esters generally represent from 0.1 to 3% by weight by volume of the suspension and preferably from 0.2% to 2.8% by weight/volume.

The surfactant system based on sucroglycerides, which may be used to prepare the suspension of active substance, preferably also contains at least one wetting agent.

The wetting agent is a compound as defined in the standard NF T 73-000.

The wetting agents are, in particular, anionic salts of surfactants and alkoxylated alcohols or alkoxylated alkylphenols represented by the following formulae:

R_1-SO_3-M

R_2-SO_4-M

$R_3-(EO)_n-H$

$R_3-(PO)_n-H$

$R_3-(EO-PO)_n-H$

$R_4-COONa$

in which:

- R_1 represents
  - an alkylphenyl radical such as dodecylphenyl or nonylphenyl,
  - an alkyl radical such as dodecyl, or
  - a 1,2-bis(octyloxycarbonyl)ethyl radical, preferably 1,2-bis(2-ethylhexyloxycarbonyl)ethyl,
- R_2 represents
  - an alkyl radical such as dodecyl,
  - an ethoxylated alkylphenol radical such as nonylphenol ethoxylated with 2 to 50 EO units, or
  - an ethoxylated alkyl radical,
- R_3 represents
  - an alkylphenyl radical such as nonylphenyl,
  - an alkylnaphthyl radical, or
  - an alkyl radical having 8 to 20 carbon atoms and preferably from 10 to 14 carbon atoms,
- n is a number from 4 to 12,
- EO represents the ethylene oxide unit and PO the propylene oxide unit,
- R_4 represents an alkyl radical having 7 to 23 carbon atoms, and
- M represents Na, K, NH_4, or a triethanolammonium,

diethanolammonium or N-methyl-cyclohexylammonium cation.

The wetting agent may also be a silicone-based surfactant, such as copolymers of polydimethylsiloxane and either ethylene glycol homopolymer or ethylene glycol/propylene glycol copolymer, or a fluorinated surfactant, such as compounds comprising a hydrophobic and oleophobic straight perfluorocarbon chain, and a hydrophilic part comprising, for example, an acid or neutralised sulphonic group, a carboxyl group or an ethoxylated alcohol radical.

The suspensions generally comprise from 0.05% to 1% by weight of wetting agent relative to the total volume of the suspension, and preferably from 0.1% to 0.8% by weight/volume.

The nonionic surfactant, which may be used to prepare the suspension of active substance, may be chosen in particular from:

- alkoxylated di(1-phenylethyl)phenols,
- alkoxylated tri(1-phenylethyl)phenols,
- alkoxylated alkylphenols,
- alkoxylated fatty amines,
- alkoxylated fatty alcohols,
- alkoxylated castor oils, and
- ethylene oxide/propylene oxide (EO-PO) or ethylene oxide/propylene oxide/ethylene oxide (EO-PO-EO) block polymers.

The alkoxy units in these surfactants are ethylene oxide and/or propylene oxide units.

Their number usually varies from 2 to 100 depending on the HLB (hydrophilic/lipophilic balance) desired.

Preferably, the number of alkoxy units is between 4 and 50.

The alkoxylated alkylphenols generally have 1 or 2 straight-chain or branched alkyl groups having 4 to 12 carbon atoms, in particular octyl, nonyl or dodecyl.

The alkoxylated fatty amines generally have from 10 to 22 carbon atoms.

The alkoxylated fatty alcohols generally have from 6 to 22 carbon atoms.

The following may be mentioned as examples of nonionic surfactants:

- ethoxylated di(1-phenylethyl)phenol containing 15 ethylene oxide (EO) units,
- ethoxylated di(1-phenylethyl)phenol containing 5 EO units,
- ethoxylated di(1-phenylethyl)phenol containing 10 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 20 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 25

EO units,

- ethoxylated tri(1-phenylethyl)phenol containing 40 EO units,
- ethoxy-propoxylated tri(1-phenylethyl)phenols containing 25 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 25 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 30 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 40 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 55 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 80 EO + PO units, and
- EO-PO-EO tri-block polymers.

The anionic surfactant, which may be used to prepare the suspension of active substance, is chosen in particular from:

- phosphoric esters of alkoxylated alkylphenols, alkoxylated di(1-phenylethyl)phenols, alkoxylated tri(1-phenylethyl)phenols and alkoxylated fatty alcohols;
- sulphuric esters of alkoxylated alkylphenols, alkoxylated di(1-phenylethyl)phenols, alkoxylated tri(1-phenylethyl)phenols and alkoxylated fatty alcohols;
- sulphonic esters of alkoxylated alkylphenols,

alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols;

- salts of polycarboxylic acids, homopolymers and copolymers of polycarboxylic acids (such as polyacrylic and polymethacrylic acids), and copolymers based on maleic anhydride and diisobutylene;
- alkylnaphthalenesulphonates and poly(alkylnaphthalenesulphonates); and
- condensation products of dihydroxydiphenylsulphonates and formol.

The alkoxyl units in these anionic surfactants are ethylene oxide and/or propylene oxide units.

Their number usually varies from 2 to 100 depending on the HLB (hydrophilic/lipophilic balance) desired.

Preferably, the number of alkoxyl units is between 4 and 50.

The following may be mentioned in particular as examples of anionic surfactants:

- triethanolamine salts of phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- potassium salts of phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the hydrogen sulphate of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,

- the potassium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 15 EO units,
- the triethanolamine salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the hydrogen phosphate of ethoxylated nonylphenol containing 9 EO units,
- sodium methylnaphthalenesulphonate and
- the sodium salt of polyacrylic acid.

It is, of course, possible to use mixtures of nonionic surfactants and/or anionic surfactants.

The aqueous suspension of the active substance comprises generally from 0.1% to 90% by weight of active substance, relative to the total volume of the suspension, and preferably from 0.5% to 85% by weight/volume.

Either it comprises from 0.2% to 15% by weight/volume of nonionic and/or anionic surfactant and preferably from 0.5% to 10% by weight/volume.

Or it comprises:

- from 0.1% to 5% by weight of sucroglycerides and phospholipid, and preferably from 0.2% to 4%,
- from 0.1% to 3% by weight of alkoxylated triglyceride and/or alkoxylated fatty acid and/or

sorbitan ester and/or alkoxylated sorbitan ester, as defined above, and preferably from 0.2% to 2.8%, and

- from 0.05% to 1% by weight of a wetting agent, and preferably from 0.1% to 0.8%,

relative to the total volume of the aqueous suspension.

Without going beyond the scope of the present invention, it is possible to prepare several aqueous suspensions of active substances, as defined above, and then to prepare a suspo emulsion using an aqueous emulsion of sucroglycerides and these various aqueous suspensions of active substances as the starting material.

The suspo emulsions according to the invention may contain, in addition to the compounds defined above, other compounds customary in plant protection compositions, such as antifoams, such as organopolysiloxanes; organic thickeners which are soluble in water or able to swell in water, such as polysaccharides, such as xanthan gum, alginates, carboxylated or hydroxylated methylcelluloses, synthetic macromolecules of the polyacrylate, polymaleate, polyvinylpyrrolidone or polyvinyl alcohol type, or inorganic macromolecules, such as bentonites, and silicas; and an antigel, such as monopropylene glycol, monoethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol or urea.

Other supplementary additives which may be

present are agents which provide protection against oxidation, UV radiation or variations in pH, dyes or bactericides.

As indicated above, the suspo emulsion may be prepared from the various constituent compounds.

Preferably, the suspo emulsion is prepared by mixing the aqueous suspension of active substance and the aqueous emulsion which have been described above.

The proportions of suspension and emulsion are such that the suspo emulsion contains a total of 0.1% to 60% by weight of active substance relative to its total volume.

The proportions of suspension and emulsion are such that the suspo emulsion contains from 0.1% to 12% by weight of nonionic and/or anionic surfactant relative to its total volume.

The proportions of suspension and emulsion are such that the suspo emulsion contains from 0.1% to 60% by weight of sucroglycerides relative to its total volume.

The proportions of suspension and emulsion are such that the suspo emulsion contains from 0% to 50% by weight of phospholipid relative to its total volume.

The proportions of suspension and emulsion are such that the suspo emulsion contains from 0% to 20% by weight of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or

alkoxylated sorbitan ester relative to its total volume.

The proportions of suspension and emulsion are such that the suspo emulsion contains from 0.05% to 0.7% by weight of wetting agent relative to its total volume.

The suspo emulsions of the invention are very stable over a wide temperature range (for example between -10°C and +54°C).

They are used as such or after dilution with water for the treatment and the protection of plants.

They have the advantage of being film-forming, which ensures a good fixation and a good permanency of the active substance on the plants to be treated or on the parasites to be destroyed.

The presence of sucroglycerides promotes the bioavailability of the active substance.

In the examples which follow and which illustrate the invention, the amounts of the various constituents of the suspensions or the emulsions are given in grams to obtain 1000 cm^3 of suspension or emulsion.

EXAMPLES OF THE PREPARATION OF SUSPENSIONS OF ACTIVE SUBSTANCE

The method used is the same for the various examples.

It consists first in dispersing the molten sucroglycerides in water at 60°C, in an amount of 10%

by weight/weight, by simple stirring.

This pre-dispersion permits swelling of the sucroglycerides.

In the examples it will be indicated simply that the sucroglycerides are used in the form of a 10% weight/weight pre-dispersion in water.

The ethoxylated triglyceride or the ethoxylated fatty acid and the wetting agent are dissolved in water.

The pre-dispersion of sucroglycerides and, where appropriate, the antigel compound are then added.

The active substance is then added in small fractions, with stirring, and, if necessary, the antifoam.

The mixture is homogenised with the aid of a turbine stirrer and is then ground for a few minutes in a ball mill (glass balls 1 mm in diameter) until an average particle size of the active substance of 3 to 4 micrometres is obtained.

The change in the diameter of the particles is followed using a granulometer.

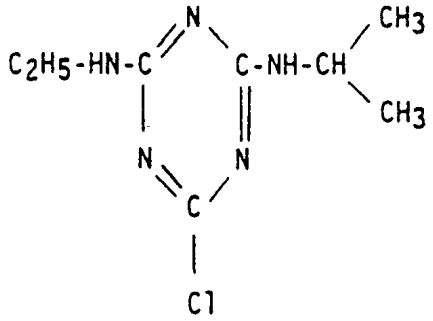
If necessary, a thickener (xanthan gum) is added and the suspension is stirred for about a further 30 minutes.

EXAMPLES 1 AND 2 AND COMPARATIVE EXAMPLE A

Preparation of aqueous suspensions of atrazine.

Atrazine is a known herbicide having a

melting point of 175°C and a solubility in water at 25°C of 0.028 g/l:



Using the method described above, four aqueous suspensions, according to the invention, of atrazine are prepared as well as an aqueous suspension of atrazine which does not contain ethoxylated triglyceride (comparative experiment A), the respective compositions of which suspensions are indicated in Table 1 below.

Table 1 also indicates, for each of the suspensions:

- the average diameter of the particles of the active substance (in micrometres)
- the value in seconds of the measurement of the flow rate of the suspension (before addition of the thickener (xanthan gum) using a No. 4 Ford cup (FC No.4)
- the abbreviation EO corresponds to the ethylene oxide unit in the formula of the triglycerides or of the ethoxylated fatty acids.

The antifoam used is a polydiorganosiloxane.

The suspensions of Examples 1 and 2 were stable:

- for more than 2 months at 45°C and
- for more than 2 months under a temperature cycle of: 24 hours at +45°C, 24 hours at -5°C.

By dilution with water they led to suspensions containing 0.5% to 2% of active substance, with neither flocculation nor sedimentation during a period of use of about 24 hours.

The suspension according to the comparative experiment is also stable on storage, but it is difficult to grind and a flocculation in water is observed on dilution.

Constituents of the suspension	Example 1	Example 2	Experiment A
Atrazine	500 g	500 g	500 g
Castor oil sucroglycerides, 10% in water	150 g	80 g	150 g
Ethoxylated castor oil (approximately 33 EO)	5 g	4 g	0 g
Ethoxylated copra oil (approximately 27 EO)	0 g	0 g	0 g
Sodium dodecylbenzenesulphonate	0 g	2 g	2 g
Sodium lauryl sulphate	2 g	0 g	0 g
Monopropylene glycol	70 g	80 g	80 g
Xanthan gum, 2% in water	50 g	50 g	50 g
Antifoam	1 g	1 g	1 g
Water (amount sufficient for 1000 cm^3)	300 g	450 g	295 g
Average diameter of the particles (in micrometres)	3.1	3.1	-
FC No.4	17 s	15 s	-

TABLE 1

EXAMPLE 3

Preparation of an aqueous suspension of atrazine.

Using the method described above, an aqueous suspension of atrazine is prepared, the composition and the properties of which are indicated below (with the same abbreviations as for Table 1).

- Atrazine	500 g
- Copra sucroglycerides, 10% in water	100 g
- Ethoxylated castor oil (approximately 33 EO)	5 g
- Sodium dodecylbenzenesulphonate	2 g
- Monopropylene glycol	80 g
- Xanthan gum, 2% in water	50 g
- Antifoam	1 g
- Water (amount sufficient for 1000 cm^3)	338 g
- Average diameter of the particles (in micrometres)	3.0
- FC No.4	20 s

As in the case of the suspensions of Examples 1 and 2, the suspension of Example 3 was stable:

- for more than 2 months at 45°C and
- for more than 2 months under a temperature cycle of: 24 hours at +45°C, 24 hours at -5°C.

By dilution with water it led to a suspension containing 1% of active substance, with neither flocculation nor sedimentation during a period of use

of about 24 hours.

EXAMPLE 4

Preparation of an aqueous suspension of diuron.

Using the method described above, an aqueous suspension of diuron is prepared, the composition of which is indicated below (with the same abbreviations as for Table 1).

- Diuron 450 g
- Butter sucroglycerides, 10% in water 100 g
- Ethoxylated castor oil (approximately 33 EO) 10 g
- Sodium dodecylbenzenesulphonate 5 g
- Monopropylene glycol 70 g
- Xanthan gum, 2% in water 60 g
- Antifoam 1 g
- Water (amount sufficient for 1000 cm^3) 455 g
- Average diameter of the particles (in micrometres) 3.5
- FC No.4 12 s

As in the case of the suspensions of Examples 1 and 2, the suspension of Example 4 was stable:

- for more than 2 months at 45°C and
- for more than 2 months under a temperature cycle of: 24 hours at +45°C, 24 hours at -5°C.

By dilution with water it led to a suspension containing 1.5% of active substance, with neither flocculation nor sedimentation during a period of use

of about 24 hours.

EXAMPLE 5

Preparation of 1000 cm^3 of an aqueous suspension of atrazine.

5 g of ethoxylated nonylphenol containing 10 EO units and 35 g of ethoxylated tri(1-phenylethyl)phenol phosphate containing 16 EO units are dissolved in a mixture consisting of 60 g of monopropylene glycol and 415 g of water. 500 g of atrazine and 1 g of polydiorganosiloxane antifoam are dispersed in this solution, with stirring. The mixture is then homogenised using a turbine stirrer and is then ground for a few minutes in a ball mill (glass balls 1 mm in diameter; 4000 rev/min) until an average particle size of the active substance of 3 to 4 micrometres is obtained.

The change in the diameter of the particles is followed with the aid of a granulometer.

After grinding, 60 g of a solution containing 2% by weight of xanthan gum in water are added, with slow stirring.

EXAMPLE 6

Preparation of 1000 cm^3 of an aqueous suspension of diuron.

Following the procedure of Example 5, a suspension of the following composition is prepared:

- Diuron 500 g
- Ethoxypropoxylated fatty alcohol

(hydroxyl number of from 107 to 117) 2 g

- Ethoxylated tri(1-phenylethyl)phenol sulphate containing 16 EO units 30 g
- Monopropylene glycol 60 g
- Antifoam 1 g
- Xanthan gum, 2% by weight in water 70 g
- Water (amount sufficient for 1000 cm^3) 480 g

EXAMPLE 7

Emulsion of castor oil sucroglycerides.

200 cm^3 of demineralised water are heated to 60°C. The castor oil sucroglyceride necessary to produce the emulsion is also brought to 60°C in order to render it liquid and sufficiently fluid to be poured.

The emulsion is produced using a laboratory homogeniser.

40 g of castor oil sucroglycerides are poured slowly (about 5 min) into the demineralised water, with stirring (turbine stirrer rotating at 2000 rev/min). At the end of the addition, the speed of the turbine stirrer is brought to 8000 rev/min for 3 min.

The emulsion thus obtained is cooled to ambient temperature, under slow stirring.

It has the following characteristics:

- average diameter of the particles: 1.6 μm
- pH: 7.7

The emulsion is stable for more than 2 months at 45°C.

EXAMPLE 8

Emulsion of butter oil sucroglycerides.

Example 7 is repeated replacing the castor oil sucroglyceride by 32 g of butter oil sucroglyceride.

The emulsion obtained has the following characteristics:

- average diameter of the particles: 2.2 μm
- pH: 6.9

The emulsion is stable for more than 2 months at 45°C.

EXAMPLE 9

Emulsion of copra oil sucroglycerides.

Example 7 is repeated replacing the castor oil sucroglyceride by 26 g of copra oil sucroglyceride.

The emulsion obtained has the following characteristics:

- average diameter of the particles: 0.6 μm
- pH: 6.9

The emulsion is stable for more than 2 months at 45°C.

EXAMPLE 10

Emulsion of castor oil sucroglycerides.

Example 7 is repeated using 70 g of castor oil sucroglyceride.

The emulsion obtained has the following characteristics:

- average diameter of the particles: 1.5 μm
- pH: 7.8

The emulsion is stable for more than 2 months at 45°C.

EXAMPLES 11 TO 29

Preparation of suspo emulsions using the aqueous suspensions of active substance and the aqueous emulsions of sucroglycerides from the preceding examples as the starting material.

Various suspo emulsions are prepared by simple mixing using, respectively, one aqueous suspension of an active substance and one aqueous emulsion of sucroglycerides, obtained in the preceding examples, as the starting materials.

The relative volumes of suspension and emulsion are indicated in Table 2 below.

Each suspo emulsion obtained was stable:

- for more than 2 months at 45°C and
- for more than 2 months under a temperature cycle of:
  - . 24 hours at +45°C,
  - . 24 hours at -5°C.

SUSPO EMULSION	SUSPENSION USED	EMULSION USED
Example 11	50 cm^3 from Ex.1	25 cm^3 from Ex.7
Example 12	25 cm^3 from Ex.1	25 cm^3 from Ex.7
Example 13	25 cm^3 from Ex.2	25 cm^3 from Ex.7
Example 14	25 cm^3 from Ex.5	25 cm^3 from Ex.7
Example 15	50 cm^3 from Ex.6	25 cm^3 from Ex.7
Example 16	25 cm^3 from Ex.1	25 cm^3 from Ex.8
Example 17	75 cm^3 from Ex.1	25 cm^3 from Ex.8
Example 18	25 cm^3 from Ex.4	25 cm^3 from Ex.8
Example 19	50 cm^3 from Ex.4	25 cm^3 from Ex.8
Example 20	25 cm^3 from Ex.3	25 cm^3 from Ex.9
Example 21	50 cm^3 from Ex.3	25 cm^3 from Ex.9
Example 22	75 cm^3 from Ex.5	25 cm^3 from Ex.9
Example 23	50 cm^3 from Ex.6	25 cm^3 from Ex.9
Example 24	75 cm^3 from Ex.1	25 cm^3 from Ex.10
Example 25	100 cm^3 from Ex.2	25 cm^3 from Ex.10
Example 26	125 cm^3 from Ex.3	25 cm^3 from Ex.10
Example 27	25 cm^3 from Ex.4	25 cm^3 from Ex.10
Example 28	50 cm^3 from Ex.5	25 cm^3 from Ex.10
Example 29	150 cm^3 from Ex.6	25 cm^3 from Ex.10

Table 2

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Aqueous suspo emulsion of solid plant protection active substance which has a melting point higher than or equal to 45°C and is essentially insoluble in water, characterised in that it comprises at least sucroglycerides, the said active substance and either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester, and water.

2. Suspo emulsion of plant protection active substance according to claim 1, characterised in that the said suspo emulsion is obtained by mixing:

- an aqueous emulsion comprising at least sucroglycerides,
- with an aqueous suspension of the said active substance, comprising at least either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester.

3. Suspo emulsion of active substance according to one of claims 1 or 2, characterised in that the said suspo emulsion is obtained by mixing:

- an aqueous emulsion comprising at least sucroglycerides,

- with an aqueous suspension of the said active substance, comprising at least either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester and a wetting agent.

4. Suspo emulsion according to any one of claims 1 to 3, characterised in that the sucroglycerides are prepared by transesterification of triglycerides by sucrose.

5. Suspo emulsion according to claim 4, characterised in that the sucroglycerides are prepared by transesterification of natural triglycerides.

6. Suspo emulsion according to claim 5, characterised in that the natural triglycerides are chosen from lard, suet, groundnut oil, butter oil, cottonseed oil, linseed oil, olive oil, palm oil, grapeseed oil, fish oil, soya oil, castor oil, colza oil, copra oil and coconut oil.

7. Suspo emulsion according to any one of claims 1 to 6, characterised in that the sucroclycerides used originate from palm oil, lard, copra oil, suet, colza oil or castor oil.

8. Suspo emulsion according to any one of claims 2 to 7, characterised in that the aqueous emulsion contains a phospholipid chosen from crude lecithins of vegetable or animal origin.

9. Suspo emulsion according to claim 8, wherein the phospholipid is chosen from soya lecithin, egg yolk

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lecithin and any lecithin fraction.

10. Suspo emulsion according to any one of claims 2 to 9, characterised in that the aqueous emulsion comprises, by weight relative to the total volume of the emulsion:

- from 0.1% to 60% of sucroglycerides,
- from 0 % to 50% of phospholipid,
- from 0 % to 20% of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester,
- and water to make up to 100%.

11. Suspo emulsion according to claim 10, characterised in that the aqueous emulsion comprises, by weight relative to the total volume of the emulsion:

- from 3% to 50% of sucroglycerides,
- from 0% to 40% of phospholipid
- from 0% to 15% of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester,
- and water to make up to 100%.

12. Suspo emulsion according to any one of claims 2 to 11, characterised in that the aqueous emulsion comprises alkoxylated triglycerides and/or alkoxylated fatty acids and/or sorbitan esters and/or alkoxylated sorbitan esters.

13. Suspo emulsion according to claim 12, characterised in that the aqueous emulsion comprises alkoxylated triglycerides and/or alkoxylated fatty acids and/or sorbitan esters and/or alkoxylated sorbitan esters chosen from ethoxylated triglycerides, ethoxylated fatty acids,

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sorbitan esters and ethoxylated sorbitan esters.

14. Suspo emulsion according to claim 13, characterised in that the ethoxylated triglycerides are ethoxylated triglycerides of vegetable or animal origin.

15. Suspo emulsion according to claim 14, wherein the ethoxylated triglycerides are chosen from lard, suet, groundnut oil, butter oil, cottonseed oil, linseed oil, olive oil, palm oil, grapeseed oil, fish oil, soya oil, castor oil, colza oil, copra oil and coconut oil.

16. Suspo emulsion according to claim 13, characterised in that the ethoxylated fatty acids are esters of ethoxylated fatty acids.

17. Suspo emulsion according to claim 16 wherein the fatty acid is oleic acid or stearic acid.

18. Suspo emulsion according to claim 13, characterised in that the sorbitan esters are cyclised sorbital esters of C_{10} to C_{20} fatty acids.

19. Suspo emulsion according to claim 18 wherein the fatty acid is lauric acid, stearic acid or oleic acid.

20. Suspo emulsion according to any one of claims 1 to 19, characterised in that the plant protection active substance is chosen from:

- deltamethrin,
- propham,
- tetramethrin,
- furalaxyl,
- heptachlor,
- propanil,

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- oxadiazon,
- triflumizole,
- dimethamethrin,
- atrazine,
- diuron,
- neburon,
- linuron,
- isoproturon,
- simazine,
- amethryne,
- phenmidipham,
- pendimethalin.

21. Suspo emulsion according to any one of claims 1 to 20, characterised in that it comprises several plant protection active substances.

22. Suspo emulsion according to any one of claims 1 to 21, characterised in that the aqueous suspension of active substance comprises a nonionic surfactant chosen from:

- alkoxylated di(1-phenylethyl)phenols,
- alkoxylated tri(1-phenylethyl)phenols,
- alkoxylated alkylphenols,
- alkoxylated fatty amines,
- alkoxylated fatty alcohols,
- alkoxylated castor oils, and
- ethylene oxide/propylene oxide (EO-PO) or ethylene oxide/propylene oxide/ethylene oxide (EO-PO-EO) block polymers.

23. Suspo emulsion according to claim 22, characterised

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in that the alkoxyl units of these surfactants are ethylene oxide and/or propylene oxide units, the number of which varies from 2 to 100.

24. Suspo emulsion according to claim 23 wherein the number varies from 4 to 50.

25. Suspo emulsion according to any one of claims 22 to 24, characterised in that the nonionic surfactant is chosen from:

- ethoxylated di(1-phenylethyl)phenol containing 15 ethylene oxide (EO) units,
- ethoxylated di(1-phenylethyl)phenol containing 5 EO units,
- ethoxylated di(1-phenylethyl)phenol containing 10 EO units
- ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 20 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 25 EO units,
- ethoxylated tri(1-phenylethyl)phenol containing 40 EO units,
- ethoxy-propoxylated tri(1-phenylethyl)phenols containing 25 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 25 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 30 EO + PO units,

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- ethoxy-propoxylated nonylphenols containing 40 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 55 EO + PO units,
- ethoxy-propoxylated nonylphenols containing 80 EO + PO units, and
- EO-PO-EO tri-block polymers.

26. Suspo emulsion according to any one of claims 1 to 21, characterised in that the aqueous suspension of active substance comprises an anionic surfactant chosen from:

- phosphoric esters of alkoxylated alkylphenols, alkoxylated di(1-phenylethyl)phenols, alkoxylated tri(1-phenylethyl)phenols and alkoxylated fatty alcohols;
- sulphuric esters of alkoxylated alkylphenols, alkoxylated di(1-phenylethyl)phenols, alkoxylated tri(1-phenylethyl)phenols and alkoxylated fatty alcohols;
- sulphonic esters of alkoxylated alkylphenols, alkoxylated di(1-phenylethyl)phenols and alkoxylated tri(1-phenylethyl)phenols;
- salts of polycarboxylic acids, homopolymers and copolymers of polycarboxylic acids, and copolymers based on maleic anhydride and diisobutylene;
- alkylnaphthalenesulphonates and poly(alkylnaphthalenesulphonates); and
- condensation products of dihydroxydiphenylsulphonates and formol.

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27. Suspo emulsion according to claim 26, wherein the polycarboxylic acids are polyacrylic or polymethacrylic acids.

28. Suspo emulsion according to claim 26 or 27, characterised in that the alkoxyl units in these anionic surfactants are ethylene oxide and/or propylene oxide units, the number of which varies from 2 to 100.

29. Suspo emulsion according to claim 28, the number varying from 4 to 50.

30. Suspo emulsion according to any one of claims 26 to 29, characterised in that the anionic surfactant is chosen from:

- triethanolamine salts of phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- potassium salts of phosphoric monoesters and diesters of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,
- the hydrogen sulphate of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- the potassium salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 15 EO units,
- the triethanolamine salt of the sulphuric monoester of ethoxylated di(1-phenylethyl)phenol containing 11 EO units,
- the ammonium salt of the sulphuric monoester of ethoxylated tri(1-phenylethyl)phenol containing 16 EO units,

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- the hydrogen phosphate of ethoxylated nonylphenol containing 9 EO units,
- sodium methylnaphthalenesulphonate and
- the sodium salt of polyacrylic acid.

31. Suspo emulsion according to any one of claims 2 to 30, characterised in that the aqueous suspension of the active substance comprises from 0.1% to 90% by weight of active substance, relative to the total volume of the suspension.

32. Suspo emulsion according to claim 31, characterised in that the aqueous suspension of the active substance comprises from 0.5% to 85% by weight/volume.

33. Suspo emulsion according to claim 31 or 32, characterised in that the aqueous suspension of the active substance comprises from 0.2% to 15% by weight of nonionic and/or anionic surfactant relative to the total volume of the aqueous suspension.

34. Suspo emulsion according to claim 33 wherein the aqueous suspension of the active substance comprises from 0.5% to 10% by weight of nonionic and/or anionic surfactant relative to the total volume of the aqueous suspension.

35. Suspo emulsion according to claim 31 or 32, characterised in that the aqueous suspension of the active substance comprises

- from 0.1% to 5% by weight of sucroglycerides and phospholipid,
- from 0.1% to 3% by weight of alkoxylated

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triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester, as defined above, and

- from 0.05% to 1% by weight of a wetting agent, relative to the total volume of the aqueous suspension.

36. Suspo emulsion according to claim 35 wherein the aqueous suspension comprises from 0.2% to 4% of sucroglycerides and phospholipid.

37. Suspo emulsion according to claim 35 or 36 wherein the aqueous suspension comprises from 0.2% to 2.8% of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester, as defined above.

38. Suspo emulsion according to any one of claims 35 to 37 wherein the aqueous suspension comprises from 0.1% to 0.8% of a wetting agent.

39. Suspo emulsion according to any one of claims 35 to 38, characterised in that the wetting agent is chosen from the anionic salts of surfactants, alkoxylated alcohols or alkoxylated alkylphenols represented by the following formulae:

R_1-SO_3-M

R_2-SO_4-M

$R_3-(EO)_n-H$

$R_3-(PO)_n-H$

$R_3-(EO-PO)_n-H$

R_4COONa

in which:

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- R_1 represents
  - . an alkylphenyl radical,
  - . an alkyl radical, or
  - . a 1,2-bis(octyloxycarbonyl)ethyl radical,
- R_2 represents
  - . an alkyl radical,
  - . an ethoxylated alkylphenol radical, or
  - . an ethoxylated alkyl radical,
- R_3 represents
  - . an alkylphenyl radical,
  - . an alkylnaphthyl radical, or
  - . an alkyl radical having 8 to 20 carbon atoms,
- n is a number from 4 to 12,
- EO represents the ethylene oxide unit and PO the propylene oxide unit,
- R_4 represents an alkyl radical having 7 to 23 carbon atoms, and
- M represents Na, K, NH_4, or a triethanolammonium, diethanolammonium or N-methyl-cyclohexylammonium cation.

40. Suspo emulsion according to claim 39 where R_3 represents an alkyl radical having from 10 to 14 carbon atoms.

41. Suspo emulsion according to any one of claims 35 to 38, characterised in that the wetting agent is chosen from silicone-based surfactants.

42. Suspo emulsion according to claim 41 wherein the wetting agent is chosen from copolymers of polydimethylsiloxane and either ethylene glycol

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homopolymer or ethylene glycol/propylene glycol copolymer.

43. Suspo emulsion according to any one of claims 35 to 38, characterised in that the wetting agent is chosen from fluorinated surfactants.

44. Suspo emulsion according to claim 43 wherein the wetting agent is chosen from compounds comprising a hydrophobic and oleophobic straight perfluorocarbon chain, and a hydrophilic part comprising an acid or neutralised sulphonic group, a carboxyl group or an ethoxylated alcohol radical.

45. Suspo emulsion according to any one of claims 35 to 38, characterised in that the sucroglyceride/phospholipid ratio by weight in the aqueous suspension of active substance is from 0 to 3.

46. Suspo emulsion according to any one of claims 1 to 45, characterised in that the proportions of aqueous suspension and aqueous emulsion are such that the suspo emulsion contains from 0.1% to 60% by weight of active substance, relative to its total volume.

47. Suspo emulsion according to any one of claims 1 to 46, characterised in that the proportions of suspension and emulsion are such that the suspo emulsion contains from 0.1% to 12% by weight of nonionic and/or anionic surfactant relative to its total volume.

48. Suspo emulsion according to any one of claims 1 to 47, characterised in that the proportions of suspension and emulsion are such that the suspo emulsion contains from 0.1% to 60% by weight of sucroglycerides relative to its total volume.

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49. Suspo emulsion according to any one of claims 1 to 48, characterised in that the proportions of suspension and emulsion are such that the suspo emulsion contains from 0% to 50% by weight of phospholipid relative to its total volume.

50. Suspo emulsion according to any one of claims 1 to 49, characterised in that the proportions of suspension and emulsion are such that the suspo emulsion contains from 0% to 20% by weight of alkoxylated triglyceride and/or alkoxylated fatty acid and/or sorbitan ester and/or alkoxylated sorbitan ester relative to its total volume.

51. Suspo emulsion according to any one of claims 1 to 50, characterised in that the proportions of suspension and emulsion are such that the suspo emulsion contains from 0.05% to 0.7% by weight of wetting agent relative to its total volume.

52. Use of the suspo emulsions according to any one of claims 1 to 51, if appropriate after dilution with water, for the treatment and the protection of plants.

53. An aqueous suspo emulsion, substantially as herein described with reference to any one of Examples 1 to 29 but excluding any comparative examples therein.

54. Use of the suspo emulsion according to claim 53, if appropriate after dilution with water, for the treatment and protection of plants.

DATED this 20th day of DECEMBER, 1993
RHONE-POULENC CHIMIE
Attorney: IAN T. ERNST
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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ABSTRACT

The present invention relates to new plant protection suspo emulsions.

More precisely, the invention consists in a suspo emulsion of solid plant protection active substance which has a melting point higher than or equal to 45°C and is essentially insoluble in water, characterised in that it comprises at least sucroglycerides, the active substance, and either a nonionic and/or anionic surfactant or a surfactant system comprising sucroglycerides, an alkoxylated triglyceride and/or an alkoxylated fatty acid and/or a sorbitan ester and/or an alkoxylated sorbitan ester, and water.