(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 210 642**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86110434.7

(22) Date of filing: 29.07.86

(51) Int. Cl.⁴: C07C 69/40 , C11D 1/08 , C07C 67/08

(30) Priority: 30.07.85 IT 2176585

(43) Date of publication of application: 04.02.87 Bulletin 87/06

(84) Designated Contracting States: BE CH DE FR GB LI NL

(71) Applicant: Raffineria Olii Lubrificanti "R.O.L." S.p.A.
31, Foro Buonaparte
Milan(IT)

(72) Inventor: Turchini, Luigi
85, via Archimede
I-20129 Milan(IT)
Inventor: Garilsi, Salvatore
32, via Aosta
I-13100 Vercelli(IT)
Inventor: Albanini, Aurelio
37, via Vigoreli
I-27045 Casteggio Pavia(IT)

(74) Representative: Barz, Peter, Dr. et al
Patentanwälte Dr. V. Schmied-Kowarzik
Dipl.-Ing. G. Dannenberg Dr. P. Weinhold Dr.
D. Gudel Dipl.-Ing. S. Schubert Dr. P. Barz
Siegfriedstrasse 8
D-8000 München 40(DE)

(54) Surfactants derived from succinic acid.

(57) Surfactants derived from succinic acid having the general formula:

$R\text{-}A_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COOR^1$ (I)

wherein:

R^1 is H, a metal ion, $-NH_4$, a cation of an organic amine base or a group having the formula:

$\text{-}A_n\text{-}R$ (II)

wherein A is an oxyethylene group $-CH_2\text{-}CH_2O-$, n is a number from 1 to 20 and R is a $C_8\text{-}C_{20}$ alkyl group.

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SURFACTANTS DERIVED FROM SUCCINIC ACID

The present invention relates to non-toxic and biodegradable surfactants derived from succinic acid.

In the large number of classes of known surfactants it is unusual for a single surfactant to combine a variety of characteristics such as biodegradability, non-toxicity, lack of irritating effect on the skin, high solubility in water with excellent detergent properties that make such a product particularly versatile and, therefore, utilizable in such different fields of use as, for instance, detergents in general, in cleansing agents, in cosmetics, in the food industry, in the textile industry, for emulsion polymerisation, etc.

It has now been found that a novel class of surfactants, derived from succinic acid more particularly, monoesters and/or diesters of succinic acid with aliphatic polyoxyethylated alcohols as well as the salts of the monoesters with organic or inorganic bases, possess the above-mentioned characteristics in combination and, therefore, are effective in a wide range of applications.

Thus, an object of the present invention is to provide esters of succinic acid having the general formula:

$R\text{-}A_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COOR^1$ (I)

wherein:

R^1 is a hydrogen atom, a metal ion, an ammonium group, the cation of an organic amine base or a group having the formula:

$\text{-}A_n\text{-}R$ (II)

wherein A is an oxyethylene group $\text{-}CH_2\text{-}CH_2O\text{-}$, n is a number from 1 to 20 and R is a C_8-C_{20} alkyl group.

The metal ion is preferably selected from sodium, potassium and magnesium.

The cation of an organic amine base is, for instance, derived from an alkanolamine such as monoethanolamine or triethanol amine.

The radical R is preferably selected from linear or branched alkyl groups containing 10 to 16 carbon atoms, n ranging preferably from 4 to 10.

A further object of the present invention is to provide a process for preparing the esters having formula I, which process comprises the esterification of succinic acid with an aliphatic polyoxyethylated alcohol of formula III:

$R\text{-}A_n\text{-}OH$ (III)

wherein R, A and n have the above-mentioned meaning, at a temperature of from 150 to 190°C under continuous distillation of water formed during the reaction and, optional subsequent conversion of the obtained product into a salt with metal bases, ammonia or amines.

In this process monoester and diesters are obtained having the following formulae:

succinic monoester: $R\text{-}A_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COOH$ - (IV)

succinic diester: $R\text{-}A_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COO\text{-}A_n\text{-}R$ (V)

According to the reaction conditions employed and, in particular, depending on the molar ratio of succinic acid to polyoxyethylated alcohol, either the mono-or the diester may be prepared as preferred.

Thus, in order to preferentially produce the monoester having the formula (IV), the acid and the polyoxyethylated alcohol are reacted in substantially equimolar ratios, whereas they are reacted in molar ratios of about 1:2 in order to produce the diester having formula (V).

In the case of preparing the monoester of succinic acid of a polyoxyethylated alcohol, the reaction may be represented by the following equation:

$$HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH + R\text{-}(OCH_2CH_2)_n\text{-}OH \xrightarrow{-H_2O} R\text{-}(OCH_2CH_2)_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COOH$$

The polyoxyethylated alcohols of formula (III) are known, commercially available products which may be prepared by reacting the alcohol with ethylene oxide, using an alkaline base as a catalyst.

Preferred alcohols are the ethoxylated alcohols having the formula: $R\text{-}(OCH_2CH_2)_n\text{-}OH$, wherein R is a linear or branched alkyl group containing 10 to 16 carbon atoms and n ranges from 4 to 8, as well as mixtures thereof.

The esters according to the present invention and, in particular, the monoesters of the aliphatic ethoxylated alcohols and their salts are very efficient surfactants which, even when used at very low percentages, result in a remarkable lowering of the surface tension and, therefore, can be used as emulsifying agents, dispersants and as detergents in general.

Besides the excellent detergent properties, they do not exhibit any noxious or irritating effects on the skin or on the eyes and do not have any acute toxicity if they are ingested. They are highly biodegradable, their biodegradability being over 90%. They are stable within a wide temperature range of up to 100°C. They show very good wetting properties and foam-forming ability and are of moderate to excellent solubility in water. In particular, their solubility increases with an increase in the number of moles of ethylene oxide contained in the alkylether chain.

The esters according to the invention proved to be compatible with most known surfactants and, therefore, they can be formulated in combination with them. Owing to their spectrum of characteristics, the esters according to the invention are very flexible in their use in the different applications of surfactants. An account of their high detergent power combined with the lack of toxic effects on the skin, hair, and eyes, they are particularly suitable for beauty care applications such as, for instance, the preparation of liquid or creamy detergents for the skin, of shampoos and bath foams.

The following example illustrates the invention without, however, limiting it in any way.

EXAMPLE 1

Monoesterification of Succinic Acid

165.3 g (1.4 moles) of succinic acid and 710.5 g (1.407 moles) of LIAL 123®.7ETO (a mixture of ethoxylated alcohols having

formula $R-(OCH_2CH_2)_n-OH$, wherein R = C_{11}, C_{12}, C_{13} and n = 7; $\overline{MW}$ = 505) were introduced under nitrogen flow into a reactor equipped with a heating system, stirrer, thermometer, feeding system for reactants and connected with a cooler provided with a manifold for collecting the reaction water.

While stirring the mixture under a nitrogen flow, the temperature was raised to 188 to 190°C over a period of about 90 minutes, which is the temperature at which the reaction water begins to distil. Thereafter, the temperature was raised to 198-200°C. After the distillation of 65% of the theoretical esterification water (corresponding to 25.2 g) the course of the esterification was monitored by determining the acid number. The esterification is completed when an acid number of 95 to 96 - (theoretical = 92.7) is reached. There after the reaction mixture was cooled to 80°C and the reactor was discharged. 848 g of a liquid product having a water content of less than 0.1%, an acid number of 95.0 and a saponification number of 180 were obtained. The analysed product consisted predominantly of the monoester of succinic acid.

Salification

234.4 g of the succinic ester thus prepared and 714.0 g of demineralised water were introduced into a vessel provided with a stirrer, thermometer, dropping funnel and water cooling system. The mixture was stirred until a homogeneous emulsion was obtained and, then, under stirring, 51.6 g of a 30% NaOH solution were introduced slowly over a period of about 1 hour by means of the dropping funnel, keeping the temperature at values not exceeding 24°C. 1000 g of a clear aqueous solution were obtained containing 25% by weight of the sodium salt of succinic monoester.

The solution thus obtained can be used either as such or in a diluted form in the different fields of use of detergents. By removal of water from the solution a product having a creamy consistency and predominantly consisting of the sodium salt of succinic monoester, having an acid number of 4.4, a saponification number of 81.2, an ester number of 76.8 and a pH at 1% of 7.2 was obtained. The salified product dissolves in water at any ratio.

The following determinations were carried out on the salified product.

Surface Tension

The surface tension measured at 20°C according to the Du Nuoy method was 34.6 dynes/cm at a concentration of 0.25 g/l and 34.2 dynes/cm at a concentration of 1 g/l.

Wetting Power

The wetting power, determined on the product at a concentration of 2 g/l in distilled water was 90 seconds.

Foam-Forming Ability

This was determined on 200 ml of aqueous solution containing 2 g/l of product, using a plunger system with bored disk, 50 strokes.

The following results were obtained:

After Minutes	ml of Foam
0	790
5	780
10	740
15	610
20	490

The salified product was highly biodegradable, non-toxic, non-irritating and endowed with a very good detergency power.

Claims

1. Esters of succinic acid, having the general formula:

$R\text{-}A_n\text{-}OOC\text{-}CH_2\text{-}CH_2\text{-}COOR^1$ (I)

wherein:

R^1 is a hydrogen atom, a metal ion, an ammonium group, the cation of an organic amine base or a group having the formula:

$-A_n\text{-}R$ (II)

wherein A is an oxyethylene group $-CH_2\text{-}CH_2\text{-}O-$, n is a number from 1 to 20 and R is a C_8-C_{20} alkyl group.

2. Esters according to claim 1, wherein, in the $-A_n\text{-}R$ group (II), n is a number from 4 to 10 and R is an alkyl group containing 10 to 16 carbon atoms.

3. Esters according to claim 1, wherein R^1 is a metal ion, an ammonium group or an amine cation.

4. Esters according to claim 1, wherein R^1 is $-A_n\text{-}R$.

5. A process for the preparation of esters having the formula (I) according to claim 1, which comprises esterifying succinic acid with an aliphatic polyoxyethylated alcohol having the formula:

$R\text{-}A_n\text{-}OH$ (III)

wherein R, A and n have the meaning given in claim 1, at temperatures of from 150 to 190°C, under continuous removal of the reaction water and, optionally, converting the product obtained into a salt with a metal base or ammonium or an amine.

6. A process according to claim 5, wherein the base is selected from sodium, potassium, magnesium or ammonium hydroxide, sodium or potassium carbonate or bicarbonate, triethanolamine or monoethanolamine.

7. Cosmetic and detergent compositions containing one or more esters of succinic acid having the formula (I) according to any one of claims 1 to 4.

8. Use of the esters of formula I according to any one of claims 1 to 4 as surfactants.