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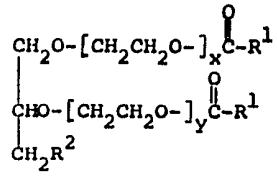
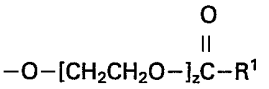
(54) **Polyoxyalkylene ethers of glycerol or 1,2-propane diol which are esterified with a fatty acid and/or isostearic acid, their preparation and their use as thickeners or solubilisers**

(57) Compounds of the general formula



wherein

is a fatty acid acyl radical having 16 or 18 carbon atoms, isostearoyl or a mixture of these radicals, R^2 is a hydrogen radical or the radical



x, y and z are integers and x + y + z is on average 50 to 60; are useful as thickeners, particularly for aqueous solutions containing surfactants, and also as solubilising agents, particularly for cosmetic preparations.

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SPECIFICATION

Polyoxyalkylene ethers of glycerol or 1,2-propane diol which are esterified with a fatty acid and/or isostearic acid, their preparation and their use as thickeners or solubilisers

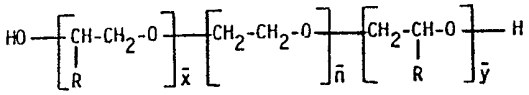
In pharmacy and especially in cosmetics frequent use is made of aqueous preparations of active compounds in circumstances in which it can be desirable, for reasons of use technology, that the preparations have a high viscosity and are present in the form of gels or pastes.

Typical examples of such cosmetic preparations are viscous or gel-like shampoos and also bath and shower gels. In addition to cosmetic active compounds, these products contain surfactants, in particular anionic surfactants, such as, for example, alkylbenzenesulphonates and sulphated alkyl ethers. In recent years betaines have also been employed as surfactants to an increasing extent.

Hitherto, anionic or cationic synthetic polymers or vegetable thickeners have been used for thickening preparations of this type. However, a disadvantage of these known thickeners is the fact that they cannot be used universally, but are specific to a system, and frequently produce turbidity and separation. In particular, the products are unsuitable for thickening aqueous solutions of betaines.

Salts, such as, for example, sodium chloride, have also already been added to anionic surfactants. These additives are ineffective in the case of sulphosuccinic acid esters and betaines. In addition, in fairly large quantities, the added mineral salts have a salting out effect on the dissolved surfactants and impair the capacity of solutions of this type to act as solubilisers.

Polyethylene glycol derivatives which have a thickening action are known from German Offenlegungsschrift 3,140,160. These compounds correspond to the general formula

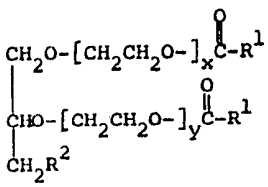


wherein R is an alkyl radical and/or alkoxymethyl radical and/or an alkenyloxymethyl radical or a mixture of these radicals; $\bar{n}$ represents an average number of groups from 20 to 500, preferably from 30 to 200; and $\bar{x}$ and $\bar{y}$ denote average number of groups from 0 to 8; it being possible for $(\bar{x} + \bar{y})$ to vary between 1 and 8.

These compounds are prepared by an addition reaction between polyethylene glycols and long-chain 1,2-alkylene oxides, such as, for example, 1,2-octadecene oxides of alkyl glycidyl ethers, such as, for example, oleyl glycidyl ether or an alkenyl glycidyl ether.

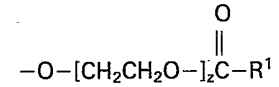
Owing to the long-chain epoxides used, the compounds of the Offenlegungsschrift mentioned above are relatively expensive. In addition, their thickening power, and especially their solubilising power, is not always adequate.

The present invention provides compounds of the general formula



wherein

is a fatty acid acyl radical having 16 or 18 carbon atoms, isostearoyl or a mixture of these radicals, R^2 is a hydrogen radical or the radical



x, y and z are integers and on average $\Sigma x + y + z$ has a value from 50 to 60.

It is thus possible to prepare compunds from readily accessible raw materials which have excellent thickening properties and are, moreover, capable of solubilising active compounds such as, for example, essential oils.

If the average of $x + y + z$ falls below 50 or if it is higher than 60, the thickening properties of these compounds are considerably reduced. It could not have been foreseen that it would be possible to find,

within the selected range, compounds having particularly advantageous thickening properties for aqueous solutions, especially surfactants.

Particularly preferred compounds are those in which

denotes entirely or predominantly (i.e.> 50%) oleoyl. Although compounds in which

is entirely or predominantly the stearoyl radical also display good thickening properties, the solubility of these compounds in aqueous systems is less than that of the corresponding oleyl derivatives.

Compounds in which

is the oleoyl radical and R^2 is a hydrogen radical are particularly preferred.

The use of the esterification products of ethylene oxide addition compounds formed from glycerol and 4-20 mol of ethylene oxide per mol of glycerol, with fatty acids having a chain length of 8-18 carbon atoms, in a ratio of 1-2 mol of fatty acid to 1 mol of glycerol/ethylene oxide adduct as fat-restoring agents in cosmetic preparations, in particularly cosmetic cleansing agents, is known from German Auslegeschrift 2,024,051.

However, these compounds differ from the compound according to the invention in their content of ethylene oxide and their lower degree of esterification. These agents do not have a thickening action in aqueous solutions of surfactants, and therefore could not suggest the subject of the present invention.

In a further embodiment of the invention, the compounds according to the invention are prepared by an addition reaction between glycerol or 1,2-propanediol and 50 to 60 mol of ethylene oxide per mol of glycerol or 1,2-propanediol in the presence of a catalyst, at a temperature of from 80 to 150°C and elevated pressure; by esterifying, transesterifying or reacting the addition reaction product at an elevated temperature with at least equivalent quantities, relative to the hydroxyl groups of the addition reaction product, of R^1COOH, R^1COOCH_3 or R^1COCl, respectively, and removing the water or methanol or neutralising the hydrogen chloride, respectively, liberated in the reaction.

The addition reaction of ethylene oxide with glycerol or 1,2-propane diol is a reaction which has been known for a long time and which can be carried out in a manner which is in itself known. The addition reaction is carried out in the presence of customary catalysts, such as, for example, small quantities of alkali metal methylates, and at temperatures from 80 to 150°C and an elevated pressure, in an autoclave.

The carboxylic acid esters are then prepared from this addition reaction product in a manner which is in itself known. The processes which are known from the state of the art can be used for this purpose:

Thus the addition reaction product can be directly esterified with the carboxylic acid or mixture of carboxylic acids, advantageously in the presence of an esterification catalyst, such as, for example, small quantities of an alkali metal hydroxide or n-butyl titanate, and with removal of the water of the reaction.

It is also possible, of course, to transesterify the addition reaction product with the corresponding carboxylic acid methyl esters, with removal of the methanol.

It is also possible to react the addition reaction product with the corresponding carboxylic acid chlorides and to neutralise the hydrogen chloride liberated. In this case it is advantageous to remove the chloride formed in order to obviate its salting out effect in the preparations.

The reaction of the polyethylene glycol addition reaction product with the carboxylic acid or a mixture or derivatives thereof is effected in quantities such that, preferably, all the hydroxyl groups of the addition reaction product are reacted. The addition reaction product is therefore reacted with at least equivalent quantities, relative to hydroxyl groups, of the carboxylic acid(s) or derivatives thereof. The compounds according to the invention are solid, wax-like substances.

It has been found, surprisingly, that the compounds according to the invention are not only excellent thickeners, but also have very good solubilising properties. In the course of this, a synergistic effect can often be observed, so that larger quantities, for example of essential oils, can be solubilised than is the case if the anionic surfactants and the compounds according to the invention are used on their own. The synergistic solubilising effect manifests itself particularly in combination with betaines and is particularly desirable, for example, in the preparation of hair shampoos and bath gels.

The compounds according to the invention can be used for thickening pharmaceutical and cosmetic preparations based on water. The field of use for which they are particularly preferred consists in thickening aqueous cosmetic preparations containing surfactant substances, in particular anionic substances or betaines. The invention thus further provides a pharmaceutical or cosmetic composition incorporating a compound of the invention as a thickener and/or solubilising agent.

The preparation of the compounds according to the invention and their technical properties in use are illustrated in greater detail in the following Examples and Tables respectively.

Example 1

2,292 g of an addition reaction product of 50 mol of ethylene oxide with glycerol (1 mol) and 882 g of oleic acid (3.15 mol) are mixed and esterified at 240-260°C for 5 hours, while stirring and in a current of nitrogen.

Example 2

2,512 g of an addition reaction product of 55 mol of ethylene oxide with glycerol (1 mol) and 924 g of oleic acid (3.3 mol) are mixed and esterified at 240-260°C for 5 hours, while stirring and in a current of nitrogen.

Example 3

2,512 g of an addition reaction product of 55 mol of ethylene oxide with glycerol (1 mol) and 980 g of isostearic acid (3.5 mol) are mixed and esterified at 240-260°C for 5 hours, while stirring and in a current of nitrogen.

Example 4

2,276 g of an addition reaction product of 50 mol of ethylene oxide with 1,2-propanediol (1 mol) and 840 g of oleic acid (3 mol) are mixed and esterified at 240-260°C for 5 hours, while stirring and in a current of nitrogen.

Example 5

2,540 g of an addition reaction product of 56 mol of ethylene oxide with 1,2-propanediol (1 mol) and 700 g of oleic acid (2.5 mol) are mixed and esterified at 240-260°C for 3 hours, while stirring and in a current of nitrogen.

Example 6

2,496 g of an addition reaction product of 55 mol of ethylene oxide with 1,2-propanediol (1 mol) are heated to 100°C in vacuo, while stirring. 650 g of oleyl chloride (2.2. mol) are added in portions in the course of 30 minutes. The mixture is left for a further hour to complete the reaction, until the hydrogen chloride formed has been removed quantitatively in vacuo.

Example 7

2,650 g of an addition reaction product of 55 mol of ethylene oxide with 1,2-propanediol (1.06 mol) and 590 g of methyl oleate (2 mol) are mixed at 100°C. 8-16 g (0.25-0.50%) of n-butyl titanate are then added as catalyst. The mixture is then heated at 180-200°C in vacuo for 4-6 hours, while stirring.

Example 8

2,496 g of an addition reaction product of 55 mol of ethylene oxide with 1,2-propanediol (1 mol) and 588 g of oleic acid (2.1 mol) are mixed at 100°C. 12 g (0.4%) of n-butyl titanate are then added and the mixture is heated at 200-220°C for 6 hours in vacuo and while stirring.

Example 9

2,276 g of an addition reaction product of 50 mol of ethylene oxide with 1,2-propanediol (1 mol) and 640 g of a mixture of palmitic and stearic acids (2.4 mol) are mixed at 100°C. 7.2 g (0.25%) of n-butyl titanate are then added, and the mixture is heated at 200-220°C for 6 hours in vacuo and while stirring.

Table 1 shows the outstanding solubilising properties of the compounds according to the invention and the synergistic effect observed.

Table 2 shows the excellent thickening properties of the compounds according to the invention.

The surfactants used have the following chemical composition:

Betaine 1	= 1-alkanoylamino-3-dimethylammoniopropane-3-carboxymethylbetaine
Betaine 4	= lauryldimethylglycine
Anionic surfactant 2	= sodium salt of sulphated lauryl polyglycol ether
Anionic surfactant 5	= Na lauryl alcohol polyglycol ether-sulphosuccinate
Cationic surfactant 3	= triethanolamine laurylsulphate
Cationic surfactant 10	= stearylpentaoxyethylammonium chloride
Nonionic surfactant 7	= polyoxyethylene(7) lauryl ether
Nonionic surfactant 8	= polyoxyethylene(10) nonylphenyl ether
Nonionic surfactant 9	= 1-alkanoylamino-3-dimethylaminopropane-3-N-oxide.

The viscosities were measured at 20°C using the Hoeppler falling ball viscometer.

TABLE 1

Solubilisation

(all figures are in g/100 g of solution)

Product, according to the invention, from Example 8	Betaine 1	Anionic surfactant 2	Cationic surfactant 3	Water	Quantity solubilised	Essential Oil
10				89.0	1.0	
	6			79.0	1.0	Menthol
10	6			66.0	4.0	
10				89.5	0.5	
	6			79.0	1.0	Peppermint oil
10	6			66.0	4.0	
10				89.5	0.5	
	6			79.0	1.0	
10	6			66.0	4.0	
		5.6		77.0	3.0	Eucalyptus oil
10		5.6		66.0	4.0	
			6	77.0	3.0	
10			6	66.5	3.5	
10				89.8	0.2	
	6			79.5	0.5	
10	6			65.0	5.0	
		5.6		79.0	1.0	Pine needle oil
10		5.6		66.5	3.5	
			6	79.0	1.0	
10			6	67.5	2.5	

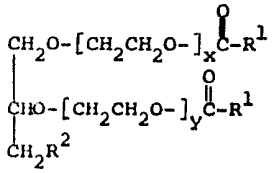
TABLE 2

Thickening surfactant solutions

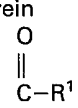
Product from Example	g/100 g of solution	surfactant	g/100 g of solution	Water g/100 g of solution	Viscosity mPas
1	7.5	betaine 1	7.5	85.0	15 000
2	7.5	betaine 1	7.5	85.0	4 000
3	7.5	betaine 1	7.5	85.0	15 000
4	5.0	betaine 1	7.5	87.5	9 000
5	5.0	betaine 1	7.5	87.5	12 000
6	5.0	betaine 1	7.5	87.5	40 000
7	5.0	betaine 1	7.5	87.5	30 000
8	5.0	betaine 1	7.5	87.5	28 000
9	5.0	betaine 1	7.5	87.5	20 000
8	5.0	betaine 4	6.25	88.75	15 000
8	5.0	anionic surfactant 5	6.25	88.75	10 000
8	5.0	anionic surfactant 6	6.25	88.75	30 000
8	5.0	nonionic surfactant 7	6.25	88.75	4 000
8	5.0	nonionic surfactant 8	6.25	88.75	4 000
8	5.0	nonionic surfactant 9	6.25	88.75	15 000
8	5.0	cationic surfactant 10	6.25	88.75	7 000

CLAIMS

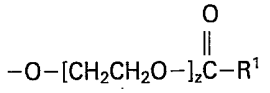
1. Compounds of the general formula



wherein



is a fatty acid acyl radical having 16 or 18 carbon atoms, isostearoyl or a mixture of these radicals, R^2 is a hydrogen radical or the radical



x, y and z are integers and on average $\Sigma x + y + z$ is from 50 to 60

2. Compounds according to claim 1 in which

$$\begin{matrix} O \\ \| \\ C-R^1 \end{matrix}$$

is oleoyl.

3. Compounds according to claim 2 in which R^2 is hydrogen.

4. Compounds according to claim 1 in which

$$\begin{matrix} O \\ \| \\ C-R^1 \end{matrix}$$

is stearoyl.

5. Any one of the compounds according to claim 1 hereinbefore described in Examples 1 to 9.

6. A process for the preparation of the compounds defined in claim 1, which process comprises carrying out an addition reaction between glycerol or 1,2-propanediol and 50 and 60 mol of ethylene oxide per mol of glycerol or 1,2-propanediol in the presence of a catalyst at a temperature of from 80 to 150°C and under elevated pressure; esterifying or transesterifying or reacting the addition reaction product at an elevated temperature with at least an equivalent amount, relative to the hydroxyl groups of the addition reaction product, of R^1-COOH, R^1COOCH_3 or R^1COCl, respectively, werein R^1CO is as defined in claim 1; and separating off the water or methanol or neutralising the hydrogen chloride, respectively, liberated in the reaction.

7. A process for the preparation of compounds as defined in claim 1, said process being substantially as hereinbefore described in any one of Examples 1 to 9.

8. A pharmaceutical or cosmetic composition incorporating a compound as defined in any one of claims 1 to 5 as a thickener and/or solubilising agent.

9. A composition according to claim 8 which is an aqueous composition.

10. A composition according to claim 8 or 9 which comprises a surfactant.

11. A composition according to claim 10 in which the surfactant is an anionic surfactant or betaine.

12. A composition according to any one of claims 8 to 11 which is a hair shampoo.

13. A composition according to any one of claims 8 to 11 which is a bath or shower gel.

14. Any one of the formulations of Table 1 hereinbefore comprising the Product from Example 8 or of the formulations of Table 2 hereinbefore.

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