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

(11) EP 0 586 323 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
10.04.1996 Bulletin 1996/15

(51) Int Cl.[6]: **C11D 1/74**

(21) Application number: **93500108.1**

(22) Date of filing: **20.07.1993**

(54) **Detergent composition and method for its preparation**

Waschmittelzusammensetzung und Verfahren zu seiner Herstellung

Composition détergente et méthode pour sa fabrication

(84) Designated Contracting States:
AT BE DE ES FR GB IT NL

(30) Priority: **20.07.1992 EP 92500092**

(43) Date of publication of application:
09.03.1994 Bulletin 1994/10

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- **DATABASE WPI Section Ch, Derwent Publications Ltd., London, GB; Class A97, AN 80-85324C [48] & JP-A-55 133 495 (LION FAT & OIL K K)**
- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 388 (C-630)1989 & JP-A-11 035 714 (LION CORP.) 29 May 1989**
- **CHEMICAL ABSTRACTS, vol. 100, no. 24, 11 June 1984, Columbus, Ohio, US; abstract no. 194041r, page 121 ;**
- **CHEMICAL ABSTRACTS, vol. 100, no. 24, 11 June 1984, Columbus, Ohio, US; abstract no. 194041r, page 121 ; & JP-A-5 901 600 (NIHON EMARUJON K K) 6 January 1984**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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EP 0 586 323 B1

Description

SPECIFICATION

Field of the invention.

The present invention relates to novel liquid detergent compositions which are biodegradable, non-toxic, and non-irritant, while improves its detergency, foam stability and colour protection in case of heavy and light duty detergent. These detergent compositions are particulary useful to formulate shampoos, body shampoos, washing up, all purpose cleaners, heavy and light duty detergents.

In fact, the present invention relates to cleaning formulations comprising a specific nonionic compound.

In addition to that, the present invention relates to a method for preparing the above mentioned nonionic.

Description of Prior Art.

Most of detergent compositions involve a combination of anionic, amphoteric and/or nonionic surfactants, in order to get better properties according to final product in terms of irritation, detergency and foam profile.

One of the current problems in the whole field of chemicals is the question of ecotoxicity and the duality cleanliness/damage, that is how to get a good performance without interact seriously with the surface (fabrics or skin).

The nonionics employed in the detergent compositions were conventionally ethoxylated nonylphenols, C_{12-18} alcohols ethoxylated with approximately 12 moles of ethylene oxides, lately C_{12-15} alcohols ethoxylated with 2 to 9 moles of ethylene oxides and EO/OP derivatives.

For instance:

Japanese Patent Laid-Open No. 55-86894, discloses the use of a secondary C_{6-14} alcohols ethoxylated with 4-15 moles of ethylene oxides on average.

Japanese Patent Laid-Open No. 52-22007, and Japanese Patent Publication No. 83037356, disclose the use of middle alcohol ethoxylated of formula $R_1O(C_2H_4O)nH$, wherein R_1 is straight chain or branched alkyl radicals and n is 1-12 on average in detergent compositions.

European Patent No. 80749, discloses the use of ethoxylated alkyl phenols in detergent compositions.

US Patent 4908150, discloses the use of polyethylene glycol ether of a glycerol ester compositions.

Japanese Patent Laid-Open No. 55-133495, discloses the use of a polyoxyethylene hardened castor oil or fatty acid ester, thereof, polyoxyethylene glyceryl ether fatty acid ester, polyoxyethylene trimethylol propane fatty acid ester and polyoxyethylene alkylether diester of N-lauroylglutamic acid etc, in detergent compositions.

However, use of such nonionics deteriorates detergency ability of detergent formulation. Also in case of heavy and light duty liquids detergents tends to cause dye transfer, especially upon repeated laundering. In addition to the above mentioned points, current nonionics cause skin and eye irritation, and values of fish toxicity, daphnia inmobilization and algae are not acceptable under the present environmental requirements.

Others patents describe the use of specific non-ionic compounds, different from the usual ones, in particular applications and/or conditions.

US Patent 4247425, discloses the use of alkoxylated partial glycerol esters of a detergent grade fatty acid in light duty detergent compositions.

EP Patent 0007120, discloses an emulsifying system, to be used in a handwashing composition, mainly consisting of mono and diglycerides of higher natural fatty acids and ethoxylated glycerine esterified by fatty acids.

US Patent 4897214, discloses the use of monoesters of fatty acids with polyoxyethylene hexitan derivatives in skin cleaning preparations.

WO Patent 92/00945, discloses the use of octadienyl glycerin ethers with polyoxyethylene.

UK Patent 2197338, discloses the use of polyoxyalkylene alkyl- or alkenyl ethers and polyoxyalkylene glycerol fatty acid esters in detergent compositions.

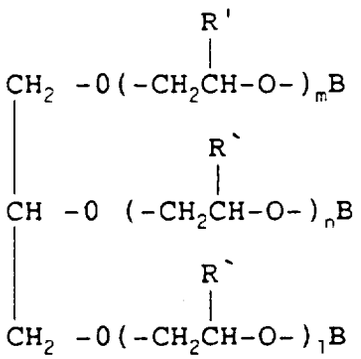
In none of disclosures mentioned above it is taught a nonionic like the one described in the present invention.

The present inventors have carried out research on the developement of a detergent composition, which will exhibit the outstanding biodegradable, non-toxic, non-irritant performance, foam stability and better dye inhibition transfer maintaining and even improving detergency.

It was unexpectedly found that the above mentioned requirements can be met when the specified nonionic compound is incorporated into detergent composition.

This finding has led to the present invention.

Accordingly, the present invention relates to a detergent compositions comprising the mono-, di- and tri-ester compounds represented by the formula (I), where the mono-di-tri-ester proportion is 46-90/9-30/1-15



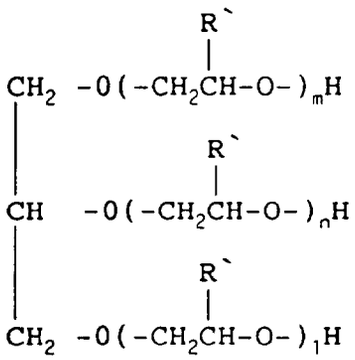
(I)

wherein:

- "B" represents "H" or the group represented by



provided that R represents alkyl or alkenyl group having C_{6-22}. Consider that at least one of "B" is an ester group.
- "n","m" and "l" may have a value between 0 and 40 provided that (n+m+l) = 2 - 100 preferebly 9 - 19.
- R` represents H or CH_3 respectively and the compound represented by the formula (II)



(II)

wherein:

- "n", "m" and "l" may have a value between 0 and 40 provided that (n+m+l) = 2 - 100 preferebly 9 - 19.
- R` represents H or CH_3 respectively.

Being the high content of ethoxylated monoester in compound (I) and ratio (I)/(II) the key parameters to get the above mentioned properties.

Ratio (I)/(II) has a value between 3 to 0.33 preferebly 1.3 to 0.75.

The compound mixture of the formula (I) + (II) in the present invention can be obtained by conventional method for preparating it.

For example the compound can be obtained by following the reaction processes.

(A) The interesterification reaction between triglyceride and glycerine, in a molar ratio in the proportion of 0.1-10/1, preferebly 0.15-3.5 (in presence of alkaline catalyst), and the reaction with alkylene oxide C_{2-3} or viceversa will lead to a mono- di- and triglyceride mixture (I) and (I)/(II) ratio of specific composition and structure, due to migration and exchange phenomena, with an HLB higher than 2.

(B) The reaction of glycerine with alkylene oxide C_{2-3}, in presence of alkaline catalysts and the later reaction with fatty acid in a molar ratio in the proportion of 0.1-10/1, preferebly 0,7-3.5/1 in presence of acidic or alkaline catalysts will lead to a mono- di-and triglyceride mixture of a specific composition and structure, due to migration and exchange phenomena, with an HLB higher than 2.

Triglyceride which can be used in process (A) includes natural fat and oil as well as a synthetic triglyceride.

The fat and oil include vegetable oil such as coconut oil, palm oil, soybean oil; and animal fat and oil such as beef tallow, bone oil; aquatic animal fat and oil; hardened oils and semihardened oil thereof.

In the present invention the compound mixture of the formula (I)+(II) can be incorporated in an amount of from 0.2% to 40%, preferebly from 3% to 20% by weight based on the whole of the detergent composition.

The reason why the present invention exhibits the outstanding biodegradable, non-toxic and non-irritant performance without deteriorating its detergeny is not certain, but it seems to applicant that good performance of the present composition comes partially from the fact that existence of fatty acid groups facilitates its biodegradability and its very low skin irritation, oral toxicity, fish toxicity, algae and daphnia inmobilization compared with conventional nonionics.

Furthermore incorporation of the formula of the new nonionic described in the patent, considerably improves its foam profile, anti dye transfer and perfume solubilization properties compared with conventional formulations, due to EO monoglyceride high ratio and the synergistic effect between (I) and (II).

The surface active agents like anionic, other nonionic, amphoteric etc and the rest of additive useful in the practice of this invention depends a great deal on kind of final product to be formulated. At the same time they are standard items of commerce so they will be not further comments upon herein.

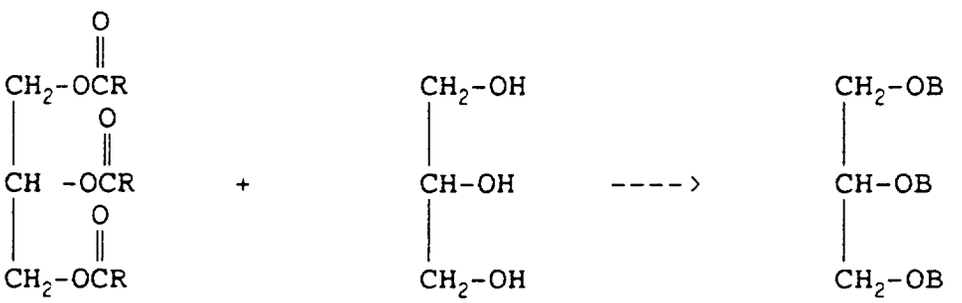
Example

The present invention is described in detail by way of the following examples. The present invention, however, is not limited to these examples.

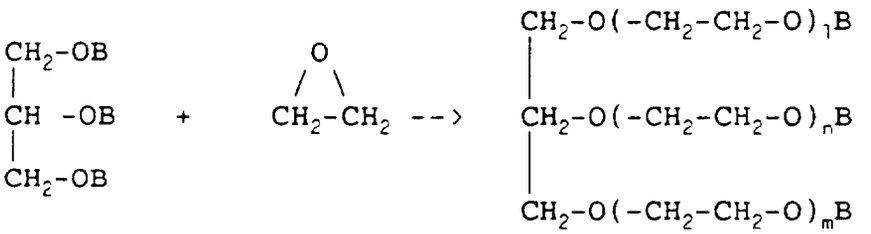
REFERENTIAL EXAMPLE 1.

The compound mixture of the formula ((I)+(II)) is obtained, for instance by means of the following process:

Step (c).



Step (d).

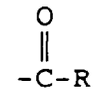


((I)+(II))

(See previous pages)

wherein:

- "B" represents "H" or the group represented by



and l+m+n = 15.

- "R" represents a coco alkyl chain.
- (I)/(II) ratio is 1.

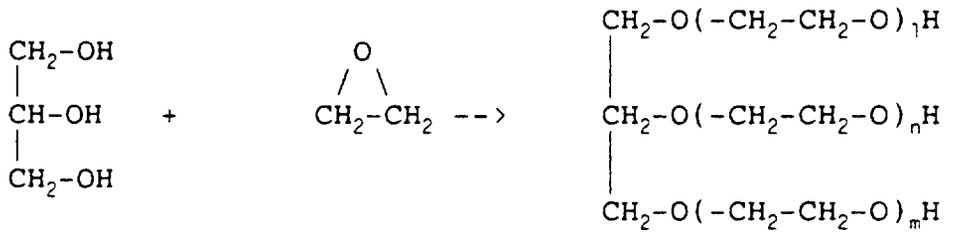
500 g (0.76 moles) of coco TRG, 210.7 g (2.29 moles) of glycerine 99% and 1.2 g of KOH 85% as catalyst are placed in a 3 kg flask properly equipped. System is purged several times with N_2, vacuum stripping till 110°C, and continued heating to 140°C. When temperature reaches 140°C the reactor is pressurized to 2-3 kg/cm^2 with ethylene oxide added until a total of 2013 gr (45.7 moles).

After the final charge of ethylene oxide the reaction mixture is allowed to react for about 1/2 hour; cooled and discharged from reactor. A product like ((I) + (II)) is obtained.

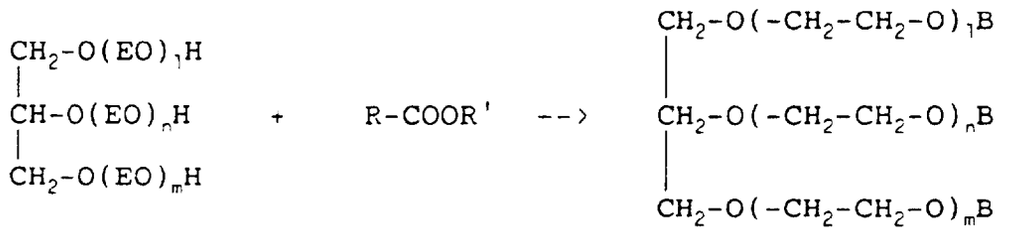
REFERENTIAL EXAMPLE 2

The compound mixture of the formula ((I)+(II)) is obtained, for instance by means of the following process:

Step (e).



Step (f).

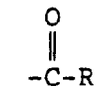


((I)+(II))

(See previous pages)

wherein:

"B" represents "H" or the group represented by



and l+m+n = 10.

R` represents CH_3.

R means tallow alkyl chain.

Ratio (I)/(II) = 1.3

14.3 g (0.1554 moles) of glycerine 99% and 1.2 g of KOH 85% as catalyst are placed in a 250 gr flask properly equipped. System is purged several times with N_2, vacuum stripping till 110°C, and continued heating to 140°C. When temperature reaches 140°C the reactor is pressurized to 2-3 kg/cm^2 with ethylene oxide added until a total of 67,9 gr (1.54 moles). After the final charge of ethylene oxide, the reaction mixture is allowed to react for about 1/2 hour; 52.3 gr (0.15 mol) of a methyl ester of fatty acid derived from tallow, is added and mixed for 45 minutes. Finally product is cooled and discharged from reactor. Thus a compound mixture of the formula (I) + (II) is obtained.

EXAMPLE 1.

HDPD

	COMPOSITION					
Raw materials	1	2	3	4	5	6
Na dodecyl benzene sulphonate	10	10	10	10	10	10
Ethoxylated (7) C_{13-15} alcohol	9	--	6	--	9	--
Nonionic of present invention. (from referential example 2)	--	9	--	6	--	9
Coco fatty acid	--	--	2	2	--	--
Silicone	0.2	0.2	0.1	0.1	0.2	0.2
Zeolite	35	35	--	--	35	35
STPP	--	--	35	35	--	--
Polycarboxilated	5	5	5	5	5	5
CMC	1.5	1.5	1.5	1.5	1.5	1.5
Perborate mono hydrate	15	15	13	13	15	15
Na Carbonate	12	12	15	15	12	12
Na Silicate	2	2	2	2	2	2
PVP	--	--	--	--	0.8	0.6
Enzyme	0.7	0.7	0.7	0.7	0.7	0.7
TAED	4	4	4	4	4	4
Sodium sulphate	B.	B.	B.	B.	B.	B.
Perfume	1	1	1	1	1	1

Note: B means balance.

Detergency evaluation test:
Washing machine:
Temperature: 30°C and 60°C.
Dosage: 6 gr/l.
Water hardness: 2 mmol/L Ca^{2+} and 4 mmol/L Ca^{2+} (20°HF and 40°HF).

Washing load: 2kg of not soiled cotton-polyester cloth and EMPA 101,104,117 + particulated soil.
No pre-washing program.

Detergent ability was evaluated on detergent compositions appearing in table 1.

All variables considered, that is, temperature, water hardness and soil type the nonionic described in this patent shows in the worst of cases equivalent eficiency in terms of detergency.

However, on the other hand, compositions containing the nonionic of the present invention provide a more superior colour care than usual ethoxylated alcohol.

The following test have been conducted at 30°C. 1.- Using Reactive dyestuff.

After 15 washings, differences appeared in terms of colour transfer.

Dye transfer was evaluated measuring delta E values $(L^2 + a^2 + b^2)^{1/2}$ by Hunter-Lab. The resulting discolouration of fabrics is shown in table below:

Table 1.

Compositions	Blue	Green	Red
1	8.0	14.0	6.0
2	5.7	10.3	5.0
3	6.0	8.0	4.5
4	5.0	6.5	4.0
5	1.3	0.9	0.5
6	1.2	1.0	0.5

The lower delta E, the better composition is able to prevent dye transfer. Therefore can be concluded from the above results that the nonionic from the present invention performs better than alcohol ethoxylated preventing dye transfer. In addition to that it is possible to save some amount of polyvinylpirrolidone (typical dye-tranfer inhibitor). The especific amount to be saved will depend on the effect of other components, that means, on formulation design. It seems to the applicant that a synergistic effect exists between the nonionic of present invention and PVP.

2.- Using Direct dyestuff.

References:

Yellow: Solar Yellow 3LG 160%
Blue: Solar Blue 2GLN 350%

Formulations:	Blue	Green	Yellow
Solar Blue 2GLN 350%	1%	1%	--
Solar Yellow 3LG 160%	--	1%	1%
SO_4Na_2	20 g/l	20 g/l	20 g/l
Sandofix R	3%	3%	3%

After 3 washings, differences appeared in terms of colour transfer.

Dye transfer was evaluated measuring delta E values $(L^2 + a^2 + b^2)^{1/2}$ by Hunter-Lab. The resulting dicoloration of fabrics is shown in table below:

Table 2.

Compositions	Blue	Green	Yellow
1	2.0	2.5	4.0
2	1.3	1.7	3.0
3	1.6	8.0	3.2
4	0.9	6.5	2.0
5	1.3	0.9	0.7
6	1.2	1.0	0.7

Those results, test 1 and 2, were corroborated using a 5 people panel, who evaluate the results according to a scale.

EXAMPLE 2.

HDL

	COMPOSITIONS			
Raw materials	1	2	3	4
Na lauryl sulphate	--	--	4	4
Na dodecyl benzene sulphonate	10	10	5	5
Ethoxylated (7) C_{13-15} alcohol.	--	5	--	15
Nonionic of present invention. (from referential example 2)	5	--	15	--
Potasium coconut soap	5	5	10	10
Ethanol	--	--	3	3
Propylenglycol	7	7	7	7
Perfum	1	1	1	1
Enzyme	0.7	0.7	0.5	0.5
Na formiate	1	1	1	1
Na phosphonate	0.8	0.8	0.8	0.8
TEA 85%	Req.	Req.	Req.	Req.
NaOH 50%	Req.	Req.	Req.	Req.
Cl_2Ca 1%	2	2	2	2
Water	B.	B.	B.	B.

Note: B means balance.
Req. means required amount.

Following the same test conditions than explained above for HDPD, (adapting the dosage according to the composition) the following results were obtained:

- Good enough detergency in all cases.
- Colour appearance results are shown in table 3.

Table 3.

Compositions	Blue	Green	Red
1	0.9	4.0	3.2
2	1.5	5.0	3.8
3	1.6	5.1	3.8
4	3.0	6.0	4.5

In short, compositions containing the nonionic of the present invention prevent better the colour transfer even in HDL where the ph is neutral and no optical brighters are used. (Note that HDL were used as colour save detergents

before appearing the new segment of colour saving H.D.P.D..

EXAMPLE 3.

WASHING UP.

	COMPOSITIONS			
Raw materials	1	2	3	4
Na lauryl ether sulphate	10	10	7	7
Na Alfa-olephine sulphonate	--	--	4	4
Alkyl amido propyl betaine	5.3	4.5	5.7	2.5
Ethoxylated (7) C_{13-15} alcohol	13	--	--	--
Nonionic of present invention. (from referential example 1)	--	7	--	7
Coconut diethanol amide	5	--	--	--
Amine oxide	--	--	3.3	--
Perfume	1	1	1	1
Water	bal.	bal.	bal.	bal.

Table 4.

Composition	1	2	3	4
Nº of dishes:	28	33	29	34
Fat dispersion (*)	R	QG	G	VG

(*) Key: R regular; QG quite good; G good enough; VG Very good.

Compositions containing Levenol® shows a better detergency and fat dispersion, allowing the supresion of nitrogen derivatives (alkanol amide and amine oxide) and also the complete substitution of ethoxylated alcohol. Other key point is the partial substitution of betaine. The nonionic of the present invention gives also a creamy foam compared to other compositions.

In order to check the effect on the skin of the nonionic of the present invention, a primary skin irritation test was conducted:

EXAMPLE 4.

	COMPOSITION		IRRITATION INDEX
1.-	Sodium lauryl sulphate	6.25%	1.88
2.-	Sodium lauryl sulphate	4.25%	
	+ Nonionic (1)	2.00%	1.00
3.-	Sodium lauryl sulphate	4.25%	1.38

EXAMPLE 5.

	COMPOSITION		IRRITATION INDEX
1.-	Sodium lauryl sulphate	4.25%	

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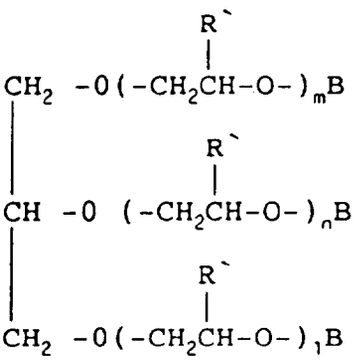
	COMPOSITION		IRRITATION INDEX
	+ Coco imidazoline betaine	2.00%	1.08
2.-	Sodium lauryl sulphate	4.25%	
	+ Alkylamide propyl betaine	2.00%	0.96
3.-	Sodium lauryl sulfate	4.25%	
	+ Nonionic (1)	2.00%	1.00

(1) Represents nonionic of the present invention from the referential example 2.

From the comparison of the above compositions, can be inferred the mild effect of the nonionic of the present invention.

Claims

1. Detergent composition comprising the mono-, di-and tri-ester compounds represented by the formula (I) wherein the weight ratio of mono, di and tri-ester is 46-90/9-30/1-15,



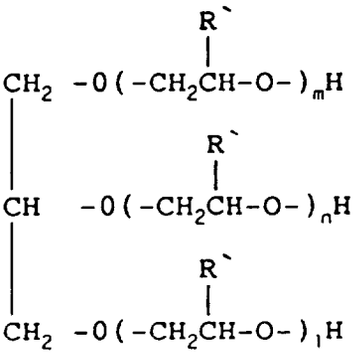
(I)

wherein:

- "B" represents "H" or the group represented by



provided that R represents alkyl or alkenyl group having C_{6-22} R' represents H or CH_3, and each of n, m and l independently represents an integer from 0 to 40; being m+n+l=2-100 preferebly 9-19, and the compound represented by the formula (II)



(II)

wherein:

- "n","m" and "l" may have a value between 0 and 40 provided that (n+m+l) = 2 - 100 preferebly 9 - 19.
- R' represents H or CH_3 respectively,

in which the weight ratio (I)/(II) has a value between 3 to 0.33.

2. Detergent composition according to claim 1 in which the ratio (I)/(II) has a value between 1.3 to 0.75.

3. Method for the preparation of a detergent composition, according to claim 1 which is produced by the following steps (a) and (b):

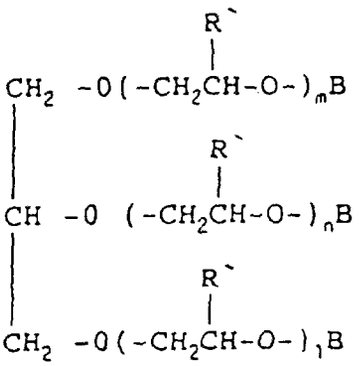
a) The mixture of triglyceride, and glycerine is subjected to a inter-esterification reaction,
b) The reaction mixture obtained in the step (a) is subjected to alkoxylation using alkylene oxide having C_{2-3} in the presence of alkaline catalyst to produce the compounds represented by the general formula (I) + (II).

4. Method for the preparation of a detergent composition, according to claim 1 which is produced by the following steps (c) and (d):

c) The mixture of glycerine and alkylene oxide C_{2-3}, in presence of alkaline catalysts,
d) The reaction mixture obtained in the step (c) reacted with methyl ester of fatty acid or fatty acid.

Patentansprüche

1. Waschmittelzusammensetzung, die Mono-, Di- und Triesterverbindungen umfaßt, dargestellt durch die Formel (I), worin das Gewichtsverhältnis von Mono-, Di- und Triester 46-90/9-30/1-15 beträgt,



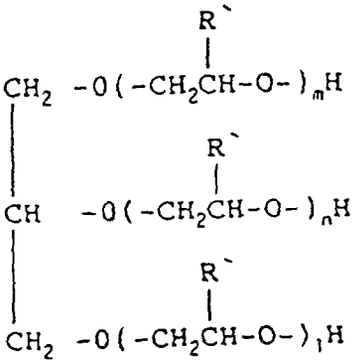
(I)

worin:

- "B" "H" oder die durch



dargestellte Gruppe darstellt, vorausgesetzt, daß R eine Alkyl- oder Alkenylgruppe mit C_{6-22} darstellt, R` H oder CH_3 darstellt, und jedes n, m und l unabhängig voneinander eine ganze Zahl von 0 bis 40 darstellt; wobei m+n+l = 2-100, vorzugsweise 9-19 beträgt, und die Verbindung, dargestellt durch die Formel (II)



(II)

worin:

- "n", "m" und "l" einen Wert zwischen 0 und 40 haben können, vorausgesetzt, daß (n+m+l) = 2-100, vorzugsweise 9-19 beträgt,

R' H bzw. CH_3 darstellt,
in welcher das Gewichtsverhältnis (I)/(II) einen Wert zwischen 3 bis 0,33 hat.

2. Waschmittelzusammensetzung nach Anspruch 1, in welcher das Verhältnis (I)/(II) einen Wert zwischen 1,3 bis 0,75 hat.

3. Verfahren zur Herstellung einer Waschmittelzusammensetzung nach Anspruch 1, die durch die folgenden Schritte (a) und (b) hergestellt wird:

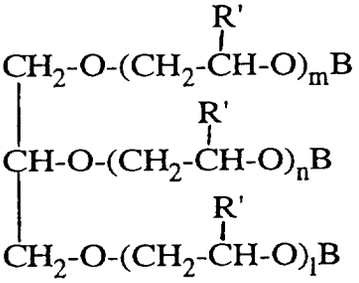
(a) die Mischung von Triglycerid und Glycerin wird einer Zwischenveresterungsreaktion unterzogen,
(b) das durch Schritt (a) erhaltene Reaktionsgemisch wird einer Alkoxylierung unter Verwendung von Alkylenoxid mit C_{2-3} in Gegenwart eines alkalischen Katalysators unterzogen, um die durch die allgemeine Formel (I) + (II) dargestellten Verbindungen herzustellen.

4. Verfahren zur Herstellung einer Waschmittelzusammensetzung nach Anspruch 1, die durch die folgenden Schritt (c) und (d) hergestellt wird:

(c) die Mischung von Glycerin und C_{2-3}-Alkylenoxid in Gegenwart eines alkalischen Katalysators,
(d) das in Schritt (c) erhaltene Reaktionsgemisch wird mit dem Methylester einer Fettsäure oder mit Fettsäure umgesetzt.

Revendications

1. Composition détergente contenant des monoesters, diesters et triesters, dans laquelle les proportions pondérales des monoesters, diesters et triesters valent 46-90/9-30/1-15, ces composés étant représentés par la formule (I):

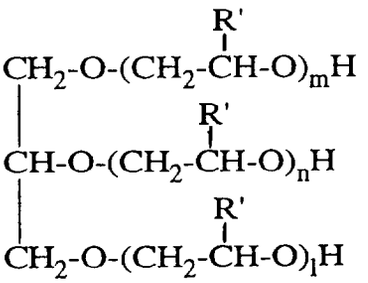


(I)

où B représente un atome d'hydrogène ou un groupe représenté par



R représentant un groupe alkyle ou alcényle en C_{6-22}, R' représente un atome d'hydrogène ou un groupe méthyle, et chacun des indices m, n et 1 est, indépendamment des autres, un nombre entier valant de 0 à 40, sous réserve que m+n+l vaille de 2 à 100, et de préférence de 9 à 19 ; et des composés représentés par la formule (II) :



(II)

où R' représente un- atome d'hydrogène ou un groupe méthyle, et chacun des indices m, n et l est, indépendamment des autres, un nombre entier valant de 0 à 40, sous réserve que m+n+l vaille de 2 à 100, et de préférence de 9 à 19 ;

et dans laquelle composition le rapport pondéral (I)/(II) vaut entre 3 et 0,33.

2. Composition détergente conforme à la revendication 1, dans laquelle le rapport pondéral (I)/(II) vaut entre 1,3 et 0,75.

3. Procédé de préparation d'une composition détergente conforme à la revendication 1, produite selon les étapes suivantes (a) et (b) :

a) on soumet un mélange de triglycérides et de glycérol à une réaction d'inter-estérification;
b) on soumet le mélange réactionnel issu de l'étape (a) à une réaction d'alcoxylation, en employant les oxydes d'alkylène en C_{2-3}, en présence d'un catalyseur alcalin, pour obtenir des composés représentés par les formules générales (I) et (II).

4. Procédé de préparation d'une composition détergente conforme à la revendication 1, produite selon les étapes suivantes (c) et (d):

c) on fait réagir un mélange de glycérol et d'oxydes d'alkylène en C_{2-3}, en présence d'un catalyseur alcalin ;
d) on fait réagir le mélange réactionnel issu de l'étape (c) avec des acides gras ou des esters méthyliques d'acide gras.