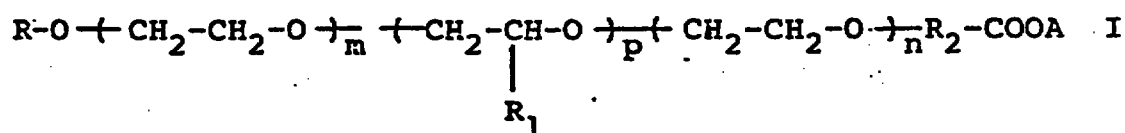


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ALKYL POLYOXYALKYLENE CARBOXYLATE SURFACTANTS

This invention relates to surface active agents. More particularly, it relates to novel alkyl polyoxyalkylene carboxylates and to their use as surface active agents.

The invention provides compounds and mixtures of formula I



where R is $n\text{-C}_{6-22}$ alkyl,

R_1 is C_{1-4} alkyl,

R_2 is C_{1-3} alkylene,

m is 0 or 0.1 to 30,

p is 0.5 to 20,

n is 0 or 0.1 to 30, and

A is hydrogen or a cation selected from

alkali metal, alkaline earth metal,

ammonium, mono-, di- and tri- C_{2-4} alkanol-

ammonium, mono-, di-, tri- and tetra- C_{1-4} -

alkylammonium, pyridinium and morpho-
linium,

with the provisos that:

1) $m + n + p$ is 1.0 to 50; and

5 2) m and n cannot both be zero.

R is preferably n - C_{8-18} alkyl, more preferably n - C_{10-18} alkyl and most preferably n - C_{10-16} alkyl.

R_1 is preferably methyl or ethyl and more preferably is methyl. When a molecule has more than one R_1 group,
10 they may be the same or different but are preferably the same.

R_2 is preferably $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH-$,
 CH_3

$-CH-$, CH_2CH- or $-CH-CH_2-$ and is more preferably $-CH_2-$.
 C_2H_5 CH_3 CH_3

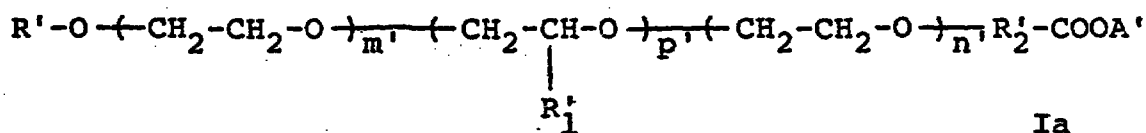
The variables m , p and n are average values. As is
15 clearly evident, the variables m , p and n must be whole numbers in the individual compounds of this invention.

The hydroxy group of any C_{2-4} hydroxyalkyl group in A is on other than the α -carbon atom. When A has more than one C_{2-4} hydroxyalkyl or C_{1-4} alkyl group, they may be the
20 same or different but are preferably the same. Preferably, A does not contain more than two tertiary butyl groups. The preferred alkali metals as A are lithium, sodium and potassium and the preferred alkaline earth metals are

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magnesium, calcium, barium and strontium.

Preferred compounds and mixtures are those of formula Ia



where R' is n-C₈₋₁₈alkyl,

5 R'₁ is C₁ or C₂alkyl,

R'₂ is C₁ or C₂ alkylene,

m' is 0 or 0.7 to 20

p' is 0.7 to 15,

n' is 0 or 0.7 to 20, and

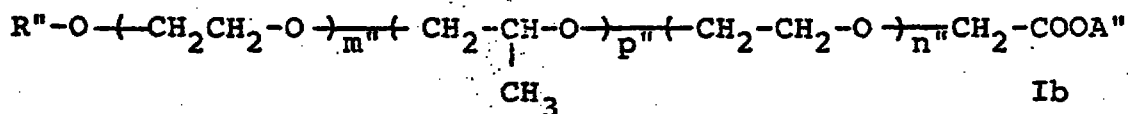
10 A' is hydrogen or a cation selected from alkali metal, alkaline earth metal, ammonium, mono-, di- and tri-C₂₋₄alkanol-ammonium and mono-, di-, tri- and tetra-C₁₋₄ alkylammonium,

15 with the provisos that

1) m' + n' + p' is 1.5 to 35; and

2) m' and n' cannot both be zero.

The more preferred compounds and mixtures are those of formula Ib



20 where R'' is n-C₁₀₋₁₈alkyl,

m'' is 0 or 1.0 to 15,

p'' is 2.0 to 10,

n'' is 0 or 1.0 to 15, and

A'' is hydrogen or a cation selected from alkali
5 metal, alkaline earth metal and ammonium,

with the provisos that

1) $m'' + n'' + p''$ is 3.0 to 25; and

2) m'' and n'' cannot both be zero.

Even more preferred compounds and mixtures are
10 those of formula Ib wherein R'' is $n\text{-C}_{10-16}$ alkyl, m'' is
0 or 1.0 to 10, p'' is 2.0 to 7, n'' is 0 or 1.0 to 10,
and A'' is hydrogen or a cation selected from alkali
metal and ammonium, with the provisos that

1) $m'' + n'' + p''$ is 3.0 to 20; and

15 2) m'' and n'' cannot both be zero.

The most preferred compounds and mixtures are
those of formula Ib wherein R'' is $n\text{-C}_{10-16}$ alkyl, m''
is 0 or 1.0 to 7, p'' is 2.0 to 5, n'' is 0 or 1.0 to 7,
and A'' is hydrogen or a cation selected from sodium,
20 potassium and ammonium, with the provisos that

1) $m'' + n'' + p''$ is 3.0 to 15; and

2) m'' and n'' cannot both be zero.

Representative compounds of each of the foregoing
groups are those wherein $m, m', \text{etc.}$ are 1 to 3, $p, p',$
25 etc. are 3 to 5 and $n, n', \text{etc.}$ are 1 to 3. Represent-
ative mixtures are those wherein such compounds are

the predominant components thereof. Preferred mixtures are those wherein such compounds comprise at least 60% of the mixtures, more preferably at least 80% of the mixtures.

5 As noted above, the R group in formula I is linear. This is important because the biodegradability of the compounds of formula I is detrimentally affected by branching.

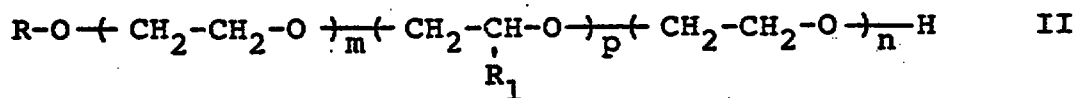
 Suitable alcohol precursors of the alkyl polyoxy-
10 alkylene carboxylates of this invention are linear, primary alkanols having from 6 to 22 carbon atoms. A mixture of such alcohols may be used and this is generally the case when using commercial alcohols which are often available as a blend of several alcohols. Consequently,
15 the number of carbon atoms in the alcohol may be referred to as an average number. Suitable alcohols are, for example n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, N-undecyl and n-dodecyl alcohols and the linear,
primary alcohols obtained from the hydrogenation of
20 vegetable or animal fatty acids such as coconut, palm kernel, tallow etc.

 The invention also provides a process for the

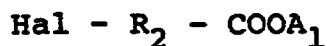
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preparation of compounds and mixtures of formula I comprising the step of reacting a compound or mixture of formula II



5 in which R, R₁, m, n and p are as defined above, with a compound of formula III



in which Hal is chlorine or bromine,

A₁ is hydrogen or an alkali metal cation

and R₂ is as defined above

10 in the presence of an alkali metal or an alkali metal hydroxide. Preferably A₁ is sodium ion and the reaction is carried out in the presence of sodium metal or sodium hydroxide. The conditions required for this carboxyalkylation reaction (the Williamson synthesis) are conventional. Where necessary, a cation A which
15 differs from A₁ above may be introduced by conventional exchange reactions.

The intermediates II are block ethylene oxide/
higher alkylene oxide adducts of linear alcohols, and are prepared in conventional manner by reaction of the
20 alcohol in two or three separate steps with ethylene oxide and with a higher alkylene oxide, preferably propylene oxide. The reaction is suitably carried out

in the presence of a catalytic amount of alkali, for example sodium or potassium hydroxide, under conditions of elevated temperature and pressure.

Optionally, a small amount of a reducing agent may
5 be added to the alcohol to be alkoxyated to minimize discoloration of the resulting polyalkoxyated alcohol. Suitable reducing agents which may be employed include sodium borohydride, lithium aluminium hydride and diborane, preferably sodium borohydride.

10 Thus, for example, the alkyl polyalkoxide intermediates II in which the polyoxyalkylene chain contains ethylene oxide blocks interrupted by a higher alkylene oxide block, e.g., a propylene oxide block, may be prepared by reacting a linear, primary alcohol having 6
15 to 22 carbon atoms with ethylene oxide in the desired amount until the ethylene oxide is consumed, as indicated by a drop in reaction pressure. A similar introduction and reaction of a calculated amount of propylene oxide or other alkylene oxide serves to provide the second block.
20 Following this, ethylene oxide is again added in the desired amount to provide the third block which completes the alkoxylation. Customarily, the alkoxyated product is treated with weak acid, e.g., glacial acetic acid, to neutralize any basic catalyst residues.

25 It should be understood that each separate alkoxylation procedure serves to introduce a desired average number of alkylene oxide units per alcohol molecule. Thus,

for example, the initial treatment of a linear, primary alcohol with m moles of ethylene oxide serves to effect the ethoxylation of each alcohol moiety with ethylene oxide to an average of m ethylene oxide moieties per alcohol moiety, although some alcohol moieties will have become combined with more than m ethylene oxide moieties and some will have become combined with less than m . The variation in the number of alkylene oxide moieties is not critical as long as the average for the number of units in each block is within the limits set out for the m , p and n terms in formula I above, which terms, as average values, are other than whole numbers in some instances. Moreover, and as can be seen from the limits set out for the m , p and n variables in formula I, nearly all of the components of the mixtures of compounds of formula I contain at least one ethylene oxide moiety and at least one higher alkylene, e.g., propylene, oxide moiety.

The reaction of the intermediates II with halocarboxylic acids or salts to form the products of formula I generally does not go to completion. Hence, the reaction product often contains minor amounts of unreacted alkyl polyalkoxide. While methods are available for separating the unreacted material as well as for assuring essentially complete reaction, they are usually tedious and expensive. Fortunately, it has been found that minor

proportions of intermediates II are not particularly harmful, and may even be advantageous.

The compounds of formula I have high activity at surfaces and interfaces, making them especially useful as surface active agents. The uses to which surface active agents can be put are numerous and well known and, as a result, the possible applications of these new compounds are extremely varied. Thus, the surface active agents of the present invention are suitable as emulsifiers, dispersing agents, lubricants, wetting agents, levelling agents, softening agents and the like in the detergent, textile, leather, paper, lacquer, personal care, e.g., toiletries and cosmetics, oil recovery, mining and rubber industries. For instance, they can be used as wetting, frothing or washing agents in the treating and refining of textiles; for converting liquid or solid substances which per se are insoluble in water (such as hydrocarbons, higher alcohols, oils, fats, waxes and resins) into creamy emulsions, clear solutions or fine, stable dispersions; for dyeing, e.g., in the pasting of dyestuffs, in dyeing acetate with insoluble dyestuffs, in the preparation of dyestuffs in finely divided form, etc.; and as an aid in softening baths for hides and skins.

In addition, these compounds are valuable emulsifiers for insecticide compositions and agricultural sprays such as DDT, 2,4-D and the like.

These compounds are valuable for use as additives to petroleum products, as additives for fuel oils, hydraulic fluids, lubricating oils, cutting oils and greases; and as additives to the water or brine used for oil recovery from oil-bearing strata by flooding techniques.

Other valuable uses are in metal cleaning compositions, dry cleaning compositions and acid pickling baths; and for use in bonding agents used in various insulating and bulking materials.

These compounds are valuable in the preparation of skin creams, lotions, salves and other cosmetic preparations. They are also of value in food products as foaming agents, emulsifying agents and softening agents.

The alkyl polyoxyalkylene carboxylates of the instant invention may also be employed as coating aids for use in coating compositions comprising a hydrophilic, film-forming colloid; and as tackifiers in the adhesive layer of adhesive tapes in, e.g., the photographic industry.

In addition, these compounds are valuable intermediates in the preparation of organic esters which in turn find use in the textile and plastic fields.

These compounds are also valuable in that they possess bactericidal and fungicidal properties and are, therefore, useful in the preparation of bactericidal

and fungicidal compositions.

The compounds also find use in shampoo compositions for application to hair and in shampoo compositions for the cleaning of carpets, rugs and upholstery.

5 The novel alkyl polyoxyalkylene carboxylates of the invention are especially suitable for formulating detergent compositions usable over a broad pH range. Accordingly, the present invention provides detergent compositions containing from 2% to 50% by weight of one
10 or more compounds of formula I, preferably from 10-40%, more preferably from 15-30%. The compounds of formula I may be the only surfactant component of the composition, but the composition may also advantageously contain one
15 surfactants. The composition may be in liquid or solid form.

 The detergent compositions of the invention may contain all manner of detergency builders commonly used in detergent compositions. However, because of the superior performance characteristics of the alkyl poly-
20 oxyalkylene carboxylates of this invention, it is possible to reduce the phosphate content to levels lower than previously possible when phosphates are used as the sole builder or in combination with other builders. It is even more surprising that by employing the alkyl poly-
25 oxyalkylene carboxylates of this invention, it is possible to formulate a detergent composition in which

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the traditional builders are completely absent.

Inorganic detergency builders include for example, water soluble salts of pyrophosphates, orthophosphates, polyphosphates, phosphonates, carbonates, bicarbonates and silicates.

Water soluble organic builders include, for example, the alkali metal, ammonium and substituted ammonium polyacetates (such as ethylenediaminetetraacetic acid sodium salt and sodium nitrilotriacetate), carboxylates, polycarboxylates and polyhydroxy-sulphonates.

The detergent compositions of the invention may optionally contain additional materials commonly found in laundering and cleaning compositions. For example, oxidizing bleaches such as sodium perborate, sodium percarbonate, etc., optionally with bleach precursors such as phthalic anhydride, may be incorporated at levels of 1% to 25% of the composition.

Defoamers such as long chain fatty acids, silicone fluids and microcrystalline waxes may be employed alone or as mixtures at levels of 0.005% to 5%, preferably 0.01% to 3%, and most preferably 0.1% to 1%, of the composition.

Viscosity modifiers and anticaking agents such as the sodium salts of lower alkyl aromatic sulfonic acids and the alkali metal salts of sulfosuccinic acid and benzene sulfonic acid are conveniently employed at levels of 0.5% to 5%, particularly if other anionic

surfactants are employed as part of the surfactant mixture.

Soil suspending agents such as sodium carboxymethyl cellulose and hydroxyethyl cellulose may also be
5 used in amounts of 0.25% to 5% by weight of the composition.

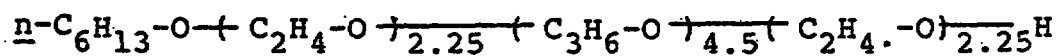
Enzymes such as the proteolytic enzymes may be incorporated at levels of up to 1% by weight, preferably from 0.25% to 0.75% by weight.

10 The compounds of formula I, although anionic in contact with water and having the desirable low foaming properties associated with anionic surfactants, also exhibit advantageous properties normally associated with nonionic surfactants. Thus like nonionic surfactants
15 but unlike most anionic surfactants, they have excellent stability in hard water. Furthermore, the compounds of formula I do not interfere with the function of cationic substances.

The following Examples illustrate the invention:

EXAMPLE 1

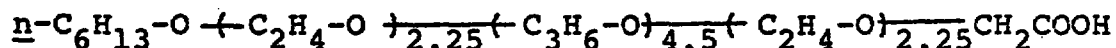
a) To a 4-necked, 5-liter round bottom flask fitted with a stirrer, dropping funnel, nitrogen inlet, condenser, vent and gas addition tube, is added 436.4 g (4.28 moles) of n-hexanol and 10.1 g of potassium hydroxide (in pellet form). The reaction flask is then evacuated to a pressure of 5 mm of mercury and kept under vacuum for thirty minutes, after which time the system is purged with nitrogen to break the vacuum. The temperature of the reaction mixture is then raised to 148°C, at which time the addition of 424.0 g of ethylene oxide (9.64 moles) to the reaction mixture is commenced. The temperature of the reaction mixture is maintained at 148°-166°C throughout the gradual addition of the ethylene oxide. Upon completion of the ethylene oxide addition, the reaction mixture is cooled and the reaction flask is evacuated to a pressure of 5 mm of mercury, after which time the system is purged with nitrogen to break the vacuum. While keeping the system under a nitrogen atmosphere, the procedure described above is repeated with 1116.0 g of propylene oxide (19.24 moles) and then with 424.0 g of ethylene oxide (9.64 moles) which completes the alkoxylation to yield the alkyl polyalkoxide intermediate of the formula



having a hydroxyl number of 103.1.

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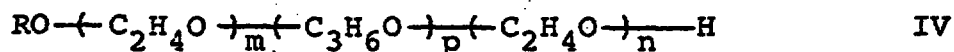
b) To 1000.0 g of the intermediate compound produced in a) above (1.78 moles), is alternately added, in small portions over a period of $3\frac{1}{2}$ hours at a temperature range of $25^{\circ}\text{--}50^{\circ}\text{C}$, 71.2 g of sodium hydroxide (1.78 moles) and 207.7 g of sodium monochloroacetate (1.78 moles). Upon completion of the addition, the temperature of the resulting reaction mixture is maintained at 50°C for 30 minutes, after which time the temperature is raised to 75°C over a period of 30 minutes. After keeping the reaction mixture at a temperature of 75°C for 90 minutes, it is cooled to 50°C and acidified with 175.0 g of sulfuric acid (50% conc.) in 600.0 g of water, after which time separation of the water-soluble salt yields an oil of the formula



having an acid number of 53.2.

EXAMPLES 2-19

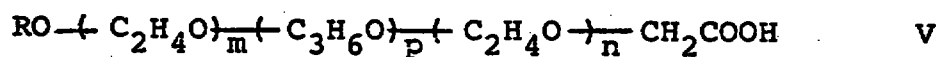
a) Following essentially the procedure of Example 1a) and employing the appropriate starting alcohol and the appropriate amounts of ethylene oxide and propylene oxide in the same sequence of addition, alkyl polyalkoxide intermediates of formula IV



are obtained, in which R, m, p and n are as shown in

Table I, and in which the hydroxyl number is as shown in column 6 of Table I.

5 b) Following essentially the procedure of Example 1b) and using in place of the intermediate compound of Example 1a), the intermediates produced as above, there is obtained the alkyl polyalkoxide carboxylates of formula V



10 in which R, m, p and n are as shown in Table I, and having an acid number as shown in column 7 of Table I.

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Table I

<u>Example No.</u>	<u>R</u>	<u>m</u>	<u>p</u>	<u>n</u>	<u>Hydroxyl No. of intermediate</u>	<u>Acid No. of product</u>
2	$\text{n-C}_{10}\text{H}_{21}$	0.15	2.4	0.45	192.4	88.6
3	"	0.45	2.4	0.15	188.0	70.7
4	"	0.9	14.4	2.7	58.4	24.7
5	"	0.6	0.6	1.8	186.7	108.0
6	"	1.8	0.6	0.6	186.9	110.8
7	"	3.6	3.6	10.8	60.0	42.6
8	"	10.8	3.6	3.6	61.3	33.3
9	$\text{n-C}_{14}\text{H}_{29}$	0.25	0.5	0.25	211.0	98.0
10	"	2.25	4.5	2.25	89.3	51.2
11	$\text{n-C}_{18}\text{H}_{37}$	0.15	2.4	0.45	130.3	45.2
12	"	0.45	2.4	0.15	132.9	44.9
13	"	0.6	0.6	1.8	134.2	83.4
14	"	1.8	0.6	0.6	132.4	81.3
15	"	2.7	14.4	0.9	61.6	31.4
16	"	3.6	3.6	10.8	55.3	38.0
17	"	10.8	3.6	3.6	55.7	36.2
18	"	0.9	7.2	0.9	83.8	18.2
19	$\text{n-C}_{22}\text{H}_{45}$	2.25	4.5	2.25	79.3	42.5

EXAMPLES 20-27

Following essentially the procedure of Example 1a) but omitting either the initial or the final ethylene oxide addition, intermediate compounds of formula IV are

obtained in which either m or n is zero. Following essentially the procedure of Example 1b), corresponding products of formula V are obtained, as shown in Table II.

Table II

<u>Example No.</u>	<u>R</u>	<u>m</u>	<u>p</u>	<u>n</u>	<u>Hydroxyl No. of intermed.</u>	<u>Acid No. of product</u>
20	n-C ₁₄ H ₂₉	0	4.5	4.5	89.7	55
21	n-C ₁₈ H ₃₇	0	0.8	0.2	174.8	69.7
22	n-C ₁₀ H ₂₁	0	0.2	0.8	275.8	88.8
23	"	0	7.2	1.8	95.5	35.0
24	"	0	0.8	0.2	268.7	99.4
25	n-C ₁₄ H ₂₉	4.5	4.5	0	90.75	21.3
26	n-C ₁₈ H ₃₇	14.4	3.6	0	57.7	14.1
27	n-C ₁₈ H ₃₇	0.5	0.5	0	172.5	60.8

Omission of the acidification step in the procedure of Example 1b) gives the corresponding products in sodium salt form.

The following represent typical formulations useful as detergent compositions:

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Solid Compositions

	Example No.		
	28	29	30
	Percent by weight		
Compound of Example 1	17	-	-
Compound of Example 20	-	17	-
Compound of Example 25	-	-	17
sodium tripolyphosphate	50	50	50
sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:2.5$)	6	6	6
sodium toluene sulfonate	2	2	2
sodium carboxymethylcellulose	0.3	0.3	0.3
sodium sulfate	13	13	13
fluorescent dye	0.16	0.16	0.16
water	8	8	8
miscellaneous	balance		

Liquid Compositions

	Example No.		
	31	32	33
	Percent by weight		
Compound of Example 1	12	-	-
Compound of Example 20	-	12	-
Compound of Example 25	-	-	12
tetrapotassium pyrophosphate	19	19	19
sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1:1.6$)	3.8	3.8	3.8
potassium toluene sulfonate	8.5	8.5	8.5
sodium carboxymethylcellulose	0.3	0.3	0.3
perfume	0.2	0.2	0.2
water	56.2	56.2	56.2

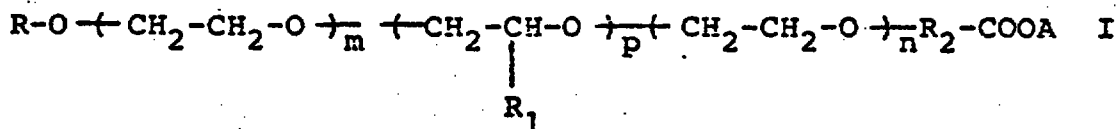
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Similar formulations useful as detergent compositions are obtained when the compounds of Examples 2-19, 21-24, 26 and 27 are used.

CLAIMS

1. Compounds of formula I



where R is $\underline{n}$ -C₆₋₂₂alkyl,

R₁ is C₁₋₄alkyl,

R₂ is C₁₋₃alkylene,

m is 0 or 0.1 to 30,

p is 0.5 to 20,

n is 0 or 0.1 to 30, and

A is hydrogen or a cation selected from

alkali metal, alkaline earth metal,

ammonium, mono-, di- and tri-C₂₋₄alkanol-

ammonium, mono-, di-, tri- and tetra-C₁₋₄-

alkylammonium, pyridinium and morpho-

linium,

with the provisos that

1) m + n + p is 1.0 to 50; and

2) m and n cannot both be zero

and mixtures thereof.

2. Compounds as claimed in Claim 1 in which R is $\underline{n}$ -C₁₀₋₁₈ alkyl.

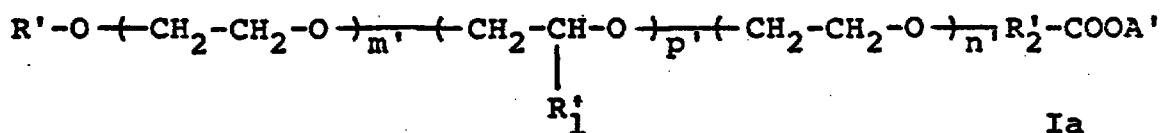
3. Compounds as claimed in Claim 1 or Claim 2 in which R₁ is methyl.



4. Compounds as claimed in any one of the preceding claims in which R_2 is methylene.

5. Compounds as claimed in any one of the preceding claims in which A is hydrogen or a cation selected from sodium, potassium or ammonium.

6. Compounds as claimed in Claim 1 of formula Ia



where R' is n - C_{8-18} alkyl,

R_1' is C_1 or C_2 alkyl,

R_2' is C_1 or C_2 alkylene,

m' is 0 or 0.7 to 20

p' is 0.7 to 15,

n' is 0 or 0.7 to 20, and

A' is hydrogen or a cation selected from alkali metal, alkaline earth metal, ammonium, mono-, di- and tri- C_{2-4} alkanol-ammonium and mono-, di-, tri- and tetra- C_{1-4} alkylammonium,

with the provisos that

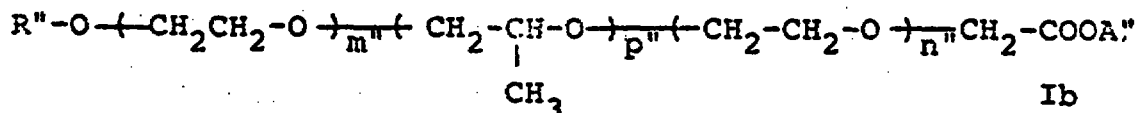
- 1) $m' + n' + p'$ is 1.5 to 35; and
- 2) m' and n' cannot both be zero.



* C L N S *

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7. Compounds as claimed in Claim 6 of formula Ib.



where R'' is $n\text{-C}_{10-18}$ alkyl,

m'' is 0 or 1.0 to 15,

p'' is 2.0 to 10,

n'' is 0 or 1.0 to 15, and

A'' is hydrogen or a cation selected from alkali metal, alkaline earth metal and ammonium,

with the provisos that

1) m'' + n'' + p'' is 3.0 to 25; and

2) m'' and n'' cannot both be zero.

8. Compounds as claimed in Claim 7 in which R'' is $n\text{-C}_{10-16}$ alkyl, m'' is 0 or 1.0 to 10, p'' is 2.0 to 7, n'' is 0 or 1.0 to 10, and A'' is hydrogen or a cation selected from alkali metal and ammonium, with the provisos that

1) m'' + n'' + p'' is 3.0 to 20; and

2) m'' and n'' cannot both be zero.

9. Compounds as claimed in Claim 8 in which R'' is $n\text{-C}_{10-16}$ alkyl, m'' is 0 or 1.0 to 7, p'' is 2.0 to 5, n'' is 0 or 1.0 to 7, and A'' is hydrogen or a cation selected from sodium, potassium and ammonium, with the provisos that

1) m'' + n'' + p'' is 3.0 to 15; and

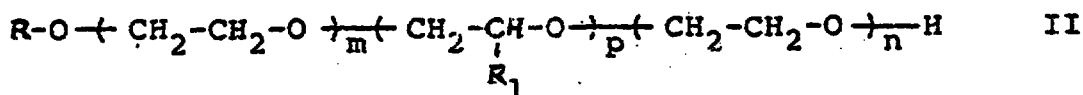
2) m'' and n'' cannot both be zero.

10. Compounds and mixtures as claimed in Claim 1,



as described in any one of Examples 1 to 27.

11. A process for the preparation of compounds and mixtures of formula I comprising the step of reacting a compound or mixture of formula II



in which R, R₁, m, n and p are as defined ^{in Claim 1} above, with a compound of formula III



in which Hal is chlorine or bromine,

A₁ is hydrogen or an alkali metal cation

and R₂ is as defined ^{in Claim 1} above

in the presence of an alkali metal or an alkali metal hydroxide.

12. A detergent composition containing from 2% to 50% by weight of one or more compounds of formula I.

13. A detergent composition containing from 15% to 30% by weight of one or more compounds of formula I.

14. A detergent composition as claimed in Claim 12 or Claim 13 containing no significant quantity of detergency builder.

15. A detergent composition as described in any one of Examples 28 to 33.

