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(54) **UTILISATION D'ESTERS QUATERNAIRES DANS LES
PRODUITS DE COLORATION DES CHEVEUX**

(54) **USE OF ESTER QUATERNARIES AS EMULSIFIERS FOR
PRODUCING PREPARATIONS FOR COLORING KERATIN
FIBERS**

(57) L'invention concerne l'utilisation d'esters quaternaires comme émulsifiants pour les produits de coloration des cheveux dans la production de préparations destinées à la coloration des fibres kératiniques. L'invention présente deux avantages: une meilleure absorption de la couleur par les cheveux et les cheveux colorés ont un contact plus doux.

(57) The invention relates to the use of ester quaternaries as emulsifiers for hair colorants for producing preparations for coloring keratin fibers. The invention provides an improved receptivity for color in the hair while, at the same time, the hair is given an improved soft touch during coloring.

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The Use of Esterquats as Emulsifiers for the Production of Formulations for Coloring Keratin Fibers

Abstract

The invention relates to the use of esterquats as emulsifiers for hair dyes for the production of formulations for coloring keratin fibers. The advantage of the invention lies in improved dye absorption by the hair. At the same time, improved softness is imparted to the hair during coloring.

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Patent Application
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**The Use of Esterquats as Emulsifiers for the Production of Formulations
for Coloring Keratin Fibers**

Field of the Invention

This invention relates to the use of esterquats as emulsifiers for the production of hair coloring formulations and to a process for coloring keratin fibers in which hair dyes and emulsifiers of the esterquat type are used.

5 Prior Art

Synthetic hair colorants can be divided into three groups, namely: substantive temporary colorants, semipermanent colorants and permanent colorants. However, natural hair colorants cannot readily be assigned to any of these three groups. Whether a temporary, semipermanent or permanent hair color is to be obtained with individual dyes also depends *inter alia* on the formulation in which it is incorporated and on how the formulations are applied.

The color obtainable with temporary substantive hair colorants is merely a temporary change of the existing hair color. Accordingly, it must be easy to wash out with shampoos. It is produced by the simple deposition of the dyes on the surface of the hair. Accordingly, this coloring treatment should not be followed by a rinsing step. Because of this, the dyes used must have the following properties: poor affinity for hair keratin, easy removability by washing with a shampoo, adequate fastness to light and high fastness to

rubbing to avoid soiling clothes and pillows. Azo dyes, triphenylmethane dyes, anthraquinone dyes or indamine dyes and leuco derivatives thereof are generally used for this purpose.

Semipermanent hair colorants provide the hair with more pronounced and permanent colors which are capable of withstanding washing 5 or 6 times. This is achieved by the use of dyes which have a high affinity for keratin and which penetrate relatively deeply into the hair fibers. These colorants perform various functions. For example, they add reflexes to a natural color, hide grey hair and eliminate the yellow tinge from grey or white hair. The substantive dyes suitable for this purpose are largely nonionic or cationic and have a relatively low molecular weight and poor solubility in water. Important representatives are the nitrophenyldiamines from which many other hair dyes can be produced by substitution reactions. The nitro dyes also include the nitroaminophenols which - depending on the position of their nitro and amino group on the phenol ring - give colors ranging from yellow through orange to red. Azo dyes or quinone imine dyes containing quaternary ammonium groups have a high affinity for hair keratin. Although they do not color as intensively as nitro dyes, they do give colors in all shades.

Finally, permanent hair colors are highly resistant to washing, light and other hair treatment methods. In their case, the dyes are formed directly on and in the hair by chemical reactions to which the uncolored intermediate products or precursors are subjected. These reactions include oxidation reactions and coupling reactions or condensations which are produced by hydrogen peroxide in the presence of ammonia or monoethanolamine. Hydrogen peroxide is preferably used as the oxidizing agent because not only does it initiate the color-forming process, it also destroys the melanin pigments in the hair and, in doing so, bleaches the hair. Besides the true oxidation hair dyes, there are also the self-oxidizing dyes which are actually oxidized by atmospheric oxygen. The oxidation dyes are divided according

to their nature into the oxidation bases (developers or primary intermediates) and the color modifiers (couplers or secondary intermediates). Oxidation bases are aromatic compounds which are nucleus-substituted by at least two electron donor groups, preferably amino and/or hydroxy groups, and which are therefore readily oxidized. Important representatives of these bases are the isomeric ortho- and para-phenyldiamines, aminophenols and dihydroxybenzenes. The couplers, too, are generally aromatic compounds which contain amino and/or hydroxy groups, but in the meta-position.

The hair dyes may be applied to the hair in various forms. In the most simple case, they may be aqueous or aqueous-alcoholic lotions which are diluted just before application and then applied to the hair. There are also the conditioning lotions which, in addition to the dyes, also contain above all cationic polymers and, accordingly, also have a hair-care effect. The same also applies to foam aerosols. A typical formulation for semipermanent coloring is the tinting shampoo whereas permanent hair colorants are generally applied as cremes or gels. However, in the production of shampoos, cremes and gels in particular, problems are involved on the one hand in stably emulsifying the dye together with hair-care additives and, on the other hand, in ensuring rapid deposition on the keratin fibers.

In this connection, a process for coloring cotton in which esterquats based on tall oil fatty acid are used is known from Russian patent application **SU 956.668**.

Accordingly, the complex problem addressed by the present invention was to provide emulsifiers for hair dyes with which it would be possible to prepare emulsions that would neither separate nor change viscosity even in the event of prolonged storage or under the effect of heat. In addition, the formulations obtainable with these emulsifiers would lead to improved dye absorption in the hair and would also have a hair-care effect, i.e. in particular would improve feel, shine and combability.

Description of the Invention

The present invention relates to the use of esterquats as emulsifiers for hair dyes for the production of formulations for coloring keratin fibers.

It has surprisingly been found that not only are esterquats capable of 5 permanently emulsifying hair dyes without the formulations changing viscosity, the use of these cationic surfactants as emulsifiers also facilitates absorption of the dye by the keratin fibers. Another advantage is that a pleasant softness and shine is imparted to the hair during coloring and static 10 charging between the fibers is reduced. Accordingly, not only the required coloring effect, but also a hair-care effect is obtained through the use according to the invention.

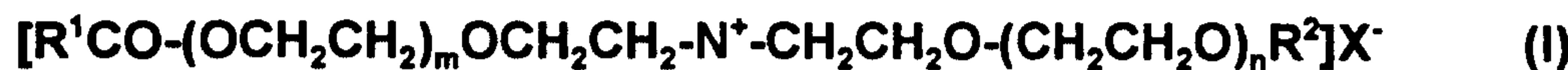
Esterquats

"Esterquats" are generally understood to be quaternized fatty acid 15 triethanolamine ester salts. They are known compounds which may be obtained by the relevant methods of preparative organic chemistry, cf. International patent application WO 91/01295 (Henkel), in which triethanol-amine is partly esterified with fatty acids in the presence of hypophosphorous acid, air is passed through the reaction mixture and the whole is then 20 quaternized with dimethyl sulfate or ethylene oxide. Overviews of this subject have been published, for example, by R. Puchta et al. in **Tens. Surf. Det.**, 30, 186 (1993), by M. Brock in **Tens. Surf. Det.**, 30, 394 (1993), by R. Lagerman et al. in **J. Am. Oil Chem. Soc.**, 71, 97 (1994) and by I. Shapiro in **Cosm. Toil.** 109, 77 (1994).

25 The quaternized fatty acid triethanolamine ester salts correspond to formula (I):

R^4

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$$|$$

$$CH_2CH_2O(CH_2CH_2O)_pR^3$$

in which R^1CO is an acyl group containing 6 to 22 carbon atoms R^2 and R^3 independently of one another represent hydrogen or have the same meaning as R^1CO , R^4 is an alkyl group containing 1 to 4 carbon atoms or a $(CH_2CH_2O)_qH$ group, m , n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and X is halide, alkyl sulfate or alkyl phosphate.

Typical examples of esterquats which may be used in accordance with the present invention are products based on caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, isostearic acid, stearic acid, oleic acid, elaidic acid, arachic acid, behenic acid and erucic acid and the technical mixtures thereof obtained, for example, in the pressure hydrolysis of natural fats and oils. Technical $C_{12/18}$ cocofatty acids and, in particular, partly hydrogenated $C_{16/18}$ tallow or palm oil fatty acids and $C_{16/18}$ fatty acid cuts rich in elaidic acid are preferably used. To produce the quaternized esters, the fatty acids and the triethanolamine may be used in a molar ratio of 1.1:1 to 3:1. With the performance properties of the esterquats in mind, a ratio of 1.2:1 to 2.2:1 and preferably 1.5:1 to 1.9:1 has proved to be particularly advantageous. The preferred esterquats are technical mixtures of mono-, di- and triesters with an average degree of esterification of 1.5 to 1.9 and are derived from technical $C_{16/18}$ tallow or palm oil fatty acid (iodine value 0 to 40). In performance terms, quaternized fatty acid triethanolamine ester salts corresponding to formula (I), in which R^1CO is an acyl group containing 16 to 18 carbon atoms, R^2 has the same meaning as R^1CO , R^3 is hydrogen, R^4 is a methyl group, m , n and p stand for 0 and X stands for methyl sulfate, have proved to be particularly advantageous.

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Besides the quaternized fatty acid triethanolamine ester salts, other suitable esterquats are quaternized ester salts of fatty acids with diethanol-alkylamines corresponding to formula (II):

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 R^4

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 R^5

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in which R^1CO is an acyl group containing 6 to 22 carbon atoms, R^2 is hydrogen or has the same meaning as R^1CO , R^4 and R^5 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate.

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Finally, another group of suitable esterquats are the quaternized ester salts of fatty acids with 1,2-dihydroxypropyl dialkylamines corresponding to formula (III):

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 $R^6 \quad O-(CH_2CH_2O)_mOCR^1$

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 R^7

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in which R^1CO is an acyl group containing 6 to 22 carbon atoms, R^2 is hydrogen or has the same meaning as R^1CO , R^4 , R^6 and R^7 independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate.

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So far as the choice of the preferred fatty acids and the optimal degree of esterification are concerned, the examples mentioned for (I) also apply to the esterquats corresponding to formulae (II) and (III). The esterquats are normally marketed in the form of 50 to 90% by weight solutions in alcohol

5 which may readily be diluted as required with water. However, it is also possible to use mixtures of esterquats with fatty alcohols which are commercially available in the form of flakes and of which the production is described in **DE-C1 43 08 794** (Henkel). The esterquats may be used in quantities of 0.1 to 5% by weight and are preferably used in quantities of 1 to 3% by

10 weight, based on the formulations.

Hair dyes

Dyes suitable for the use according to the invention are, for example, **substantive dyes**, for example from the group of nitrophenylenediamines,

15 nitroaminophenols, anthraquinones or indophenols, such as for example the compounds known under the international names or trade names of HC Yellow 2, HC Yellow 4, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16,

20 Basic Brown 17, picramic acid and Rodol 9 R and also 4-amino-2-nitrodi-phenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, (N-2,3-dihydroxypropyl-2-nitro-4-trifluoromethyl)-aminobenzene and 4-N-ethyl-1,4-bis-(2'-hydroxyethylamino)-2-nitrobenzene hydrochloride. In addition,

25 naturally occurring dyes, for example henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, buckthorn bark, sage, logwood, madder root, catechu, sedre and alkanet may also be used.

In addition to substantive dyes, **oxidation dyes** consisting of primary and secondary intermediates may also be used. The primary intermediates used include, for example, primary aromatic amines containing another free

30 or substituted hydroxy or amino group in the para or ortho position, diamino-

pyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives and 2,4,5,6-tetraaminopyrimidine and derivatives thereof. Special representatives are inter alia p-toluylenediamine, p-aminophenol, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenoxy)-ethanol, 1-phenyl-3-carboxyamido-4-amino-5-pyrazolone and 4-amino-3-methylphenol, 2-(2-hydroxyethyl)-1,4-aminobenzene and 2,4,5,6-tetraaminopyrimidine. The secondary intermediates used are generally m-phenylenediamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones, m-amino-phenols and pyridine derivatives. Suitable secondary intermediates are, in particular, 1-naphthol, pyrogallol, 1,5-, 2,7- and 1,7-dihydroxynaphthalene, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 1-phenyl-3-methyl-5-pyrazolone, 2,4-dichloro-3-aminophenol, 1,3-bis-(2,4-diaminophenoxy)-propane, 2-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methyl resorcinol, 2,5-dimethyl resorcinol, 2,6-dihydroxypyridine and 2,6-diaminopyridine.

Other suitable dye components can be found in the Colipa List published by the Industrieverband Körperpflege und Waschmittel, Frankfurt. The hair dyes may be used in quantities of 0.001 to 1% by weight and are preferably used in quantities of 0.3 to 0.7% by weight, based on the formulations.

Other auxiliaries and additives

In one particularly simple embodiment of the invention, the formulations for coloring keratin fibers only contain oils besides the hair dyes, the esterquat emulsifiers and water. However, the formulations may also be made up, for example, in the form of tinting or coloring shampoos which may contain other ingredients typical of the particular nature of the formulation, such as for example mild surfactants, coemulsifiers, superfatting agents, pearlescent waxes, stabilizers, consistency regulators, thickeners, cationic polymers, silicone compounds, biogenic agents, antidandruff agents, film

formers, preservatives, hydrotropes, solubilizers, UV filters, perfume oils, dyes and the like.

Typical examples of suitable mild surfactants, i.e. surfactants particularly compatible with the skin, are fatty alcohol polyglycol ether sulfates, monoglyceride sulfates, monoalkyl and/or dialkyl sulfosuccinates, fatty acid isethionates, fatty acid sarcosinates, fatty acid taurides, fatty acid glutamates, ether carboxylic acids, alkyl oligoglucosides, fatty acid gluc-amides, alkylamidobetaines and/or protein fatty acid condensates (preferably based on wheat proteins).

Suitable oils are, for example, Guerbet alcohols based on fatty alcohols containing 6 to 18 and preferably 8 to 10 carbon atoms, esters of linear C₆₋₂₂ fatty acids with linear C₆₋₂₂ fatty alcohols, esters of branched C₆₋₁₃ carboxylic acids with linear C₆₋₂₂ fatty alcohols, esters of linear C₆₋₂₂ fatty acids with branched alcohols, more particularly 2-ethyl hexanol, esters of linear and/or branched fatty acids with polyhydric alcohols (for example propylene glycol, dimer diol or trimer triol) and/or Guerbet alcohols, triglycerides based on C₆₋₁₀ fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆₋₁₈ fatty acids, esters of C₆₋₂₂ fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, more particularly benzoic acid, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear C₆₋₂₂ fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C₆₋₂₂ alcohols (for example Finsolv® TN), dialkyl ethers, ring-opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons. The quantity of oils in the formulations is typically from 10 to 70% by weight and preferably from 25 to 50% by weight.

Suitable co-emulsifiers are, for example, nonionic surfactants from at least one of the following groups:

(1) products of the addition of 2 to 30 moles of ethylene oxide and/or 0 to

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5 moles of propylene oxide to linear fatty alcohols containing 8 to 22 carbon atoms, to fatty acids containing 12 to 22 carbon atoms and to alkylphenols containing 8 to 15 carbon atoms in the alkyl group;

(2) C_{12/18} fatty acid monoesters and diesters of products of the addition of 1 to 30 moles of ethylene oxide to glycerol;

(3) glycerol monoesters and diesters and sorbitan monoesters and diesters of saturated and unsaturated fatty acids containing 6 to 22 carbon atoms and ethylene oxide adducts thereof;

(4) alkyl mono- and oligoglycosides containing 8 to 22 carbon atoms in the alkyl group and ethoxylated analogs thereof;

(5) adducts of 15 to 60 moles of ethylene oxide with castor oil and/or hydrogenated castor oil;

(6) polyol esters and, in particular, polyglycerol esters such as, for example, polyglycerol polyricinoleate or polyglycerol poly-12-hydroxystearate.

15 Mixtures of compounds from several of these classes are also suitable;

(7) products of the addition of 2 to 15 moles of ethylene oxide to castor oil and/or hydrogenated castor oil;

(8) partial esters based on linear, branched, unsaturated or saturated C_{6/22} fatty acids, ricinoleic acid and 12-hydroxystearic acid and glycerol,

20 polyglycerol, pentaerythritol, dipentaerythritol, sugar alcohols (for example sorbitol), alkyl glucosides (for example methyl glucoside, butyl glucoside, lauryl glucoside) and polyglucosides (for example cellulose);

(9) trialkyl phosphates and mono-, di- and/or tri-PEG-alkyl phosphates;

(10) wool wax alcohols;

25 (11) polysiloxane/polyalkyl polyether copolymers and corresponding derivatives;

(12) mixed esters of pentaerythritol, fatty acids, citric acid and fatty alcohol according to DE-PS 11 65 574 and/or mixed esters of fatty acids containing 6 to 22 carbon atoms, methyl glucose and polyols, preferably glycerol, and

(13) polyalkylene glycols.

The addition products of ethylene oxide and/or propylene oxide with fatty alcohols, fatty acids, alkylphenols, glycerol monoesters and diesters and 5 sorbitan monoesters and diesters of fatty acids or with castor oil are known, commercially available products. They are homolog mixtures of which the average degree of alkoxylation corresponds to the ratio between the quantities of ethylene oxide and/or propylene oxide and substrate with which the addition reaction is carried out. C_{12/18} fatty acid monoesters and diesters 10 of addition products of ethylene oxide with glycerol are known as refatting agents for cosmetic formulations from DE-PS 20 24 051.

C_{8/18} alkyl mono- and oligoglycosides, their production and their use as surfactants are known from the prior art. They are produced in particular by reaction of glucose or oligosaccharides with primary alcohols containing 8 to 15 18 C atoms. So far as the glycoside component is concerned, both monoglycosides, in which a cyclic sugar unit is attached to the fatty alcohol by a glycoside linkage, and oligomeric glycosides with a degree of oligomerization of preferably up to about 8 are suitable. The degree of oligomerization is a statistical mean value on which a homolog distribution typical of such 20 technical products is based.

Zwitterionic surfactants may also be used as emulsifiers. Zwitterionic surfactants are surface-active compounds which contain at least one quaternary ammonium group and at least one carboxylate and one sulfonate group in the molecule. Particularly suitable zwitterionic surfactants are the 25 so-called betaines, such as the N-alkyl-N,N-dimethyl ammonium glycinate, for example cocoalkyl dimethyl ammonium glycinate, N-acylaminopropyl-N,N-dimethyl ammonium glycinate, for example cocoacylaminopropyl dimethyl ammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxyethyl imidazolines containing 8 to 18 carbon atoms in the alkyl or acyl group and 30 cocoacylaminooethyl hydroxyethyl carboxymethyl glycinate. The fatty acid

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amide derivative known by the CTFA name of *Cocamidopropyl Betaine* is particularly preferred. Other suitable emulsifiers are ampholytic surfactants. Ampholytic surfactants are surface-active compounds which, in addition to a C_{8/18} alkyl or acyl group, contain at least one free amino group and at least one -COOH or -SO₃H group in the molecule and which are capable of forming inner salts. Examples of suitable ampholytic surfactants are N-alkyl glycines, N-alkyl propionic acids, N-alkylaminobutyric acids, N-alkyliminodipropionic acids, N-hydroxyethyl-N-alkylamidopropyl glycines, N-alkyl taurines, N-alkyl sarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids containing around 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacyl-aminoethyl aminopropionate and C_{12/18} acyl sarcosine.

The **superfatting agents** used may be such substances as, for example, lanolin and lecithin and polyethoxylated or acylated lanolin and lecithin derivatives, polyol fatty acid esters, monoglycerides and fatty acid alkanolamides, the latter also serving as foam stabilizers.

Suitable pearlescent waxes are, for example, alkylene glycol esters, particularly ethylene glycol distearate; fatty acid alkanolamides, especially cocofatty acid diethanolamide; partial glycerides, especially stearic acid monoglyceride; esters of polybasic, optionally hydroxysubstituted carboxylic acids with fatty alcohols containing 6 to 22 carbon atoms, especially long-chain esters of tartaric acid; fatty compounds, for example fatty alcohols, fatty ketones, fatty aldehydes, fatty ethers and fatty carbonates which contain a total of at least 24 carbon atoms, especially laurone and distearyl ether; fatty acids, such as stearic acid, hydroxystearic acid or behenic acid, ring opening products of olefin epoxides containing 12 to 22 carbon atoms with fatty alcohols containing 12 to 22 carbon atoms and/or polyols containing 2 to 15 carbon atoms and 2 to 10 hydroxyl groups; and mixtures thereof.

Suitable **consistency regulators** are, above all, fatty alcohols containing 12 to 22 and preferably 16 to 18 carbon atoms and, in addition,

partial glycerides. These substances are preferably used in combination with alkyl oligoglucosides and/or fatty acid-N-methyl glucamides of the same chain length and/or polyglycerol poly-12-hydroxystearates. Suitable **thickeners** are, for example, polysaccharides, more particularly xanthan gum, guar guar, 5 agar agar, alginates and tyloses, carboxymethyl cellulose and hydroxyethyl cellulose, relatively high molecular weight polyethylene glycol monoesters and diesters of fatty acids, polyacrylates (for example Carbopol® [Goodrich] or Synthalens® [Sigma]), polyacrylamides, polyvinyl alcohol and polyvinyl pyrrolidone, surfactants such as, for example, ethoxylated fatty acid glycerides, esters of fatty acids with polyols such as, for example, pentaerythritol or trimethylol propane, narrow-range fatty alcohol ethoxylates or alkyl oligoglucosides and electrolytes such as sodium chloride and ammonium chloride.

Suitable **cationic polymers** are, for example, cationic cellulose 15 derivatives such as, for example, the quaternized hydroxyethyl cellulose available under the name of Polymer JR 400® from Amerchol, cationic starch, copolymers of diallyl ammonium salts and acrylamides, quaternized vinyl pyrrolidone/vinyl imidazole polymers such as, for example, Luviquat® (BASF), condensation products of polyglycols and amines, quaternized collagen 20 polypeptides such as, for example, Lauryldimonium Hydroxypropyl Hydrolyzed Collagen (Lamequat®L Grünau), quaternized wheat polypeptides, polyethyleneimine, cationic silicone polymers such as, for example, Amidomethicone, copolymers of adipic acid and dimethyl aminohydroxypropyl diethylenetriamine (Cartaretine®, Sandoz), copolymers of acrylic acid with 25 dimethyl diallyl ammonium chloride (Merquat® 550, Chemviron), polyamino-polyamides as described, for example, in **FR-A 2252840** and crosslinked water-soluble polymers thereof, cationic chitin derivatives such as, for example, quaternized chitosan, optionally in microcrystalline distribution, condensation products of dihaloalkyls such as, for example, dibromobutane 30 with bis-dialkylamines such as, for example, bis-dimethylamino-1,3-propane,

cationic guar gum such as, for example, Jaguar® CBS, Jaguar® C-17, Jaguar® C-16 of Celanese, quaternized ammonium salt polymers such as, for example, Mirapol® A-15, Mirapol® AD-1, Mirapol® AZ-1 of Miranol.

Suitable **silicone compounds** are, for example, dimethyl polysiloxanes, methyl phenyl polysiloxanes, cyclic silicones and amino-, fatty acid-, alcohol-, polyether-, epoxy-, fluorine- and/or alkyl-modified silicone compounds which may be both liquid and resin-like at room temperature. Typical examples of **fats** are glycerides while suitable **waxes** are *inter alia* beeswax, carnauba wax, candelilla wax, montan wax, paraffin wax or microwaxes, optionally in combination with hydrophilic waxes, for example cetostearyl alcohol, or partial glycerides. Suitable **stabilizers** are metal salts of fatty acids such as, for example, magnesium, aluminium and/or zinc stearate. **Biogenic agents** in the context of the invention are, for example, tocopherol, tocopherol acetate, tocopherol palmitate, ascorbic acid, retinol, bisabolol, allantoin, phytantriol, panthenol, AHA acids, amino acids, ceramides, pseudoceramides, essential oils, plant extracts and vitamin complexes. Suitable **antidandruff agents** are climbazol, octopirox and zinc pyrethion. Typical **film formers** are, for example, chitosan, microcrystalline chitosan, quaternized chitosan, polyvinyl pyrrolidone, vinyl pyrrolidone/vinyl acetate copolymers, polymers of the acrylic acid series, quaternary cellulose derivatives, collagen, hyaluronic acid and salts thereof and similar compounds. Suitable **swelling agents** for aqueous phases include montmorillonites, clay minerals, Pemulen and alkyl-modified Carbopol types (Goodrich).

In the context of the invention, **UV filters** are organic compounds which are capable of absorbing ultraviolet rays and of releasing the energy absorbed in the form of longer wave radiation, for example heat. Typical examples are 4-aminobenzoic acid and esters and derivatives thereof (for example 2-ethylhexyl-p-dimethylaminobenzoate or p-dimethylaminobenzoic acid octyl ester), methoxycinnamic acid and derivatives thereof (for example 4-methoxycinnamic acid-2-ethylhexyl ester), benzophenones (for example

oxybenzone, 2-hydroxy-4-methoxybenzophenone), dibenzoyl methanes, salicylate esters, 2-phenyl benzimidazole-5-sulfonic acid, 1-(4-tert.butyl-phenyl)-3-(4'-methoxyphenyl)-propane-1,3-dione, 3-(4'-methyl)-benzylidene-bornan-2-one, methylbenzylidene camphor and the like. Other suitable UV 5 filters are finely disperse metal oxides and salts, for example titanium dioxide, zinc oxide, iron oxide, aluminium oxide, cerium oxide, zirconium oxide, silicates (talcum) and barium sulfate. The particles should have an average diameter of less than 100 nm, preferably from 5 to 50 nm and more preferably from 15 to 30 nm. They may be spherical in shape although ellipsoidal 10 particles or other non-spherical particles may also be used. Besides the two above-mentioned groups of primary light filters, secondary light filters of the antioxidant type, which interrupt the photochemical reaction chain initiated when UV radiation penetrates into the skin, may also be used. Typical examples of these secondary light filters are Superoxid-Dismutase, tocopherols (vitamin E) and ascorbic acid (vitamin C). 15

In addition, **hydrotropes** such as, for example, ethanol, isopropyl alcohol or polyols may be used to improve flow behavior. Suitable polyols preferably contain 2 to 15 carbon atoms and at least two hydroxyl groups. Typical examples are

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- glycerol;
- alkylene glycols such as, for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol and polyethylene glycols having an average molecular weight of 100 to 1,000 dalton;
- 25 • technical oligoglycerol mixtures with a degree of self-condensation of 1.5 to 10 such as, for example, technical diglycerol mixtures with a diglycerol content of 40 to 50% by weight;
- methylol compounds such as, in particular, trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- 30 • lower alkyl glucosides, particularly those containing 1 to 8 carbon atoms

in the alkyl group, for example methyl and butyl glucoside;

- sugar alcohols containing 5 to 12 carbon atoms such as, for example, sorbitol or mannitol;
- sugars containing 5 to 12 carbon atoms such as, for example, glucose or sucrose and
- aminosugars such as, for example, glucamine.

Suitable **preservatives** are, for example, phenoxyethanol, formaldehyde solution, parabens, pentanediol or sorbic acid.

Examples of **perfume oils** include the extracts of blossoms (lavender, rose, jasmine, neroli), stems and leaves (geranium, patchouli, petitgrain), fruits (anise, coriander, caraway, juniper), fruit peel (bergamot, lemon, orange), roots (nutmeg, angelica, celery, cardamon, costus, iris, calamus), woods (sandalwood, pockwood, cedarwood, rosewood), herbs and grasses (tarragon, lemon grass, sage, thyme), needles and branches (spruce, fir, pine, dwarf pine), resins and balsams (galbanum, elemi, benzoin, myrrh, olibanum, opopanax). Animal raw materials, for example musk, civet and beaver, may also be used. Suitable synthetic and semisynthetic perfume oils are Ambroxan, eugenol, isoeugenol, citronellal, hydroxycitronellal, geraniol, citronellol, geranyl acetate, citral, ionone and methyl ionone.

The total percentage content of auxiliaries and additives may be from 1 to 50% by weight and is preferably from 5 to 40% by weight, based on the particular formulation. The formulations may be prepared by standard cold or hot processes and are preferably produced by the phase inversion temperature method.

Finally, the present invention also relates to a process for coloring keratin fibers in which human hair is contacted with formulations which contain esterquats as emulsifiers in addition to oxidation or substantive hair dyes.

Examples

Example 1

5 An emulsion containing 33.3 g of Dehyquart® AU-46 (methyl-
quaternized dipalm oil fatty acid triethanolamine ester, methyl sulfate salt,
Pulcra S.A., Barcelona), 9 g of C_{8/18} alkyl glucoside, 9 g of colloidal silica, 3
g of ammonium chloride, aqueous ammonia solution to 100 g (pH = 10.5) was
prepared by mixing at 70°C. 7.5 mmoles of a primary intermediate (N,N'-bis-
10 (4-aminophenyl)-piperidine) and 7.5 mmoles of a secondary intermediate
(resorcinol) were then stirred into the emulsion at 20°C. Oxidative develop-
ment was then carried out with hydrogen peroxide. The hair color obtained
was dark blond.

15 **Example 2**

An emulsion containing 33.3 g of Dehyquart® AU-46, 9 g of C_{8/18} alkyl
glucoside, 9 g of colloidal silica, 3 g of ammonium chloride, aqueous
ammonia solution to 100 g (pH = 10.5) was prepared as in Example 1. 7.5
mmoles of 2,4,5,6-tetraaminopyridine and 7.5 mmoles of 2,6-bis-(2-hydroxy-
20 ethylamino)-toluene were stirred into the PIT emulsion at 20°C. Oxidative
development was again carried out with hydrogen peroxide. The hair color
obtained was deep red.

Examples 3 to 15

25 The following hair coloring creme emulsions were then "cold"-prepared
on the basis of these Examples (water to 100% by weight):

creme base of Example 1 or 2	: 50.0% by weight
primary intermediate	: 7.5 mmoles
30 secondary intermediate	: 7.5 mmoles
Na ₂ SO ₃ (inhibitor)	: 1.0% by weight

H 3015

18

(NH₄)₂SO₄ : 1.0% by weight
conc. ammonia solution : to pH 10

The components were mixed in the above order. After addition of the
5 oxidation dye precursors and the inhibitor, the pH value of the emulsion was
first adjusted to 10 with concentrated ammonia solution, after which the
emulsion was made up with water to 100 g. Oxidative development of the
color was carried out with hydrogen peroxide solution as the oxidizing
solution. To this end, 50 g of hydrogen peroxide solution (1, 3 or 9%) were
10 added to and mixed with 100 g of the emulsion. The coloring creme was
applied to approximately 5 cm long tresses of standardized, 90% grey but not
specially pretreated human hair and left thereon for 30 minutes at 32°C. After
the coloring process, the hair was rinsed, washed with a standard shampoo
and then dried. The colors listed in Table 1 were obtained:

Table 1

Hair colors

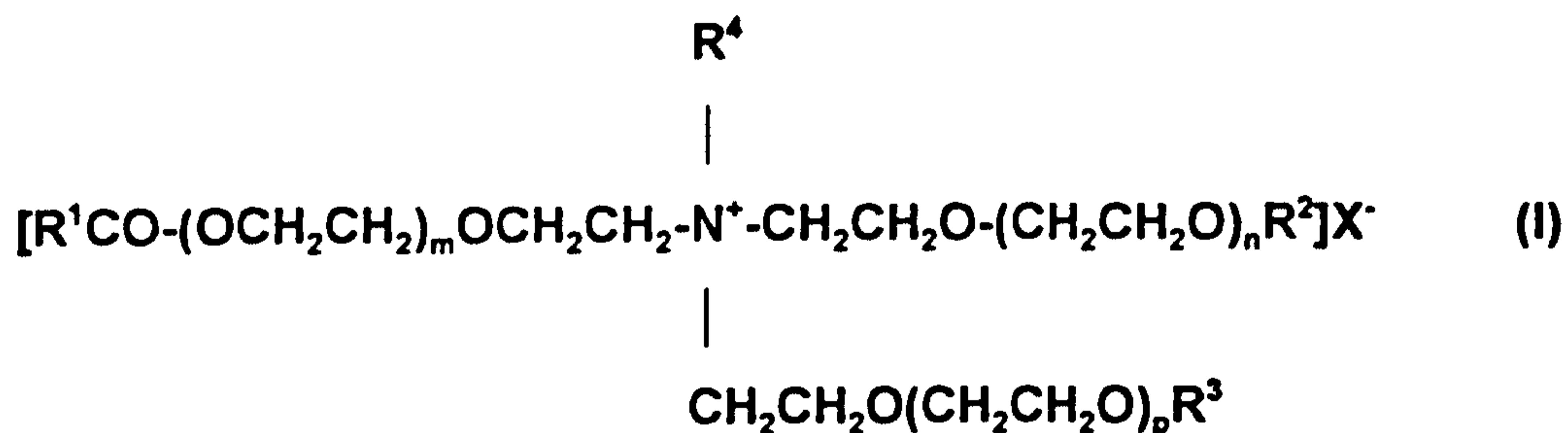
Secondary Intermediate	Primary Intermediate	Substantive Dye	c[H ₂ O ₂]	Color
2,6-Bis-(2-hydroxyethylamino)-toluene	2,4,5,6-Tetraamino-pyrimidine	-	3	Deep red
2,6-Bis-(2-hydroxyethylamino)-toluene	4-Hydroxy-2,5,6-triaminopyrimidine	-	3	Madder red
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Dimethylamino-4,5,6-triaminopyrimidine	-	3	Brown-red
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Methylamino-4,5,6-triaminopyrimidine	-	3	Red
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Piperidyl-4,5,6-triaminopyrimidine	-	3	Madder red
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Morpholino-4,5,6-triaminopyrimidine	-	3	Madder red
2-Morpholino-4,5,6-triaminopyrimidine + 2,7-dihydroxynaphthalene	2,4,5,6-Tetraamino-pyrimidine	-	3	Copper red
2,6-Bis-(2-hydroxyethylamino)-toluene	2-(2-Hydroxyethyl)-1,4-diaminobenzene	-	1	Violet
2,6-Bis-(2-hydroxyethylamino)-toluene	2-(2-Hydroxyethyl)-1,4-diaminobenzene	-	9	Violet
2,6-Bis-(2-hydroxyethylamino)-toluene	2,4,5,6-Tetraamino-pyrimidine + 2,5-diaminotoluene	-	1	Grey-ruby
2,6-Bis-(2-hydroxyethylamino)-toluene	2,4,5,6-Tetraamino-pyrimidine + 2,5-diaminotoluene	-	9	Deep magenta
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Dimethylamino-4,5,6-triaminopyrimidine	4-(3'-Trimethyl ammonium phenyl azo)-1-phenyl-3-methyl pyrazolone chloride	1	Cinnabar
2,6-Bis-(2-hydroxyethylamino)-toluene	2-Dimethylamino-4,5,6-triaminopyrimidine	4-(3'-Trimethyl ammonium phenyl azo)-1-phenyl-3-methyl pyrazolone chloride	9	Orange-red

Article 34 Amendment

CLAIMS

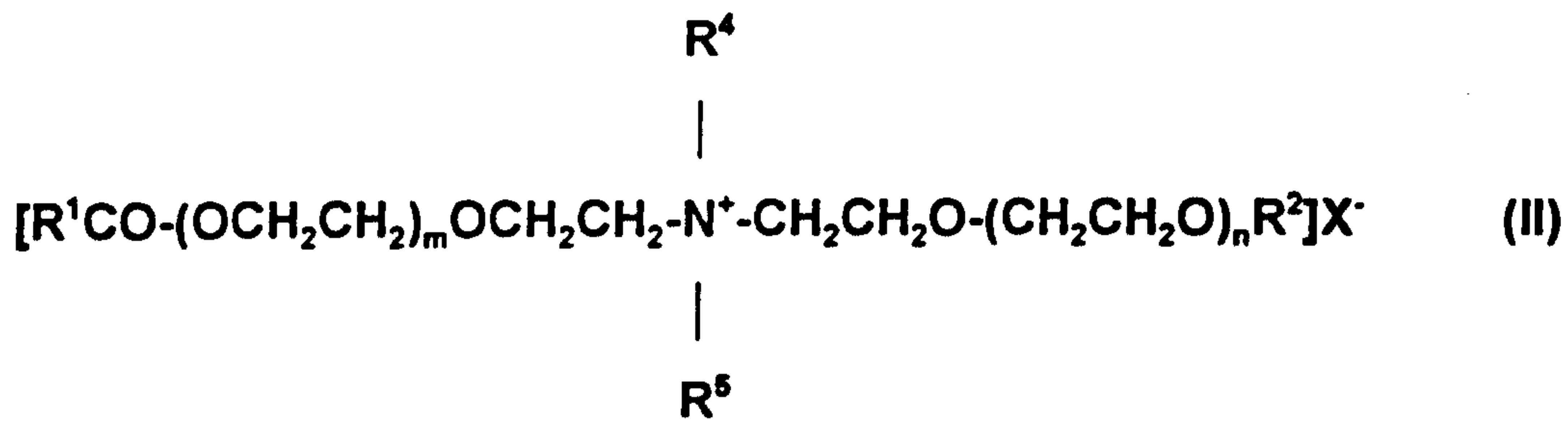
1. The use of esterquats as emulsifiers for hair dyes for the production of formulations for coloring keratin fibers.

2. The use claimed in claim 1, characterized in that esterquats corresponding to formula (I):



in which $\mathbf{R^1CO}$ is an acyl group containing 6 to 22 carbon atoms $\mathbf{R^2}$ and $\mathbf{R^3}$ independently of one another represent hydrogen or have the same meaning as $\mathbf{R^1CO}$, $\mathbf{R^4}$ is an alkyl group containing 1 to 4 carbon atoms or a $(\mathbf{CH_2CH_2O})_q\mathbf{H}$ group, m , n and p together stand for 0 or numbers of 1 to 12, q is a number of 1 to 12 and $\mathbf{X^-}$ is halide, alkyl sulfate or alkyl phosphate, are used.

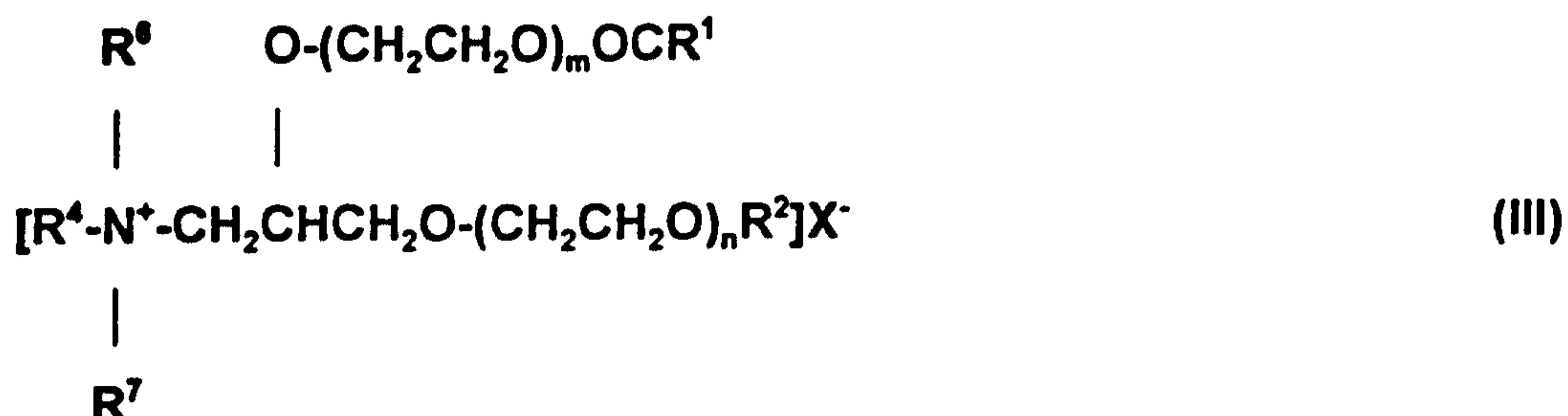
3. The use claimed in claim 1, characterized in that esterquats corresponding to formula (II):



in which $\mathbf{R^1CO}$ is an acyl group containing 6 to 22 carbon atoms, $\mathbf{R^2}$ is hydrogen or has the same meaning as $\mathbf{R^1CO}$, $\mathbf{R^4}$ and $\mathbf{R^5}$ independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together

stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate,
are used.

4. The use claimed in claim 1, characterized in that esterquats corresponding to formula (III):



in which R¹CO is an acyl group containing 6 to 22 carbon atoms, R² is hydrogen or has the same meaning as R¹CO, R⁴, R⁶ and R⁷ independently of one another are alkyl groups containing 1 to 4 carbon atoms, m and n together stand for 0 or numbers of 1 to 12 and X stands for halide, alkyl sulfate or alkyl phosphate,

are used.

5. The use claimed in claims 1 to 4, characterized in that the esterquats are used in quantities of 0.1 to 5% by weight, based on the formulations.

6. The use claimed in claims 1 to 5, characterized in that substantive hair dyes or oxidation hair dyes are used.

7. The use claimed in claims 1 to 6, characterized in that the hair dyes are used in quantities of 0.001 to 1% by weight, based on the formulation.

25 8. The use claimed in claims 1 to 7, characterized in that oils selected from the group consisting of Guerbet alcohols based on fatty alcohols containing 6 to 18 carbon atoms, esters of linear C₆₋₂₂ fatty acids with linear C₆₋₂₂ fatty alcohols, esters of branched C₆₋₁₃ carboxylic acids with linear C₆₋₂₂ fatty alcohols, esters of linear C₆₋₂₂ fatty acids with branched alcohols, esters of linear and/or branched fatty acids with polyhydric alcohols and/or Guerbet

alcohols, triglycerides based on C₆₋₁₀ fatty acids, liquid mono-/di-/triglyceride mixtures based on C₆₋₁₈ fatty acids, esters of C₆₋₂₂ fatty alcohols and/or Guerbet alcohols with aromatic carboxylic acids, vegetable oils, branched primary alcohols, substituted cyclohexanes, linear C₆₋₂₂ fatty alcohol carbonates, Guerbet carbonates, esters of benzoic acid with linear and/or branched C₆₋₂₂ alcohols, dialkyl ethers, ring-opening products of epoxidized fatty acid esters with polyols, silicone oils and/or aliphatic or naphthenic hydrocarbons are additionally used.

9. The use claimed in claim 7, characterized in that the oils are used in quantities of 10 to 70% by weight, based on the formulations.