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SHAMPOOS

Armin Hiestand, Binningen, Switzerland, assignor to Ciba Limited, Basel, Switzerland, a Swiss company

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14 Claims. (Cl. 252—152)

This is a continuation-in-part of application Ser. No. 232,608, filed Oct. 23, 1962, now abandoned.

The present invention provides shampoos that contain

(*a*) A cationic compound containing at least one aliphatic hydrocarbon residue with more than 7, preferably 11 to 18, carbon atoms, as well as at least one tertiary or quaternary nitrogen atom present in salt-like form, and

(*b*) A water-soluble reaction product of an alcohol with 6 to 11 carbon atoms having a branched hydrocarbon radical and whose main chain contains at least 5 carbon atoms, with up to 15 molecular proportions of ethylene oxide.

It is known to use in shampoos simultaneously cationic compounds and ethylene oxide adducts derived from linear higher fatty alcohols, for example n-dodecyl alcohol. Compared with such known shampoos the preparations of the invention are distinguished by a vastly superior lathering power and stability of the lather.

The outstanding lathering power of the new shampoos is all the more surprising as the above-mentioned cationic components (*a*) and the non-ionic components (*b*) by themselves either have a completely inadequate or no lathering power at all on hair.

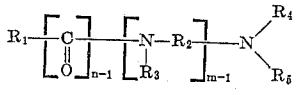
It is another surprising advantage of the preparations of the invention that their washing power is such that it ensures on one hand a completely adequate washing effect on dirty hair, while on the other hand this is not accompanied by an undesirable defatting, drying, irritation or the like of the hair or scalp respectively such as is connected with an excess washing effect.

The so-called "poissage-effect" which often occurs on application of shampoos containing cationic ingredients and which finds its expression in hair sticking together, more especially when it is subsequently rinsed, practically does not crop up with the present shampoos. It is another of their advantages that they have no unpleasant odour of their own or one that would render perfuming difficult.

Hair treated with one of the new shampoos has a soft, fluffy feel and a pleasing silky sheen, it has no electrostatic charge and is easy to brush and comb.

The afore-mentioned valuable properties of the hair are obtained more especially with those preparations of the invention which contain a hair shampoo preparation which contains

(1) As cation active component a member selected from the group consisting of (*a*) a tertiary amine salt of the compound of the formula



in which

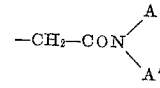
n represents a number of at most 2,

m represents a number of at most 3,

R_1 represents an aliphatic hydrocarbon radical with 11 to 18 carbon atoms,

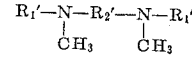
R_2 represents an alkalene with 2 to 6 carbon atoms,

R_3, R_4 and R_5 each represent a member selected from the group consisting of a hydrogen atom, an alkyl radical with at most 2 carbon atoms, a hydroxyalkyl radical with at most 3 carbon atoms, and the radical



where A and A′ each represents a member selected from the group consisting of a hydrogen atom, the methyl radical and the hydroxyethyl radical with a cosmetically acceptable acid,

(*b*) A tertiary amine salt of a compound of the formula

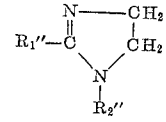


in which R_1' represents an aliphatic hydrocarbon radical with 11 to 18 carbon atoms, and

R_2' represents a member selected from the group consisting of an alkylene radical containing 2 to 6 carbon atoms and the radical $-CH_2-CHOH-CH_2-$, with a cosmetically acceptable acid,

(*c*) A quaternary ammonium salt of a compound of the formulae set forth above under (*a*) and (*b*) with a member selected from the group consisting of methyl iodide, dimethyl sulfate, benzyl chloride, a polyglycol chloride containing at most 6 carbon atoms and ethylene chlorohydrine,

(*d*) A compound of the formula



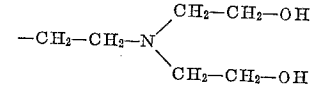
in which

R_1'' represents a hydrocarbon radical with 11 to 18 carbon atoms, and

R_2'' represents a member selected from the group consisting of a hydrogen atom, a radical of the formula

$$-CH_2-CH_2-NH_2$$

and a radical of the formula



(2) As nonionic component a water-soluble reaction product of an alcohol which contains 6 to 11 carbon atoms, whose hydrocarbon radical is branched and whose

main-chain contains at least 5 carbon atoms, with at most 15 mols of ethylene oxide,

(3) Water, and

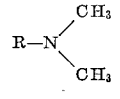
(4) A cosmetically acceptable acid in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0, and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

With regard to their non-ionic ingredient (2) those preparations of the invention deserve to be given preference which contain a compound obtained by reacting 5 to 10 molecular proportions of ethylene oxide with 1 molecular proportion of the alcohol referred to above under (2).

Particularly useful are those new mixtures whose non-ionic ingredient has been prepared by adding 5 to 10 molecular proportions of ethylene oxide on to a secondary or preferably primary aliphatic alcohol of the kind described above.

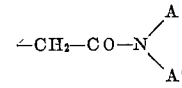
Surprisingly, it has further been found that those shampoos of the invention possess particularly good properties and are distinguished, for example, by the absence of an unpleasant odour of their own even when examined critically, which contain as the non-ionic ingredient an ethylene oxide adduct which, before being incorporated in the shampoo, has been subjected to a special purifying treatment, for example by expulsion of undesired substances by distillation. Such a purification operation may consist, for example, in the distillative expulsion from a commercial ethylene oxide adduct under a very good water-jet vacuum at about 160 to 180° C. or in a falling-film distillation. It has further been found that particularly valuable, purified products are obtained in this manner when the commercial ethylene oxide adduct liquefied by heating is mixed in the undiluted form with a sufficiency of an inorganic or organic acid to establish a weakly acidic reaction of the resulting solution of 10% strength. This may be achieved with concentrated acids, such as phosphoric acid of 85% strength, lactic acid of 90% strength, tartaric acid or citric acid. It is of special advantage to heat the batch to a distillation temperature corresponding to the boiling point of the monohydroxyethyl compound or of the monoglycol or diglycol ether of the alcohol selected as starting material.

The amine compound on which the cationic ingredient (*a*) is based can be prepared by methods known in the art from the corresponding amine bases or their reaction products with fatty acids or derivatives thereof, hydroxyalkylation agents, for example ethylene oxide, alkylating and acylating agents, for example chloracetic acid or with derivatives thereof, and then converted in known manner by reaction with acids into the amine salts or with quaternating agents into the quaternary ammonium salts. Suitable starting materials for the manufacture of the cationic ingredient to be used according to the invention are tertiary amines of the formula

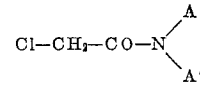


wherein R represents an alkyl with 12–16 carbon atoms, for example, N-dimethyl-dodecylamine, N-dimethyl-hexadecylamine and their hydroxyalkylation products, also diamines, for example N-dodecyl-ethylenediamine, tetramethylenediamine and hexamethylenediamine, N-octadecyl-ethylenediamine, N-dodecyl-propylenediamine, N-hexadecyl-propylenediamine and N-octadecyl-propylenediamine; also reaction products of such N-alkylene-polyamines with an alkylene oxide, such as ethylene oxide or propylene oxide, for example N-dodecyl-N:N'-dihydroxyethyl-ethylenediamine, N - dodecyl-N:N'-dihydroxyethyl-propylenediamine and N-octadecyl-N:N'-dihydroxyethyl-propylenediamine. Furthermore, there may be used as starting material for the cationic ingredient (*a*) contained in the new preparations the following: mono-acylation products from 1 molecular proportion of a higher fatty acid (for example lauric, myristic, palmitic, stearic or oleic acid) and 1 molecular proportion of an alkylene-polyamine such as ethylenediamine or propylenediamine and diethylenetriamine; likewise suitable are reaction products of these monoacyl derivatives with a halohydrin or alkylene oxide, such as N-lauroyl-N'-hydroxyethyl-ethylenediamine, N - palmitoyl-N'-hydroxyethyl-ethylenediamine, N-stearoyl-N'-hydroxyethyl-ethylenediamine, N-lauroyl-N'-hydroxyethyl-propylenediamine and N-lauroyl-hydroxyethyl-diethylenetriamine.

Those compounds of the general Formula 1, which are used in the form of their salts as cationic ingredient (*a*) of the new preparations and contain a radical of the formula



(in which formula A and A' have the above meanings) are accessible by reacting the amine concerned with chloracetic acid or with a compound of the general formula



(in which A and A' have the above meanings), more especially with chloracetamide or N:N-[di-(β-hydroxyethyl)]-chloracetamide.

The conversion of the selected tertiary amines into salts used as cationic ingredient of the new preparations is achieved by the usual formation of salts with cosmetically acceptable acids which may be inorganic, such as hydrochloric acid, and phosphoric acid, or organic acids as acetic acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycolic acid and mixtures of the above-mentioned acids. Quite generally speaking, any acid may be used that furnishes with the harmless amine salts that are neither toxic nor irritate the scalp, more especially the salts mentioned specifically below, such as are used in the present invention to establish the desired pH range.

To convert the tertiary amine compounds into quaternary ammonium compounds—which may likewise and with special advantages be used as cationic ingredient of the new preparations—they are reacted in known manner with a quaternating agent, for example methyl iodide, dimethyl sulfate, benzyl chloride or with ethylene chlorohydrin or with a polyglycol chloride.

It has further been found that the above-mentioned valuable properties of the new shampoos are particularly evident in those preparations in which the ratio of the cationic ingredient (*a*) to the non-ionic ingredient (*b*) ranges from 1:1 to 1:30, preferably from 1:2 to 1:10. More especially at a ratio of (*a*):(*b*) of 1:3 it was found that the new preparations had surprisingly advantageous properties insofar as their lathering power and the stability of the lather, good washing power, gentleness towards the skin and absence of the poissage-effect are concerned.

When the above-mentioned ratios are used, the new preparations have a particularly long shelf-life.

The preparations of the invention should have a moderately acidic to neutral reaction, for example ranging from pH 3.0 to 7.0. The desired pH value may be adjusted with any inorganic or organic acidic compound acceptable for use in cosmetics, for example with acetic acid or phosphoric acid, or with acid phosphates, or adipic, tartaric, malic, nitrilotriacetic, ethylene-diamine-tetraacetic, citric, lactic or glycolic acid.

Likewise suitable for this purpose are mixtures of inorganic and organic acids, for example mixtures of phosphoric acid and citric acid.

The new shampoos containing the new combinations are obtained by simply mixing and dissolving the ingredients, if desired with further addition of compounds conventionally contained in shampoos, such as perfume, dyestuffs, bleaching agents or thickening agents.

There may be further added fatty acid alkanol-amides, for example coconut oil fatty acid hydroxyethyl-amide. The new preparations may be prepared in solid, pasty or liquid form. They are applied in the known hairdressing manner.

Very favourable results were obtained with hair shampoos of the composition set forth above in this application, wherein the weight ratio of cation-active component (1) to nonionic component (2) ranges from 1:1 to 1:100.

Parts in the following examples are parts by weight.

Example 1

(*a*) The non-ionic polyglycol ethers listed in the following Tables I to V were examined for their lathering power. The results are shown in the tables under "Lather volume I."

(*b*) The cationic compounds listed in the following

Tables I to V were examined for their lathering power. The results are shown in the tables under "Lather volume II."

(*c*) Combinations of the cationic and non-ionic compounds shown in Tables I to V were examined for their lathering power. The results are shown in the tables under "Lather volume C."

The amounts of the ingredients making up the combinations are shown in the tables under "C"; "I" refers to the percentage of the non-ionic share of the total weight of the shampoo solution, and "II" refers to the cationic share of the total weight of the solution. The remainder of the total weight is accounted for by water and the amount of acid necessary to establish the pH value.

The shampoo solutions listed in the following Tables I, II and V were prepared by dissolving the non-ionic compound and the cationic compound in water with addition of a sufficiency of citric acid to establish a pH value of 4 to 4.5 of the individual solutions.

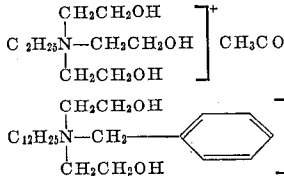
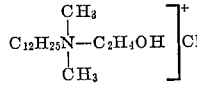
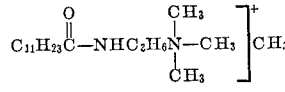
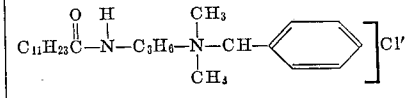
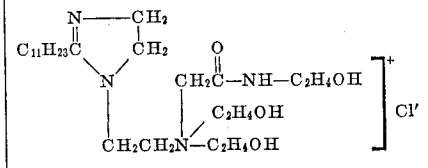
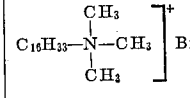
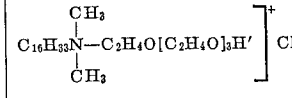
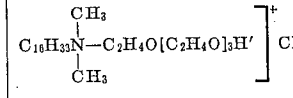
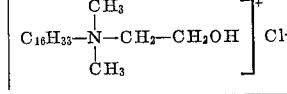
The term "lather volume" in the following Tables I to V refers to the amount of lather in cc. produced by twice washing 10 g. of homogeneously dirtied raw wool, moistened with 30 g. water at 35° C. with 2.7 cc. of the individual shampoo solution in each case. The indices "1" and "2" underneath "lather volume" in Tables I to V refer to the first and second wash each performed in the method employed for determining the lather volume.

TABLE I

	Non-ionic compounds	Lather volume in cc. I		Cationic compounds containing a quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C in cc.	
		1	2		1	2		1	2
1	2-ethylhexanol +5 mols ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	12+4	140	260
2	2-ethylhexanol +5 mols ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	13+3	100	240
3	2-ethylhexanol +5 mols ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	10+6	100	170
4	Isooctanol +5 mols ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	12+4	135	275
5	3:5:5-trimethylhexanol +5 mol ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	12+4	140	300
6	3:5:5-trimethylhexanol +10 mol ethylene oxide	0	0	$C_{16}H_{33}-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+Cl'$	5	5	12+4	70	120

The cationic compound used in the mixtures shown in Table I was obtained by heating the compound $C_{16}H_{33}N(CH_3)_2$ for 24 hours at 100° C. with excess of 10% by weight of ethylene chlorohydrin above the stoichiometrically required amount.

TABLE II

	Non-ionic compounds	Lather volume I		Cationic compounds containing a quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
1	2-ethylhexanol +5 mol ethylene oxide	0	0		0	0	12+4	100	210
2	do	0	0		0	0	12+4	85	110
3	do	0	0		5	10	12+4	130	320
4	do	0	0		5	10	12+4	150	330
5	do	0	0		0	0	12+4	105	275
6	do	0	0		0	0	12+4	40	150
7	do	0	0		0	0	12+4	80	170
8	do	0	0		0	0	12+4	60	130
9	2-ethylhexanol +5 mol ethylene oxide with addition of 2% by weight of polyvinyl pyrrolidone of mean molec. weight of 400,000 to 700,000.	0	0		0	0	12+4	70	150
10	2-ethylhexanol +5 mol ethylene oxide.	0	0		0	0	[1] 12+4	125	240

[1] The pH value of the solution is adjusted to 6.9.

TABLE IIa

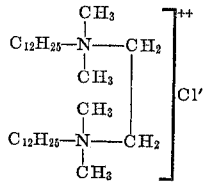
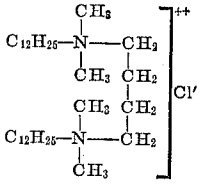
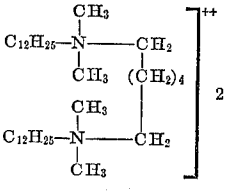
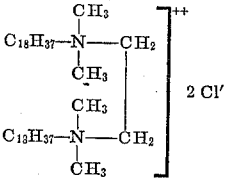
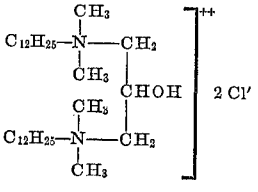
	Non-ionic compounds	Lather volume I		Cationic compounds containing more than one quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
1	2-ethylhexanol +5 mol ethylene oxide	0	0		10	10	12+4	250	500
2	do	0	0		0	0	12+4	150	350
3	do	0	0		5	5	12+4	110	340
4	do	0	0		0	0	12+4	70	200
5	do	0	0		0	0	12+2 12+4 10+6	30 105 85	110 235 170

TABLE III

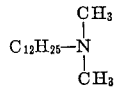
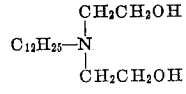
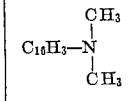
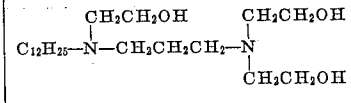
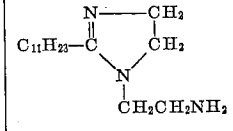
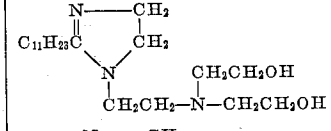
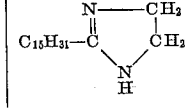
	Non-ionic compounds	Lather volume I		Cationic compounds containing at least one tertiary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
1	2-ethylhexanol+5mol ethylene oxide	0	0		25	75	12+4	160	340
2	do	0	0		0	0	12+4	60	220
3	do	0	0		0	0	12+4	130	360
4	do	0	0		10	25	12+4	150	340
5	do	0	0		25	35	12+4	90	180
6	do	0	0		35	65	12+4	190	500
7	do	0	0		0	0	12+4	120	220

TABLE IIIa

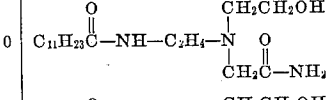
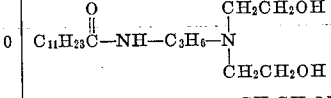
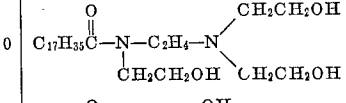
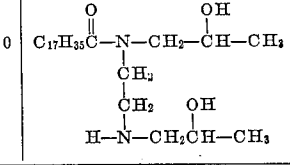
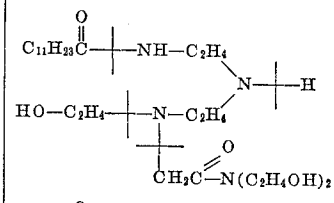
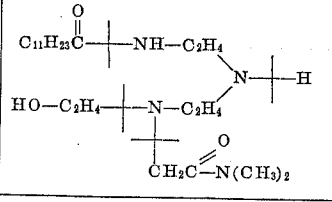
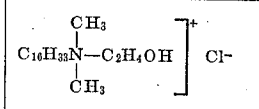
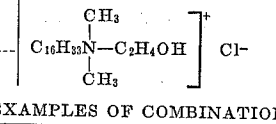
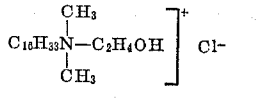
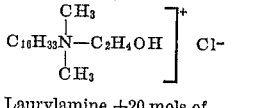
	Non-ionic compounds	Lather volume I		Cationic compounds containing at least one tertiary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
8	2-ethylhexanol +5 mol ethylene oxide	0	0		0	0	12+4	150	350
9	do	0	0		10	10	12+4	170	450
10	do	0	0		0	15	12+4	90	220
11	do	0	0		5	5	12+4	35	125

TABLE III*b*

	Non-ionic compounds	Lather volume I		Cationic compounds containing at least one tertiary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
------	2-ethylhexanol +5 mol ethylene oxide---	0	0		5	5	12+4	260	500
2------	------do------	0	0		5	10	12+4	240	50

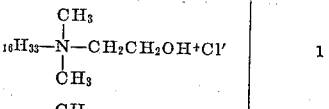
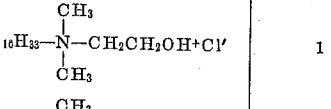
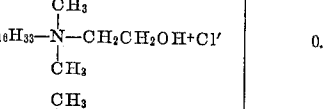
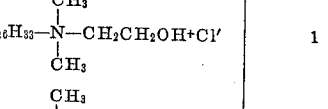
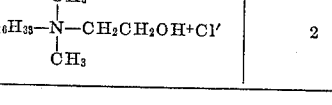
Similar results are obtained by adjusting the combinations of Tables I to III*b* to a pH value from 4 to 4.5, instead of with citric acid, with one of the following acids: adipic, tartaric, phosphoric, lactic, acetic, ethylenediamine-tetraacetic, nitrilotriacetic or glycollic acid.

Similar, very advantageous results with regard to lathering power and washing power were obtained with aqueous solutions adjusted with citric acid to a pH value from 4 to 4.5, containing the following combinations of a non-ionic compound with a cationic compound:

(I) Non-ionic compound	(II) Cationic compound
2-ethylhexanol +10 mols of ethylene oxide.	
Isodecanol +5 mols of ethylene oxide---	
2-propylheptanol +5 mols of ethylene oxide.	
1-ethyl-, 3-ethyl-, 1-heptanol +8 mols of ethylene oxide.	
2-ethylhexanol +5 mols of ethylene oxide.	Laurylamine +20 mols of propylene oxide.

The weight ratios between the component I and the component II are the same as those set forth above in Tables I to III.

TABLE IV.—EXAMPLES OF COMBINATIONS OF (*a*) AND (*b*) USING DIFFERENT ACIDS

	Share in percent of weight of the solution	Non-ionic compound I	Share in percent of weight of the solution	Cationic compound II	Share in percent of weight of the solution	Acid component III	Lather volume C 1+II+III	
							1	2
1------	12	3:5:5-trimethylhexanol +5 mols ethylene oxide.	4		1	Adipic acid (100%)-------	175	380
2 ----	12	-----do[1]------	4		1	Tartaric acid (100%)------	190	420
3------	12	-----do------	4		0.1	Phosphoric acid (85%)----	160	320
4------	12	-----do------	4		1	Ethylenediaminotetra-acetic acid (100%).	180	380
5------	12	-----do------	4		2	Nitrilotriacetic acid (100%).	180	360

[1] With 2% coconut oil fatty acid ethanolamide.

The following Table V shows that combinations in which the non-ionic ingredient is a compound derived from a linear alcohol or from a branched alcohol having a side-chain of fewer than 5 carbon atoms or derived from an alkylphenol do not possess the advantageous properties of the preparations of the invention.

TABLE V

Non-ionic compounds	Lather volume I		Cationic compounds containing a quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C	
	1	2		1	2		1	2
2-ethylbutanol +5 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
n-Octanol +5 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	5	10
Tert. nonylphenol +8 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
Lauryl alcohol +7 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
Lauryl alcohol +12 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
Stearyl alcohol +8 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
Do [1]	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
Do [2]	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0
2-ethylbutanol +5 mol ethylene oxide +160 mol ethylene oxide	0	0	$C_{16}H_{35}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-C_2H_4OH]^+ \ Cl'$	5	5	12+4	0	0

[1] Plus 35 mol ethylene oxide.
[2] Plus 80 mol ethylene oxide.

Example 2

A shampoo was made of the composition of the product 1 in Table I. This shampoo was further admixed in each case with the thickening agents shown in Tables VI and VII:

TABLE VI

	Non-ionic compound I	Cationic compound II	Substance acting as thickening agent III	C I+II+III	Viscosity, 25° in centipoises
0	2-ethylhexanol +5 mols ethylene oxide.	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl		12 4 0	3
1	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Stearyl alcohol +80 mols ethylene oxide	12 4 10	15
2	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Stearyl alcohol +200 mols ethylene oxide	12 4 20	78
3	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Hydroabietyl alcohol +200 mols ethylene oxide.	12 4 10 12 4 20	22 61
4	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Reaction product of (a) oleyl alcohol +80 mols of ethylene oxide with (b) hexamethylene diisocyanate.	12 4 5 12 4 7.5 12 4 10 12 4 20	22 68 200 1,600
5	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Polyethylene glycol (mean molec. wt. 20,000)	12 4 5 12 4 10	15 72
6	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	A hydroxylated cellulose	12 4 1	35
7	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl	Finely "dispersed silicic acid (Aerosil", reg. trade name).	12 4 5 12 4 10	40 (1)

[1] Paste (brushable).

TABLE VII

	Non-ionic compound I	Cationic compound II	Substance acting as thickening agent III	C I+II+III	Viscosity, 25° in centipoises
1	2-ethylhexanol +5 mol ethylene oxide.	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl′	Stearylamine +80 mol ethylene oxide	12 4 10	15
2	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl′	Oleylamine +80 mol ethylene oxide	12 4 10	17
3	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl′	Stearylamine +160 mol ethylene oxide	12 4 10 12 4 20	18 50
4	do	$C_{16}H_{33}N(CH_3)_2CH_2CH_2OH]^+$ Cl′	A reaction product of 1 mol coconut oil fatty acid and 2 mols diethanolamine, with elimination of 1 mol water.	12 4 5	64

Mixtures having very valuable properties are also obtained by adding 2%, 4% and 8% of polyvinylpyrrolidone (molecular weight 400,000 to 700,000).

Example 3

The shampoos listed in Tables I to IV of Example 1 were examined as to whether they displayed the so-called pissage-effect. As is known, this effect consists in the following: When hair washed with a shampoo containing a cationic compound and then rinsed with water, salve-like, water-insoluble deposits form on the hair and, more especially in the case of women's long hair, cause it to stick. The occurrence of this sticking effect ("pissage") seems to be due to the anionic constituents of the dirt found on human hair.

In the in vitro tests 18 g. of hair dirtied with 10% of oleic acid was washed in each case with 5 g. of the shampoos listed in the Tables I to IV and then rinsed. It was found that after washing at 35° C. and rinsing, the combinations listed in Tables I to IV produced substantially no sticking of the hair.

Example 4

(*a*) The non-ionic polyglycol ether, listed in the following Tables VIII to X, was freed in a falling-film evaporator from the unreacted alcohol and the monoglycol and diglycol ethers and then examined for its lathering power. The results are shown in the Tables VIII to X under the heading "Lather volume I."

(*b*) The cationic compounds listed in the following Tables VIII to X were examined for their lathering power. The results are shown in the Tables VIII to X under the heading "Lather volume II."

(*c*) The combinations of cationic compound and non-ionic compound listed in the Tables VIII to X were examined for their lathering power. The result is listed in Tables VIII to X under "Lather volume C." The amounts of the ingredients are shown in the Table under "C," in which "I" is the percentage share of the non-ionic compound of the total weight of the shampoo solution, and "II" is that of the cationic compound. The remainder of the total weight is accounted for by water and the amount of acid needed to adjust the pH value.

TABLE VIII

	Non-ionic compounds	Lather volume I		Cationic compounds containing a quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
1	2-ethy hexanol +5mol ethylene oxide	0	0	$C_{12}H_{25}-\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CONH_2]Cl'$	0	0	12+4	115	240
2	do	0	0	$C_{12}H_{25}-\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CONHC_2H_4OH]^+Cl'$	0	0	12+4	195	380
3	do	0	0	$C_{12}H_{25}-\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CON(C_2H_5)(CH_2CH_2OH)]^+Cl$	0	0	12+4	70	160
4	do	0	0	$C_{12}H_{25}-\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CONH_2]^+Cl'$	0	0	12+4	115	240
5	do	0	0	$C_{16}H_{33}\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CONHC_2H_4OH]^+Cl'$	0	0	12+4	105	190

TABLE IX

	Non-ionic compounds	Lather volume I		Cationic compounds containing a quaternary nitrogen atom	Lather volume II		C I+II	Lather volume C	
		1	2		1	2		1	2
1	2-ethylhexanol +5 mol ethylene oxide.	0	0	$C_{11}H_{23}\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-(CH_2)_3-\overset{\overset{CH_3}{|}}{N}(CH_3)-\overset{\overset{O}{\|}}{C}-NH_2$	0	0	12+4	150	280
2	do	0	0	$C_{11}H_{23}CONH(CH_2)_3\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CONHC_2H_4OH]^+ Cl'$	0	0	12+4	140	240
3	do	0	0	$C_{17}H_{35}CONH(CH_2)_3\overset{\overset{CH_3}{|}}{N}(CH_3)-CH_2CH_2OH]^+ Cl'$	0	0	12+4	105	210

The shampoos set forth above in Tables VIII and IX were adjusted with citric acid to a pH-value of 4.0 to 4.5, with the exception of those signified by (+) which were adjusted with citric acid to pH-value of 6.9.

Good results were also obtained with shampoos of the compositions set forth above in Tables I to IV and VI to IX when the nonionic (1) and the cationic (2) compounds were used in weight proportions different from those set forth specifically in the said tables but lying within the range of 2:1 to 10:1.

Example 5

(*a*) The following mixture was prepared:

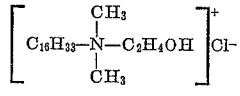
4 parts of a mixture of 1 mol of coconut fatty acid diethanolamide and 1 mol of diethanolamine,
25 parts of a condensatoin product containing 1 mol of 2-ethylhexanol and about 8 mols of ethylene oxide,
0.25 part of cetyldimethyl-(2-hydroxyethyl)-ammonium chloride,
2.5 parts of about 88% lactic acid,
3 parts of polyethylene glycol having a molecular weight of about 20,000.

The mixture was made up to 100 parts with water and a shampoo obtained to which perfumes can be added, if desired.

What is claimed is:

1. A hair shampoo preparation which consists essentially of

(1) the cationic compound of the formula



(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

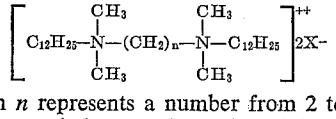
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

2. A hair shampoo preparation which consists essentially of

(1) a cationic compound of the formula



wherein *n* represents a number from 2 to 6 and X− represents a halogen anion selected from the group consisting of chlorine and bromine,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

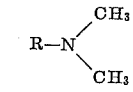
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

3. A hair preparation which consists essentially of

(1) a tertiary amine salt of a cationic compound of the formula



wherein R represents alkyl with 12 to 16 carbon atoms with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid; malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-souble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

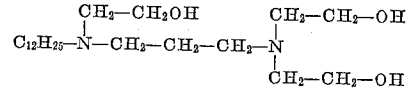
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:2 to 1:100.

4. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

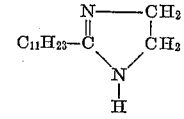
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

5. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon

atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

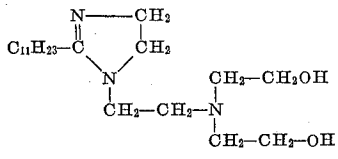
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-vaue of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

6. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

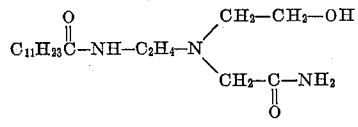
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

7. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

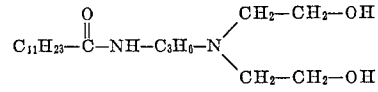
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

8. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

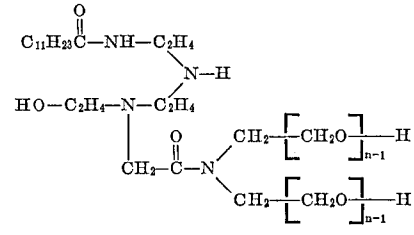
(3) water, and

(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

9. A hair shampoo preparation which consists essentially of

(1) a tertiary amine salt of the cationic compound of the formula



wherein *n* represents a whole number of at most 2, with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

(3) water, and

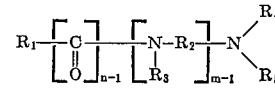
(4) a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylenediamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

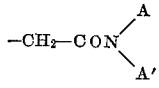
10. A hair shampoo preparation which consists essentially of

(1) a cationic compound selected from the group consisting of

(a) a tertiary amine salt of a compound of the formula



in which n represents a number of at most 2, m represents a number of at most 3, R_1 represents alkyl with 11 to 18 carbon atoms, R_2 represents alkylene with 2 to 6 carbon atoms, R_3, R_4 and R_5 each represent a member selected from the group consisting of hydrogen, alkyl with at most 2 carbon atoms, hydroxyalkyl with at most 3 carbon atoms,



where A and A' each represents a member selected from the group consisting of hydrogen, methyl and hydroxyethyl, with a cosmetically acceptable acid selected from the group consisting of acetic acid, phosphoric acid, adipic acid, tartaric acid, malic acid, nitrilotriacetic acid, ethylene-diamine-tetraacetic acid, citric acid, lactic acid, glycollic acid and mixtures thereof, and

(b) a quaternary ammonium salt of a compound of the formula set forth above under (a) with a member selected from the group consisting of methyl iodide, dimethyl sulfate, benzyl chloride, a polyglycol chloride containing at most 6 carbon atoms and ethylenechlorohydrine,

(2) a nonionic watersoluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms, whose main-chain consists of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

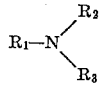
(3) water, and

(4) a cosmetically acceptable acid, as defined above in this claim under (a) in an amount which is sufficient to effect in the aqueous shampoo preparation a pH-value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

11. A hair shampoo preparation which consists essentially of

(1) a cationic quaternary ammonium salt of a compound of the formula



wherein R represents alkyl with 11 to 18 carbon atoms and R_2 and R_3 represents alkyl with at most 2 carbon atoms with ethylenechlorohydrine,

(2) a nonionic water-soluble reaction product of a saturated branched-chain alcohol with 6 to 11 carbon atoms whose main-chain consist of at least 5 carbon atoms, with 5 to 15 mols of ethylene oxide,

(3) water, and

(4) a cosmetically acceptable acid as defined above in claim **10** under (a) in an amount which is sufficient to effect in the aqueous shampoo preparation a pH value of 3.0 to 7.0,

and in which shampoo preparation the weight ratio of component (1) to component (2) ranges from 1:1 to 1:100.

12. A preparation as claimed in claim **10** which contains as further component approximately 5% by weight of a mixture of coconut fatty acid diethanolamide and diethanolamine.

13. A preparation as claimed in claim **10** which contains as a further component an effective amount of a mixture of coconut fatty acid diethanolamide and diethanolamine as a thickening agent.

14. A preparation as claimed in claim **10** which contains as a further component approximately 1–20% by weight of a thickening agent.

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LEON D. ROSDOL, *Primary Examiner.*

ALBERT T. MEYERS, *Examiner.*

S. E. DARDEN, *Assistant Examiner.*