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HAIR RINSE COMPOSITIONS OF POLYOXYPROPYLENE QUATERNARY AMMONIUM COMPOUNDS

Harry Hilfer, Port Washington, N.Y., assignor to Witco Chemical Company, Inc., New York, N.Y., a corporation of Delaware

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14 Claims. (Cl. 167—87)

My invention relates to new and improved hair rinses and is particularly concerned with the preparation of such hair rinses in the form of concentrates for use, upon dilution with water, after shampooing the hair. The invention relates, also, to the treatment of hair on the human head, after shampooing the same, to improve the combing properties of the hair, while permitting the hair to retain its curl characteristics, by subjecting the hair after shampooing to rinsing with a dilute aqueous solution containing the combination of ingredients described in detail hereafter.

Numerous hair rinse products, in the form of aqueous solutions as well as in the form of creams or lotions, have heretofore been suggested. Conventional types of rinses, long known in the art, comprise so-called acid hair rinses as, for example, ordinary lemon juice. While reasonably satisfactory so far as neutralizing the alkali left in the hair from soap or similar detergents, they are unsatisfactory in a number of respects including, for example, their inability to remove insoluble calcium and magnesium salts left in the hair after washing with soap and similar type shampoos. Various other types of hair rinses have also been suggested but, so far as I am aware, all of them have at least certain significant deficiencies which have militated against their widespread acceptance. Thus, for example, quaternary ammonium compound rinses which are conventionally used cause a relaxation in the hair thereby tending to shorten the life of permanent waves and other wave or curl treatments to which the hair has previously been subjected.

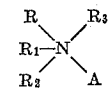
In accordance with my present invention, substantially improved hair rinse products have been produced which utilize certain particular types of compounds, as described in detail hereafter. Hair rinses made in accordance with my invention act to bring about effective removal of the soap or shampoo residues left in the hair after shampooing and rinsing, they act as lubricants to reduce tangling of the hair, and they serve to soften the hair and to facilitate or improve its combing properties. What is more, my hair rinses achieve these objects while permitting retention in the hair of the benefits imparted to it by hair curling treatments such as, for example, permanent waving.

The hair rinse compositions of the present invention, in their particularly advantageous embodiments, include (*a*) certain particular types of chemical compounds, or mixtures of such chemical compounds, which structurally are of the quaternary ammonium type, but in their activity in my hair rinse preparations manifest completely unpredictable properties in that they have no adverse effect on the curl characteristics of the hair after use, a result which is not only not realized with hair rinse compositions containing conventional quaternary ammonium compounds as an active hair conditioning ingredient, but on the contrary, is antithetical thereto, (*b*) one or more opacifying agents and lubricants, exemplified by cetyl alcohol or other higher fatty alcohols such as stearyl alcohol, lauryl alcohol and mixtures of higher fatty alcohols which are preferably solid at room temperatures; and (*c*) one or more innocuous inorganic salts which have the property of salting out the aforementioned chemical compounds so as to cause the formation of a suspension or dispersion which furnishes to the composition a cloudy effect. The

remaining ingredients comprise water and, if desired, perfume. Various supplemental ingredients can, of course, be utilized in relatively small proportions for obtaining special effects.

Certain of the quaternary ammonium type compounds having utility for the purposes of this invention are derived from low molecular weight alkyl secondary amines and cyclic amines, and can be represented by the formula

(I)

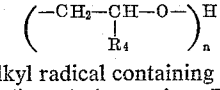


wherein R is an alkyl radical containing from 1 to 3 and more particularly from 1 to 2 carbon atoms, R_1 is an alkyl radical containing from 1 to 3 carbon atoms, or

may be a radical of a cyclic amine containing not more than 6 carbon atoms, R_2 is a polyoxyalkylene radical containing at least 18 carbon atoms and derived from an α-epoxide containing at least 3 carbon atoms, especially propyleneoxide. In those cases where R_2 is derived from propyleneoxide, there will be at least 6 of such propyleneoxide groups in R_2 and, more particularly, it is desired that R_2 contain from 8 to 30 oxypropylene groups. Where R_2 is derived from α-epoxides containing more than 3 carbon atoms, a lesser number of such oxyalkylene groups can be present, subject to the limitation of R_2 containing at least 18 atoms. R_3 is advantageously a lower alkyl or alkenyl radical containing from 1 to 4 carbon atoms; or a lower aliphatic-aryl radical containing 7 to 9 carbon atoms notably an alkaryl radical; and A is an anion. It is important for the achievements of the results to which my invention is directed that the R radical, where it is alkyl, contain not more than 3 carbon atoms and especially that it contain from 1 to 2 carbon atoms and, hence, that it be methyl or ethyl. Likewise, except where

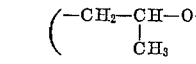
is derived from a cyclic amine, as hereafter pointed out, it is important that the R_1 radical does not contain over 3 carbon atoms, and, in any event, the maximum number of carbon atoms in R and R_1 does not exceed a total of 4 or 5. While R_2 may contain a minimum of 6 of the aforesaid oxyalkylene, particularly oxypropylene, groups, and may contain 40, 50 or 60 or even 100 or more of said groups, it is especially advantageous that the minimum number of said groups be 8 and the preferred range is 8 to 25 or 30 of said groups. The term "α-epoxide," as used herein, is intended to cover those compounds, of the type here involved, where there are two vicinal carbon atoms connected to one oxygen atom independently of the position of such group in the molecule.

The terms "polyoxyalkylene," "polyoxypropylene" and "polyoxyethylene," to the extent that they are used herein or in the claims, are employed in their usual or conventional manner. Thus, in the case of the polyoxyalkylene radical derived from α-epoxides containing from 3 to 6 carbon atoms, to wit, R_2 in the above formula, the same may be represented by



where R_4 is an alkyl radical containing from 1 to 4 carbon atoms, and, as indicated above, since R_2 contains a minimum of 18 carbon atoms, *n* is at least 6 in the case of the polyoxyalkylene radical being polyoxypropylene and

n is at least 3 in the case of the polyoxyalkylene radical being polyoxyhexylene. As indicated above, n is usually up to 60 or more. Where the polyoxyalkylene radical is polyoxypropylene, it may be represented by the formula

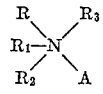


n advantageously being from 6 to 30.

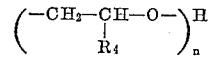
The foregoing illustrate the polyoxyalkylene and polyoxypropylene radicals where the vicinal carbons are terminal. However, the vicinal carbons need not be terminal. A typical illustration of the latter is a polyoxyalkylene radical derived from 2,3-butylene oxide.

At least most of those of the particularly preferred quaternary ammonium type compounds having utility in my hair rinse compositions which are derived from lower monoalkyl amines can be represented by the formula

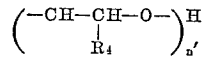
(II)



where R is an alkyl radical containing from 1 to 3, and especially from 1 to 2, carbon atoms, R_1 is



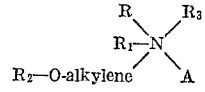
and R_2 is



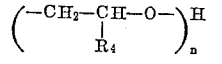
where R_4 is an alkyl radical containing from 1 to 4 carbon atoms, n and n' are numbers the sum of which preferably does not exceed 60, the total number of carbon atoms in R_1 and R_2 being at least 18; R_3 is a hydrocarbon radical selected from the group consisting of alkyl and alkenyl radicals containing not more than 4 carbon atoms, or a lower aliphatic-aromatic hydrocarbon radical containing from 7 to 9 carbon atoms; and A is an anion.

Various of those particularly preferred quaternary ammonium type compounds employed in my invention which are derived from lower dialkyl monoalkanolamines can be represented by the formula

(III)



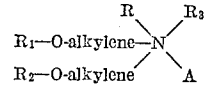
where R is an alkyl radical containing from 1 to 3, and especially from 1 to 2, carbon atoms; R_1 is an alkyl radical containing from 1 to 3 carbon atoms; alkylene contains not more than 3 carbon atoms, R_2—O is



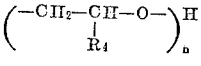
where R_4 is an alkyl radical containing from 1 to 4 carbon atoms, n is a number up to and preferably not exceeding 60, the total number of carbon atoms in R_2 being at least 18; R_3 is a hydrocarbon radical selected from the group consisting of alkyl and alkenyl radicals containing not more than 4 carbon atoms, or a lower aliphatic-aromatic hydrocarbon radical containing from 7 to 9 carbon atoms; and A is an anion.

Again, various of those of the particularly preferred quarternary ammonium type compounds used in my hair rinse compositions which are derived from lower monoalkyl dialkanolamines can be represented by the formula

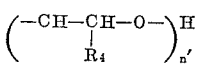
(IV)



where R is an alkyl radical containing from 1 to 3, and especially from 1 to 2, carbon atoms, alkylene contains not more than 3 carbon atoms, R_1—O is



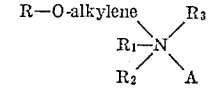
and R_2 is



where R_4 is an alkyl radical containing from 1 to 4 carbon atoms, n and n' are numbers the sum of which preferably does not exceed 60, the total number of carbon atoms in R_1 and R_2 being at least 18; R_3 is a hydrocarbon radical selected from the group consisting of alkyl and alkenyl radicals containing not more than 4 carbon atoms, or a lower aliphatic-aromatic hydrocarbon radical containing from 7 to 9 carbon atoms; and A is an anion.

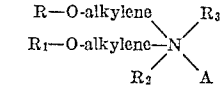
Still others of the quaternary ammonium compounds having utility in my hair rinse compositions can be represented by the formulae

(V)

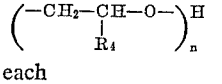


and

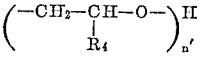
(VI)



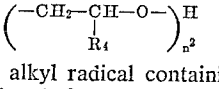
where alkylene contains not more than 3 carbon atoms, R—O is



R_1 and R_1—O are each



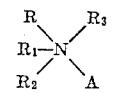
and R_2 is



in which R_4 is an alkyl radical containing from 1 to 4 carbon atoms, n, n' and n^2 are numbers the sum of which preferably does not exceed 60, the total number of carbon atoms in R, R_1 and R_2 being at least 18; R_3 is a hydrocarbon radical selected from the group consisting of alkyl and alkenyl radicals containing not more than 4 carbon atoms, or a lower aliphatic-aromatic hydrocarbon radical containing from 7 to 9 carbon atoms; and A is an anion.

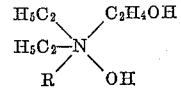
Most of the quaternary ammonium type compounds having utility in the present invention fall into the category of or correspond to reaction products of quaternizing esters having a hydrocarbon alkyl or alkenyl radical containing not more than 4 carbon atoms, or a benzyl radical or a dimethylbenzyl radical or a lower alkyl substituted or chloro or nitro substituted benzyl radical, and an anion, with adducts of (*a*) aliphatic amines or cyclic amines containing a reactive hydrogen and a total of not more than 6 carbon atoms and in which no single aliphatic radical contains more than 3 carbon atoms, with (*b*) an α-epoxide containing at least 3 and advantageously from 3 to 8 carbon atoms, the molal ratio of (*a*) to (*b*) being 1 of (*a*) to at least 6 of (*b*) when said α-epoxide contains 3 carbon atoms and ranging down to at least 2.5 or (*b*) when said α-epoxide contains 8 carbon atoms.

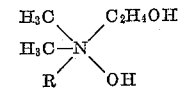
Still others of the quaternary ammonium compounds that may be employed in the hair rinse compositions of this invention can be represented by the formula



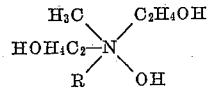
where R is an alkyl radical containing from 1 to 3 carbon atoms, R_1 is an alkyl radical containing from 1 to 3 carbon atoms or is the same as R_3, R_2 is a polyoxyalkylene radical containing at least 18 carbon atoms and derived from an α-epoxide containing from 3 to 8 carbon atoms, R_3 is a hydroxy-alkyl radical containing from 2 to 4 car-

bon atoms, and A is hydroxyl or other anion. Such compounds are readily produced by reacting the adducts, such as those described hereafter in Examples *a* to *v*, with ethyleneoxide in an aqueous medium in accordance with known quaternizing techniques. Typical of such compounds are those corresponding to the formulae





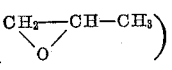
and



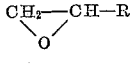
where R is a polyoxypropylene or polyoxybutylene radical containing say from 6 to 30 oxypropylene or oxybutylene groups.

While, as indicated, many of the quaternary ammonium type compounds having utility for the purposes of this invention can be represented by the above formulae, they may, in general, best be described in the form of reaction products of identified ingredients, as hereafter pointed out. Thus, for example, although this will be described in more detail hereafter, quaternary ammonium compounds which are particularly useful are reaction products of quaternizing esters in the form of alkyl and alkenyl halides, sulfates and sulfonates containing from 1 to 4 carbon atoms, exemplified by methyl cholride, ethyl chloride, methyl chloracetate, and 1 and 2 carbon atom alkyl sulfates; or aromatic quaternizing esters in the form of halides, sulfates and sulfonates advantageously containing from 7 to 9 carbon atoms, exemplified by benzyl chloride, dimethylbenzyl chloride, and phenyl ethyl chloride, with adducts of (*a*) alkyl amines having a reactive hydrogen and containing from 1 to 4 carbon atoms, such as dimethylamine and diethylamine, with (*b*) propyleneoxide or butyleneoxides, said adducts containing 1 mol of (*a*) to from 6, and preferably from 8, to 30 mols of (*b*).

It is important to note that it is critical to the successful formulation of the hair rinse compositions of the present invention that the oxyalkylene groups substituted on the quaternary ammonium type compounds be derived from an α-epoxide containing at least 3 carbon atoms. Ethyleneoxide, for instance, is not operative in the practice of my invention since it produces compounds whose properties are radically different from those described hereinabove and which would be useless for the purposes for which the quaternary ammonium type compounds above described are utilized in accordance with my invention. The most important embodiment of the α-epoxide whose use is contemplated herein in the production of the desired quaternary ammonium type compounds is propyleneoxide



The α-epoxides containing 4, 5, 6 or more carbon atoms can be used but, for general reasons of lack of economy or commercial availability, are not preferred. Typical of such latter α-epoxides are butyleneoxides such as 1,2-butyleneoxide, pentylene epoxides, hexylene epoxides, heptylene epoxides, octylene epoxides, dodecylene epoxides, and C_{16}–C_{18} olefin oxides or epoxides, and, as well, styrene epoxide. It will be seen that most of those of the α-epoxides in which the vicinal carbons are terminal can conveniently be represented by the formula



where R is an alkyl radical. In the case of propylene oxide, R is CH_3, and in the representation of the group of propyleneoxide, butyleneoxides, pentyleneoxide and hexyleneoxide R contains from 1 to 4 carbon atoms. In the higher molecular weight alkylene oxides, R may contain as high as 16 carbon atoms.

While, as I have stated above, the use of ethyleneoxide as the sole alkylene oxide is inoperative for my purposes, minor proportions thereof, not to exceed 25% and better still not to exceed 20% by weight of the propyleneoxide or other α-epoxide employed, can be utilized as hereafter described. Mixtures of two or more of the α-epoxides containing at least 3 carbon atoms can, of course, be used as such, as well as in conjunction with ethyleneoxide, subject to the limitation that the ethyleneoxide must not exceed the aforesaid 20% to 25% of the weight of said α-epoxides.

The quaternary ammonium type compounds having utility for the purposes of this invention are advantageously prepared by initially condensing a lower molecular weight amine, for instance, one containing at least one alkyl radical having from 1 to 3 carbon atoms and no radical containing more than 3 carbon atoms linked to the nitrogen atom of the amine, or by initially condensing a cyclic amine, such as piperidine, containing not more than 6 carbon atoms, with propyleneoxide or other α-epoxide containing at least 3 carbon atoms, advantageously in the presence of a conventional oxyalkylation catalyst such as sodium hydroxide or potassium hydroxide, whereby to produce an intermediate or adduct containing at least 6 oxypropylene groups. The amines used in the reaction to produce said adducts must contain a reactive hydrogen, which may be hydrogen directly attached to the nitrogen of the amine or which may be in the form of hydroxyl hydrogen, secondary alkyl amines being especially desirable, particularly dimethylamine, diethylamine and methylethylamine. The resulting adduct is then reacted with a quaternizing ester in the form of lower alkyl or alkenyl halides or lower alkyl esters of sulfuric acid or lower alkyl esters of sulfonic acids, or lower alkyl and alkenyl haloacetates, or an aromatic or lower aliphatic-aromatic quaternizing ester, to convert said adduct into the compounds employed in my invention. Illustrative examples of the lower molecular weight alkyl halides, haloacetates, sulfates, etc. are methyl chloride, ethyl chloride, methyl bromide, ethyl bromide, methyl iodide, allyl chloride, allyl bromide, methyl chloracetate, ethyl chloracetate, vinyl chloracetate, dimethyl sulfate, and diethyl sulfate. In order to obtain quaternary ammonium type compounds having the required properties for use in my invention, the quaternizing alkyl and alkenyl esters, for instance, the halides, sulfates and sulfonates, should contain not more than 4 carbon atoms and, better still, should contain only 1 to 2 carbon atoms.

Illustrative examples of the quaternizing alkaryl halides are benzyl chloride and dimethylbenzyl chloride, as well as their corresponding bromides; methylbenzyl chloride and bromide; phenylmethyl halides such as the chloride and bromide; phenylethyl chloride and bromide; substituted phenyl lower alkyl (from 1 to 4 carbon atoms) halides as, for example, o-chlorbenzyl chloride and *p*-nitrobenzyl chloride and bromide; and monocyclic arylsulfonic acid lower alkyl esters such as the methyl and ethyl esters of benzene sulfonic acid, *p*-toluene sulfonic acid, and o-toluene sulfonic acid. It will be seen that all of the quaternizing esters which are utilized contain an aryl radical, more particularly a benzene radical which is connected to a divalent hydrocarbon radical such as $—CH_2—$ of $—CH_2—CH_2—$ or to a lower alkyl radical, that is one containing not more than 4 carbon atoms, especially $—CH_3$ or $—C_2H_5$. In order to obtain quaternary ammonium type compounds having the required properties, the aromatic or lower aliphatic-aromatic quaternizing esters, for best results, should contain from 7 to 9 carbon atoms.

Illustrative examples of the intermediate condensation products or adducts which are subsequently converted into the quaternary ammonium type compounds utilized in the practice of my present invention are the following:

a. Condensation products of 1 mol of dimethylamine with 6 to 10 mols of propyleneoxide.

b. Condensation product of 1 mol of dimethylamine with 20 mols of propyleneoxide.

c. Condensation product of 1 mol of dimethylamine with a mixture of 25 mols of propyleneoxide and 5 mols of ethyleneoxide.

d. Condensation products of 1 mol of dimethylamine with 1 to 2 mols of ethyleneoxide, reacted with 20 mols of propyleneoxide.

e. Condensation products of 1 mol of dimethylamine with 1 to 2 mols of ethyleneoxide, reacted with 20 mols of propyleneoxide.

f. Condensation products of 1 mol of methylethylamine with 10 to 60 mols of propyleneoxide.

g. Condensation products of 1 mol of diethylamine with 30 mols of propyleneoxide.

h. Condensation products of 1 mol of dimethylamine with 10 to 20 mols of propyleneoxide and then with 1 mole of ethyleneoxide.

i. Condensation products of 1 mol of methylpropylamine with 10 to 25 mols of propyleneoxide.

j. Condensation products of 1 mol of dimethylamine with 10 to 15 mols of butyleneoxide.

k. Condensation products of 1 mol of diethylamine with 10 to 18 mols of butyleneoxide.

l. Condensation products of 1 mol of piperidine with 10 to 25 mols of propyleneoxide.

m. Condensation products of 1 mol of methylpiperidine with 10 to 25 mols of propyleneoxide.

n. Condensation products of 1 mol of pyrrolidine with 10 to 25 mols of propyleneoxide.

o. Condensation products of ½ mol of methylamine and ½ mol of diethylamine with 6 to 30 mols of propyleneoxide.

p. Condensation products of ⅓ mol of dimethylamine and ⅔ mol of diethylamine with 10 to 25 mols of propyleneoxide.

q. Condensation products of 1 mol of morpholine with from 6 to 30 mols of propyleneoxide.

r. Condensation products of 1 mol of diethylethanolamine with 8 to 20 mols of propyleneoxide.

s. Condensation products of 1 mol of diallylethanolamine with 8 to 25 mols of propyleneoxide.

t. Condensation products of 1 mol of furfurylamine with 8 to 25 moles of propyleneoxide.

u. Condensation products of 1 mol of 2-amino-1,3-propanediol with 8 to 25 mols of propyleneoxide.

v. Condensation products of 1 mol of diethylamine with 6 to 25 mols of propyleneoxide.

The amines which are utilized in the production of the intermediate adducts or condensation products with the propylene oxide or other α-epoxides are particularly advantageously of aliphatic or acyclic character, although they also include cyclic secondary amines. In all cases, as pointed out above, they contain at least one reactive hydrogen directly attached to nitrogen or in a hydroxy group. Illustrative examples of such amines are alkyl amines, e.g., methylamine, dimethylamine, ethylamine, diethylamine, methylethylamine, propyl amine, dipropylamine; alkyl hydroxy amines, e.g., monomethylethanolamine, mono ethylethanolamine, monomethyldiethanolamine, dimethylethanolamine, diethylethanolamine and diallylethanolamine; polyamines such as ethylenediamine, diethylenetriamine and triethylenetetraamine and higher polyamines in which there is at least one short chain alkyl group, as, for instance, monomethyl ethylenediamine, dimethyl ethylenediamine and trimethyl ethylenediamine; N,N-dimethyl-N',N'-diisopropanol propylenediamine-1,3; furfurylamine; cyclic secondary amines containing not more than 6 carbon atoms, typical examples of which are morpholine, piperidine, methylpiperidine, and pyrrolidine. Such amines may contain nonreactive substitutes such as nitro groups, ether and thioether groups, CN groups, and the like, but, in general, best results will be obtained with the unsubstituted amines. Compatible mixtures of any two or more of said amines, in various proportions, can, of course, be utilized in the production of the intermediate condensation products.

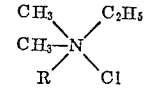
The radical A can be any negative or salt-forming radical as, for instance, halogen such as chlorine, bromine and iodine; hydroxy; sulfate, alkyl-sulfuric acid such as methyl sulfuric acid or ethyl surfuric acid (methosulfate of ethosulfate); nitrate; phosphate; acetate; formate; carbonate; lower alkyl (1 to 4 carbon atoms) sulfonic acids; and the like. Of particular importance are those of the quaternary ammonium type compounds in which the anion is chlorine, bromine, methyl chloracetate, methosulfate, and ethosulfate. Various of said anionic radicals can be introduced directly into the molecules; and, in the case of others, they can be made, for instance, by substitution for halogen in the quaternary ammonium type compounds employed in my hair rinses by known techniques as, for instance, by metathesis procedures.

The following examples are illustrative of the production of typical quaternary ammonium type compounds having utility in my invention.

Example 1

(*a*) 46 grams (1 mol) of dimethylamine were placed in an autoclave from which the air was displaced by nitrogen. 58 grams (1 mol) of propyleneoxide were pumped into the dimethylamine in said autoclave and reacted while maintaining the temperature below 25° C. The resulting compound was heated to about 150° C. and 25 mols of propyleneoxide were added to the autoclave over a period of 6 hours while maintaining a nitrogen pressure in the autoclave, said reaction being advantageously carried out in the presence of 2 to 3 grams of potassium hydroxide as a catalyst. The rate of addition of the propyleneoxide was controlled so that the pressure in the autoclave did not exceed 2 atmospheres and the temperature controlled so as not to exceed 200° C. and preferably at about 150° C. Upon completion of the reaction, the reaction mixture was cooled to below 100° C. and flushed out with gaseous nitrogen.

(*b*) to 77 grams of the intermediate condensation product or adduct of part (*a*) hereof there were added 8 grams of methanol and 4 grams of ethyl chloride and the resulting mixture was refluxed, with stirring, for 5 hours. During this period, the temperature of reflux rose somewhat and the viscosity of the reaction mixture increased appreciably. A yield in excess of 90% of theoretical of the following product was obtained:



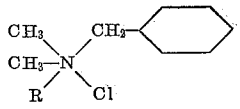
wherein R is a polyoxypropylene radical containing about 25 oxpyropylene groups.

Example 2

(*a*) 46 grams (1 mol) of dimethylamine were placed in an autoclave from which the air was displaced by nitrogen. 58 grams (1 mol) of propyleneoxide were pumped into the dimethylamine in said autoclave and reacted while maintaining the temperature below 25° C. The resulting compound was admixed with an alkaline catalyst, say 2 to 3 grams of KOH, and was heated to about 150° C. and 25 mols of propyleneoxide were added to the autoclave over a period of 6 hours while maintaining a nitrogen pressure in the autoclave. The rate of addition of the propyleneoxide was controlled so that the pressure in the autoclave did not exceed 2 atmospheres

and the temperature controlled so as not to exceed 200° C. and perferably at about 150° C. Upon completion of the reaction, the reaction mixture was cooled to below 100° and flushed out with gaseous nitrogen.

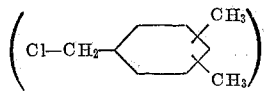
(*b*) To 77 grams of the intermediate condensation product or adduct of part (*a*) hereof there were added 8 grams of methanol and 8 grams of benzyl chloride and the resulting mixture was refluxed, with stirring, for 5 hours. During this period, the temperature of reflux rose somewhat and the viscosity of the reaction mixture increased appreciably. A yield of 96% of theoretical of the following product was obtained:



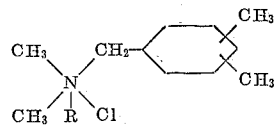
wherein R is a polyoxypropylene radical containing about 25 oxypropylene groups.

Example 3

50 grams of the adduct of part (*a*) of Example 2 were reacted with 3 grams of dimethyl benzyl chloride



in the manner described in part (*b*) of Example 2 to produce a product having the following formula:



where R is a polyoxypropylene radical containing about 25 oxypropylene groups.

Various innocuous inorganic salts which have the property of salting out the quaternary ammonium type compounds herein described having utility for the purposes of this invention can be utilized as, for example, chlorides, bromides and sulfates such as sodium chloride, potassium chloride, lithium chloride, sodium bromide, potassium bromide, lithium bromide, sodium sulfate, potassium sulfate, lithium sulfate, and the like. Especially satisfactory is sodium chloride.

The proportions of ingredients utilized in the preparation of my hair rinse concentrates are, as will be apparent, somewhat variable but, in general, said proportions will fall into the range of the following, by weight:

Quaternary ammonium type compound	1 to 4, preferably 1 to 3.
Opacifier	0.2 to 1, preferably 0.3 to 0.8.
Innocuous inorganic salt	0.4 to 1.5, preferably 0.5 to 1.
Water	90 to 100, preferably 95 to 98.

The following examples are illustrative of hair rinse concentrates made in accordance with the invention. It will be understood that these are given simply by way of illustration and are not in any way to be construed as limitative of the full scope of the invention. All parts listed are by weight.

Example 1

(*a*) The compound formed by quaternizing a condensation product of 1 mol of diethyl ethanolamine and 25 mols of propyleneoxide with methyl chloride	2
(*b*) Cetyl alcohol	0.5
(*c*) Sodium chloride	0.8
(*d*) Water (distilled)	97

Example 2

(*a*) The compound formed by quaternizing a condensation product of ½ mol of methylamine, ½ mol of diethylamine and 20 mols of propyleneoxide with dimethyl sulfate	2.2
(*b*) Stearyl alcohol	0.4
(*c*) Potassium chloride	0.7
(*d*) Water (distilled)	97

Example 3

(*a*) The compound formed by quaternizing a condensation product of 1 mol of diethyl ethanolamine and 20 mols of propyleneoxide with methyl chloride	2
(*b*) Sodium chloride	0.6
(*c*) Water (distilled)	98

Example 4

(*a*) The compound formed by quaternizing a condensation product of 1 mol of diethylamine and 30 mols of propyleneoxide with phenylmethyl chloride	1.8
(*b*) Cetyl alcohol	0.5
(*c*) Water (distilled)	98

Example 5

(*a*) The compound formed by quaternizing a condensation product of 1 mol of dimethylamine and 20 mols of propyleneoxide and 1 mol of ethyleneoxide with ethyl chloride	2.1
(*b*) Water (distilled)	98

Example 6

(*a*) The compound formed by quaternizing a condensation product of 1 mol of pyrrolidine and 30 mols of propyleneoxide with o-chlorobenzyl chloride	3.0
(*b*) Cetyl alcohol	0.8
(*c*) Sodium bromide	0.5
(*d*) Water (distilled)	96

Example 7

(*a*) The compound formed by quaternizing a condensation product of 1 mol of diethylethanolamine and 25 mols of propyleneoxide with ethyl chloride	1.6
(*b*) Potassium chloride	0.6
(*c*) Water (distilled)	98

Example 8

(*a*) The compound formed by quaternizing a condensation product of 1 mol of diethylamine and 12 mols of butyleneoxide with ethyl chloride	2.5
(*b*) Lauryl alcohol	0.5
(*c*) Water (distilled)	97

Example 9

(*a*) The compound formed by quaternizing a condensation product of 1 mol of methylpropylamine and 25 mols of propyleneoxide with methyl chloracetate	2.1
(*b*) Stearyl alcohol	0.4
(*c*) Sodium chloride	0.6
(*d*) Water (distilled)	97

Example 10

(*a*) The compound formed by quaternizing a condensation product of 1 mol of 2-amino-1,3-propanediol and 18 mols of propyleneoxide with methyl chloride	1.6
(*b*) Cetyl alcohol	0.6
(*c*) Water (distilled)	98

The ingredients are mixed together in any desired manner. Thus, for example, the sodium chloride and the compound formed by quaternizing the condensation product of 1 mol of diethyl ethanolamine and 20–25 mols

of propyleneoxide with methyl chloride, or the like quaternary ammonium type compound are dissolved in the water. The cetyl alcohol is melted and added gradually, with good stirring, to the water solution, the latter being preliminarily heated to about 80° C., and the resulting composition is allowed to cool while continuing the stirring. A homogeneous opalescent product is obtained.

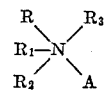
In the use of such concentrates, they are diluted in the proportion of about 1 tablespoon to a cup of water, which represents approximately a dilution of 1 part of the concentrate to 8 parts of water. It will, thus, be seen that the hair rinse concentrates, after dilution with water so as to render them ready for use on the hair after shampooing, will not, at least in most cases, contain in excess of about 1%, by weight, of the quaternary ammonium type compound as disclosed herein above, or not more than a total of about 1%, by weight, of such compound and inorganic salt, or not more than a total of about 1%, by weight, of such compound, the inorganic salt and the opacifier. In general, after dilution with water, the hair rinse will ordinarily contain from about 0.2% to about 0.6% of the said compound, and not more than about 0.1% each of the inorganic salt and the opacifier. The diluted hair rinse is poured onto the hair, in the usual way in which hair rinses are utilized, after the hair is shampooed.

While I have disclosed numerous examples of quaternary ammonium type compounds which can be utilized to achieve the objects of my invention, I find it to be especially satisfactory to employ such compounds or reaction products which result from quaternizing condensation products of 1 mol of diethyl ethanolamine and from about 20 to 25 mols of propyleneoxide with methyl chloride. The use of such compounds or reaction products represents especially preferred, though limited, embodiments of my invention.

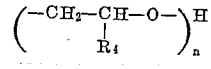
For obtaining the most desirable and commercial hair rinse preparations in accordance with my present invention, said preparations should contain, in the form of an aqueous opalescent product, the quaternary ammonium type compound, for example, the compound formed by quaternizing the condensation product of 1 mol of diethyl ethanolamine and 20 to 25 mols of propyleneoxide with methyl chloride, the inorganic salt, and the opacifier and lubricant. In the broadest phases of the invention, however, the hair, after shampooing, can be treated with dilute aqueous solutions from which the inorganic salt or the opacifier or both have been omitted, with the obtaining of some limited advantages.

What I claim as new and desire to protect by Letters Patent of the United States is:

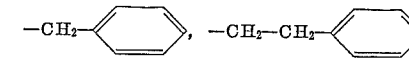
1. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing a chemical compound corresponding to the formula



wherein R is alkyl containing from 1 to 2 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a member of the group consisting of piperidine, methyl piperidine and pyrrolidine; R_2 is

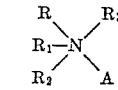


where R_4 is alkyl containing from 1 to 4 carbon atoms, n is a number up to and including 60, the total number of carbon atoms in R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

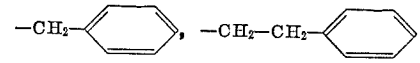


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

2. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula

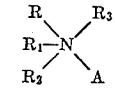


wherein R is alkyl containing from 1 to 2 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a member of the group consisting of piperidine, methyl piperidine and pyrrolidine; R_2 is a polyoxypropylene-polyoxyethylene substituent in which the ethylene oxide constitutes not more than 20% by weight of said substituent; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

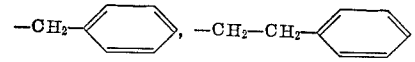


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

3. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula

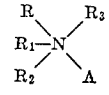


where R is alkyl containing from 1 to 3 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a cyclic amine containing not more than 6 carbon atoms, with the proviso that the total number of carbon atoms in R and R_1 does not exceed 6; R_2 is a polyoxalkylene substituent containing at least 18 carbon atoms and derived from an α-epoxide containing from 3 to 6 carbon atoms, R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

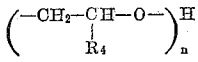


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

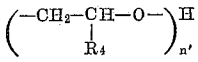
4. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing a chemical compound corresponding to the formula



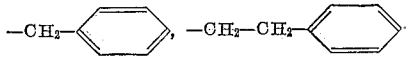
where R is alkyl containing from 1 to 3 carbon atoms, R_1 is



and R_2 is

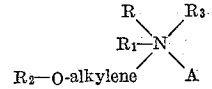


where R_4 is alkyl containing from 1 to 4 carbon atoms, n and n' are numbers the sum of which does not exceed 60, the total number of carbon atoms in R_1 and R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

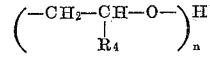


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

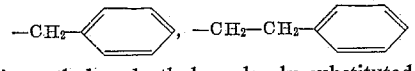
5. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula



where R is alkyl containing from 1 to 3 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, alkylene contains not more than 3 carbon atoms, R_2—O is

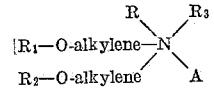


where R_4 is alkyl containing from 1 to 4 carbon atoms, n is a number up to and including 60, the total number of carbon atoms in R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

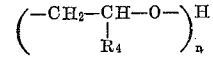


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

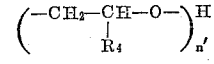
6. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula



where R is alkyl containing from 1 to 3 carbon atoms, alkylene contains not more than 3 carbon atoms, R_1—O is

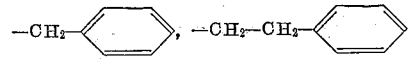


and R_2—O is



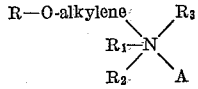
where R_4 is alkyl containing from 1 to 4 carbon atoms, n and n' are numbers the sum of which does not exceed 60, the total number of carbon atoms in R_1 and R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than

4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

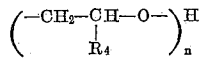


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

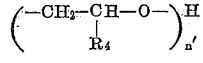
7. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula



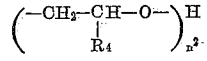
where alkylene contains not more than 3 carbon atoms, R—O— is



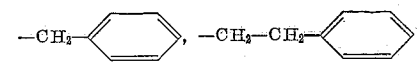
R_1 is



and R_2 is

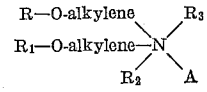


in which R_4 is alkyl containing from 1 to 4 carbon atoms, n, n' and n^2 are numbers the sum of which does not exceed 60, the total number of carbon atoms in R, R_1 and R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

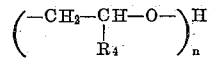


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

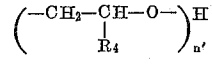
8. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula



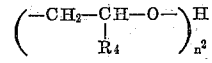
where alkylene contains not more than 3 carbon atoms, R—O is



R_1—O is

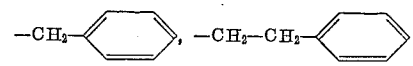


and R_2 is



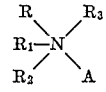
in which R_4 is alkyl containing from 1 to 4 carbon atoms, n, n' and n^2 are numbers the sum of which does not exceed 60, the total number of carbon atoms in R, R_1 and R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not

more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;

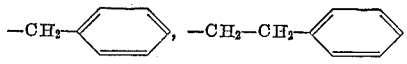


and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

9. A method of treating hair on the human head after shampooing the same to improve its combing properties, which comprises rinsing the shampooed hair with a dilute aqueous solution containing from about 0.2% to about 1%, by weight, of a chemical compound corresponding to the formula



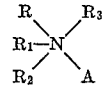
where R is alkyl containing from 1 to 3 carbon atoms, R_1 is selected from the group consisting of alkyl containing from 1 to 3 carbon atoms and hydroxyalkyl containing from 2 to 4 carbon atoms, R_2 is a polyoxyalkylene substituent containing at least 18 carbon atoms and derived from an α-epoxide containing from 3 to 8 carbon atoms, R_3 is a member selected from the group consisting of (1) a hydroxyalkyl containing from 2 to 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



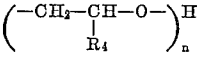
and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion.

10. A hair rinse concentrate for use, upon dilution with water, after shampooing of the hair, comprising the following ingredients in substantially the stated proportions by weight:

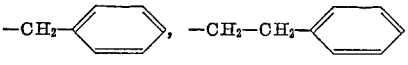
(*a*) A quarternary ammonium type compound corresponding to the formula



wherein R is alkyl containing from 1 to 2 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a member of the group consisting of piperidine, methyl piperidine and pyrrolidine; R_2 is



where R_4 is alkyl containing from 1 to 4 carbon atoms, *n* is a number up to and including 60, the total number of carbon atoms in R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion—1 to 4

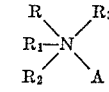
(*b*) Opacifier—0.2 to 1

(*c*) Inorganic water-soluble innocuous salt—0.4 to 1.5

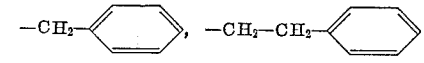
(*d*) Water—90 to 100

11. A hair rinse concentrate for use, upon dilution with water, after shampooing of the hair, comprising the following ingredients in substantially the stated proportions by weight:

(*a*) A quaternary ammonium type compound corresponding to the formula



wherein R is alkyl containing from 1 to 2 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a member of the group consisting of piperidine, methyl piperidine and pyrrolidine; R_2 is a polyoxypropylene-polyoxyethylene substituent in which the ethylene oxide constitutes not more than 20% by weight of said substituent; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion—1 to 4

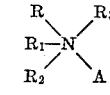
(*b*) Opacifier—0.2 to 1

(*c*) Inorganic water-soluble innocuous salt—0.4 to 1.5

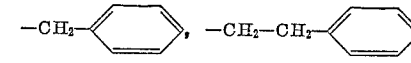
(*d*) Water—90 to 100

12. A hair rinse concentrate for use, upon dilution with water, after shampooing of the hair, comprising the following ingredients in substantially the stated proportions by weight:

(*a*) A quarternary ammonium type compound corresponding to the formula



where R is alkyl containing from 1 to 3 carbon atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, and compounds wherein R and R_1 are joined together to form with the N atom a cyclic amine containing not more than 6 carbon atoms, with the proviso that the total number of carbon atoms in R and R_1 does not exceed 6; R_2 is a polyoxyalkylene substituent containing at least 18 carbon atoms and derived from an α-epoxide containing from 3 to 6 carbon atoms, R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion—1 to 4

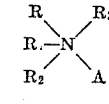
(*b*) Higher fatty alcohol opacifier—0.2 to 1

(*c*) Sodium chloride—0.4 to 1.5

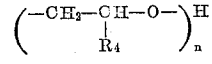
(*d*) Water—90 to 100

13. A hair rinse concentrate for use, upon dilution with water, after shampooing of the hair, comprising the following ingredients in substantially the stated proportions by weight:

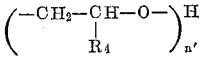
(*a*) A quarternary ammonium type compound corresponding to the formula



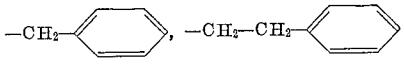
where R is alkyl containing from 1 to 3 carbon atoms, R_1 is



and R_2 is



where R_4 is alkyl containing from 1 to 4 carbon atoms, n and n' are numbers the sum of which does not exceed 60, the total number of carbon atoms in R_1 and R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion—1 to 4

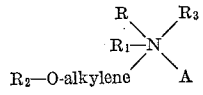
(*b*) Opacifier—0.2 to 1

(*c*) Inorganic water-soluble innocuous salt—0.4 to 1.5

(*d*) Water—90 to 100

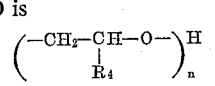
14. A hair rinse concentrate for use, upon dilution with water, after shampooing of the hair, comprising the following ingredients in substantially the stated proportions by weight:

(*a*) A quaternary ammonium type compound corresponding to the formula

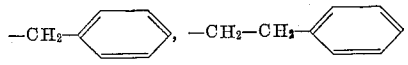


where R is alkyl containing from 1 to 3 carbon

atoms, R_1 is alkyl containing from 1 to 3 carbon atoms, alkylene contains not more than 3 carbon atoms, R_2—O is



where R_4 is alkyl containing from 1 to 4 carbon atoms, n is a number up to and including 60, the total number of carbon atoms in R_2 being at least 18; R_3 is a member selected from the group consisting of (1) alkyl and alkenyl containing not more than 4 carbon atoms, and (2) benzene; methyl benzenes; ethyl benzenes;



and their methyl and ethyl nuclearly substituted derivatives; and the mono-halo and mono-nitro nuclearly substituted derivatives of the foregoing; and A is an innocuous anion—1 to 4

(*b*) Opacifier—0.2 to 1

(*c*) Inorganic water-soluble innocuous salt—0.4 to 1.5

(*d*) Water—90 to 100

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