

1

3,208,911

## PROCESS FOR TREATING HAIR WITH IONIC OIL-IN-WATER EMULSIONS OF POLYORGANOSILOXANES

Paul E. Oppliger, Midland, Mich., assignor to Dow Corning Corporation, Midland, Mich., a corporation of Michigan

No Drawing. Filed June 13, 1962, Ser. No. 202,097

3 Claims. (Cl. 167-87)

This invention relates to a process for treating hair to improve the appearance, manageability and softness of the hair. In particular, this process relates to rinsing long hair after shampooing.

It has been desirable for a long time to develop an improved hair rinse which imparts to the hair superior manageability, a softer feel and a more lustrous appearance than present hair rinses. The term "manageability" refers to the tendency of the hair to snarl after it has been washed. The process of this invention minimizes the snarling tendencies of freshly shampooed hair. In addition to the prevention of snarling, this process also imparts to the hair a soft feel which means that the hair has a feeling of silkiness to the touch. This process also imparts a more lustrous appearance to the hair which means that the hair has highlights which may bring out any tints that are present. Hair treated by this process has more gloss and shine and is aesthetically more appealing.

It is an object of this invention to develop a process for treating hair to improve the appearance, manageability and softness of the treated hair. In particular, it is an object of this invention to develop an improved process for rinsing hair after shampooing which imparts these characteristics to the hair.

These objects are satisfied by a process for treating hair to improve the appearance, manageability and softness of the hair which comprises submitting said hair to the action of an ionic oil-in-water emulsion, said emulsion having been prepared by polymerizing and copolymerizing organosiloxanes of the formula

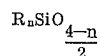


wherein R is selected from the group consisting of monovalent hydrocarbon and halogenated hydrocarbon radicals and hydrogen atoms, there being an average of no more than one hydrogen atom per silicon atom and  $n$  has an average value of from 1.9 to 2.1 inclusive while said siloxane is emulsified in an aqueous medium by polymerizing said siloxane in the presence of an alkaline catalyst until the siloxane reaches the desired molecular aggregation of between 6.5 and  $2.5 \times 10^6$  cs. at 25° C., said ionic oil-in-water emulsion containing an ionic emulsifying agent, the siloxane being present in said ionic oil-in water emulsion in an amount of from .01 to 90 percent by weight based upon the total weight of the ionic oil-in-water emulsion.

The essential ingredient of the ionic oil-in-water emulsion is the siloxane. This siloxane can be present in an amount from .01 to 90 percent by weight based upon the total weight of the emulsion. However, it is preferred that this emulsion contain at least 1 percent by weight of the siloxane and no particular advantage is gained by employing more than 10 percent by weight of the siloxane.

2

The siloxanes that can be used in this invention have the unit formula



wherein R is either a monovalent hydrocarbon or halogenated hydrocarbon radical or a hydrogen atom. Suitable examples of monovalent hydrocarbon radicals are alkyl radicals such as methyl, ethyl and octadecyl; alkenyl radicals such as vinyl, allyl and hexenyl; cycloaliphatic radicals such as cyclohexyl and cyclohexenyl; aryl hydrocarbon radicals such as phenyl, tolyl and xylyl and aralkyl hydrocarbon radicals such as benzyl. R is also halogenated monovalent hydrocarbon radicals such as chlorophenyl, 3,3,3-trifluoropropyl,  $\alpha,\alpha,\alpha$ -trifluorotolyl, trifluorovinyl, trifluorochlorocyclobutyl, and tetrabromoxenyl. The R groups on the siloxane can also be hydrogen, although there should be an average of no more than one hydrogen atom per silicon atom. Preferably, R is a monovalent hydrocarbon radical. The best results are obtained when R is an alkyl radical such as methyl.

The subscript  $n$  has an average value of from 1.9 to 2.1 inclusive. However, it is preferred that  $n$  have an average value of from 1.95 to 2.05. The operative siloxanes in this invention can have a viscosity of from 6.5 to  $2.5 \times 10^6$  cs. at 25° C. The best results are obtained with siloxanes with a viscosity of from 10 to 10,000 cs.

It is essential that the siloxanes used in this invention be polymerized by an emulsion polymerization technique and that this emulsion is used to treat the hair. The solids content of the emulsion can be varied by the addition of the necessary water and additional ingredients, such as cationic or anionic emulsifying agents, can be added to the emulsion. Siloxanes polymerized by conventional techniques do not impart the desired characteristics to hair when they are emulsified and then used to treat hair. It is also essential that the emulsion that is used to treat the hair be an ionic emulsion. A method of emulsion polymerization of siloxanes is disclosed in the Hyde and Wehrly U.S. Patent 2,891,920 (June 23, 1959), which is hereby incorporated by reference. Since it is necessary that the treating emulsion be ionic, it is preferable to use an ionic emulsifying agent in the polymerization of the siloxane and the ionic emulsifying agent is present in an amount of from 2 to 25 percent by weight based upon the weight of the organosiloxane although the usual amount is less than 10 percent by weight. However, it should be realized that any one of the nonionic emulsifying agents disclosed in the Hyde patent can be used to prepare the emulsion. When a nonionic emulsifying agent is used, the treating emulsion can be made either cationic or anionic by the addition of a suitable ionic emulsifying agent. The emulsion polymerization technique disclosed in Hyde basically consists of emulsifying a siloxane in water with the use of an emulsifying agent and then adding a catalyst and allowing the emulsion to stand with or without agitation at the desired temperature until the siloxane has reached the desired molecular aggregation of between 6.5 and  $2.5 \times 10^6$  cs. at 25° C. Since cationic treating emulsions are preferred, it is preferable to use a cationic emulsifying agent in the emulsion polymerization of the siloxane. Suitable cationic emulsifying agents include aliphatic fatty amines and their derivatives such as dodecylamine acetate, octadecylamine acetate and acetates of the amines of tallow fatty acids;

homologues of aromatic amines having fatty chains such as dodecylanalin; fatty amides derived from aliphatic diamines such as undecylimidazoline; fatty amides derived from disubstituted amines such as oleylaminodiethylamine; derivatives of ethylene diamine; quaternary ammonium compounds such as dioctadecyldimethyl ammonium chloride, didodecyldimethyl ammonium chloride and dibexadecyldimethyl ammonium chloride; amide derivatives of amino alcohols such as  $\beta$ -hydroxy-ethylstearylamine; amine salts of long chain fatty acids; quaternary ammonium bases derived from fatty amides of disubstituted diamines such as oleylbenzylaminoethylene diethylamine hydrochloride; quaternary ammonium bases of the benzimidazolines such as methylheptadecyl benzimidazolines such as methylheptadecyl benzimidazol hydrobromide; basic compounds of pyridinium and its derivatives such as cetylpyridinium chloride; sulfonium compounds such as octadecylsulfonium methyl sulfate; quaternary ammonium compounds of betaine such as betaine compounds of diethylamino acetic acid and octadecylchloromethyl ether; urethanes of ethylene diamine such as the condensation products of stearic acid and diethylene triamine; polyethylene diamines; and polypropanolpolyethanol amines.

It is preferred that an alkaline catalyst be used to effect the emulsion polymerization and in an amount of from one alkaline molecule per 100 silicon atoms to one alkaline molecule per 50,000 silicon atoms. The preferred alkaline catalysts are quaternary ammonium hydroxides having at least one alkyl radical of at least 12 carbon atoms attached to the nitrogen. These hydroxides are preferred because they provide both the emulsifying agent and polymerization catalyst for the siloxane. The quaternary ammonium hydroxides can be employed either as a hydroxide, per se, or in the form of a salt such as the quaternary ammonium chlorides, nitrates, sulfates, acetates, etc. The alkaline catalyst is selected from the group consisting of (a)  $R'NOH$  and (b)  $R'NX$  admixed with Q wherein  $R'$  is an alkyl radical, X is an acid anion and Q is an alkaline compound selected from the group consisting of ammonia, alkali metal hydroxide, alkali metal carbonates and organic amines and where the preferred acid anion is a halogen. It is preferred that the salts be employed because of their greater flexibility. It should be realized that when the salts are used, excellent emulsions are formed but polymerization is not obtained unless the emulsion is rendered alkaline by the addition of some alkaline material such as ammonia, sodium carbonate or organic amines. When the emulsion is rendered alkaline, some of the quaternary ammonium hydroxide is generated "in situ" and catalyzes the polymerization of the siloxane. The salts of quaternary ammonium hydroxide have the general formula  $R'NX$ , wherein  $R'$  is an alkyl radical, at least one of the  $R$ 's having at least 12 carbon atoms and X is an acid anion.

Specific examples of the preferred alkaline catalysts are octadecyltrimethyl ammonium hydroxide, didodecyl-diethyl ammonium hydroxide, tetradodecyl ammonium hydroxide, tritetradecylmethyl ammonium hydroxide and hexadecyloctadecyldimethyl ammonium hydroxide. The chlorides, nitrates, sulfates and acetates of these alkaline catalysts are preferred with the best results being obtained by the quaternary ammonium chlorides, such as octadecyltrimethyl ammonium chloride.

It should be realized that an anionic emulsion can be prepared when a cationic emulsifying agent has been used in the emulsion polymerization. These anionic emulsions are prepared merely by adding a suitable anionic emulsifying agent after the siloxane has been polymerized. When an ionic emulsifier has been used, the emulsion can be used to treat hair without modifying the emulsion in any manner. If desired, the siloxane solids concentration in the emulsion can be lowered or increased merely by the addition or removal of some of the water.

The process of this invention is of particular importance in rinsing the hair after shampooing. Although the hair rinse can contain from 0.1 to 90 percent by weight siloxane, the preferred concentration is from 1 to 10 percent siloxane solids. This hair rinse emulsion is used merely by applying the emulsion to the hair and then flooding the hair with excess water. Apparently a large amount of the siloxane remains as a coating on the individual hair strands. This process for rinsing hair improves the manageability of the hair and imparts a marked softness and feeling of silkiness to the touch. This process also brings out the highlights in the hair. These same characteristics are imparted to hair when a siloxane emulsion is used as an after-permanent rinse.

It should be realized that additional ingredients can be added to the siloxane emulsion. Additional ingredients, such as methylcellulose, can be added to the siloxane hair rinse emulsion. The siloxane emulsion can be added to a conventional wave set lotion or hair tonic in order to impart the above characteristics to hair.

These siloxane emulsions have been tested extensively on the hair of numerous people with various types of hair. These tests have demonstrated the excellent utility of the siloxane emulsion in improving manageability, softness and appearance of hair.

The following examples are illustrative only and should not be construed as limiting the invention which is properly delineated in the appended claims.

#### EXAMPLE 1

An emulsion of 31.5 percent by weight of cyclic dimethylsiloxane and 1.5 percent dioctadecyldimethyl ammonium chloride (said material known as Arquad 2-HT), 65.1 percent by weight water and 1.9 percent by weight ammonium hydroxide (at a concentration of 29 percent by weight  $NH_3$ ) was prepared by agitating the above compounds. The emulsion was heated at 100° C. overnight. The ammonium was then stripped off at reduced pressure and additional water added to bring the total solids to approximately 30 percent by weight (some water was lost during stripping) whereupon the viscosity of the siloxane was about 2,000 cs.

#### EXAMPLE 2

A dimethylsiloxane with a viscosity of 600 cs. was prepared in accordance with the procedure of Example 1, except that the emulsion was heated in a sealed bomb at 130° C. for 20 hours.

#### EXAMPLE 3

A dimethylsiloxane with a viscosity of 5,000 cs. was prepared by following the procedure of Example 1 except that the emulsion was heated at 90° C. for about 60 hours.

#### EXAMPLE 4

A dimethylsiloxane with a viscosity of 1,000,000 cs. was prepared following the procedure of Example 1, except that the emulsion was heated at 75° C. for 24 hours, then at 60° C. for 2 days and then allowed to stand at room temperature for several months prior to the removal of the ammonia. Additional water was added to this emulsion to bring the total solids to approximately 34 percent by weight.

#### EXAMPLE 5

An emulsion containing about 31.5 percent by weight of a fluid trimethylsilyl-endblocked methylhydrogensiloxane, 1.5 percent Arquad 2-HT and 67 percent water was prepared by agitating the above compounds. The emulsion was allowed to stand at room temperature, whereupon the polymerization of the methylhydrogensiloxane to a gel took place. Hydrogen gas evolved during the polymerization.

## EXAMPLE 6

The emulsion-polymerized siloxanes prepared in the preceding examples were tested as hair rinses at various siloxane solids concentrations. These siloxane-containing hair rinses were compared with other siloxane formulations and with commercial hair rinses. In each case the hair rinse was applied to locks of freshly shampooed wet hair and the hair was then flushed with water. The characteristics imparted to the hair by each of the rinses were then evaluated and rated on a scale from excellent to poor. The manageability of the hair was rated both while the hair was wet and after drying at room temperature. The manageability was determined by the ease with which the hair could be combed. The wet and dry feel (softness of the hair to the touch) was also evaluated. The appearance of the hair was evaluated after drying. The luster of the hair was one of the main factors considered in judging the appearance. The fly-away resistance of the hair was determined by combing the hair while observing the tendency of strands of hair to be repelled by the main body of hair.

The percentage figure in the hair rinse composition column in Table I indicates the percent by weight siloxane solids in the emulsion. In some cases the percent of siloxane solids in the emulsion was obtained by adding additional water to the siloxane emulsion that had been prepared.

The following additional material was used in the examples:

(A) an emulsion containing 30 percent by weight solids of a phenylmethylsiloxane and 5 percent by weight Arquad 2-HT. This emulsion was prepared after the phenylmethylsiloxane had been polymerized by a conventional process.

Table I

| Hair rinse composition                | Manageability |           | Feel      |           | Dry appearance | Fly-away resistance |
|---------------------------------------|---------------|-----------|-----------|-----------|----------------|---------------------|
|                                       | Wet           | Dry       | Wet       | Dry       |                |                     |
| (1) 22.3% solids—Example 3            | good          | excellent | excellent | good      | fair           | fair.               |
| (2) 32.7% solids—Example 4            | fair          | fair      | do        | poor      | do             | good.               |
| (3) 31.5% solids—Example 5            | good          | good      | good      | fair      | poor           | excellent.          |
| (4) 4.85% solids—Example 3            | excellent     | excellent | excellent | good      | excellent      | fair.               |
| (5) Non-silicone hair rinse           | fair          | poor      | poor      | fair      | poor           | Do.                 |
| (6) Commercial nonsilicone hair rinse | good          | fair      | fair      | good      | good           | good.               |
| (7) 30% solids (A)                    | poor          | poor      | poor      | poor      | poor           | poor.               |
| (8) 2.42% solids—Example 3            | good          | excellent | excellent | excellent | fair           | Do.                 |
| (9) 2.42% solids—Example 3            | fair          | do        | do        | poor      | poor           | good.               |
| (10) 4.85% solids—Example 3           | poor          | fair      | do        | excellent | good           | excellent.          |
| (11) 4.85% solids—Example 2           | do            | excellent | do        | do        | fair           | good.               |
| (12) 5% solids—Example 1              | do            | good      | good      | good      | good           | Do.                 |

Good results were obtained when sample No. 4 was tried by individuals on their hair. This hair rinse imparted a soft feel, excellent gloss, manageability and appearance to the hair.

## EXAMPLE 7

An excellent hair rinse is obtained when any of the following siloxanes are prepared from the appropriate cyclic siloxanes in accordance with the procedure of Example 3 and are diluted with sufficient water so that there are 4.85 percent by weight siloxane solids:

- (1) Phenylmethylsiloxane,
- (2) Methylvinylsiloxane,
- (3) Cyclohexylsiloxane.

That which is claimed is:

1. A method for treating hair to improve the appearance, manageability and softness of the hair consisting essentially of submitting the hair to the action of an ionic oil-in-water emulsion, said emulsion being composed of an organosiloxane in an amount of from 0.01 to 90 percent by weight based upon the total weight of the emulsion and an ionic emulsifying agent in an amount of from 2 to 25 percent by weight based upon the weight

of the organosiloxane and an alkaline catalyst in an amount of from one alkaline molecule per 100 silicon atoms to one alkaline molecule per 50,000 silicon atoms inclusive and the necessary water to give the desired solids content; the organosiloxane being of the unit formula



wherein R is selected from the group consisting of monovalent hydrocarbon and halogenated hydrocarbon radicals and hydrogen, there being an average of no more than one hydrogen atom per silicon atom and  $n$  having an average value of from 1.9 to 2.1 inclusive and said alkaline catalyst is selected from the group consisting of (a)  $\text{R}'_4\text{NOH}$  and (b)  $\text{R}'_4\text{NX}$  admixed with Q wherein R' is alkyl, X is an acid anion and Q is an alkaline compound selected from the group consisting of ammonia, alkali metal hydroxides, alkali metal carbonates and organic amines, said ionic oil-in-water emulsion being prepared by polymerizing the organosiloxane in an aqueous medium in the presence of said alkaline catalyst until the siloxane reaches a molecular aggregation of between  $6.5$  and  $2.5 \times 10^6$  cs. at  $25^\circ \text{C}$ . said ionic oil-in-water emulsion containing an ionic emulsifying agent.

2. A method for rinsing hair to improve the appearance, manageability and softness of the hair consisting essentially of submitting the hair to the action of a cationic oil-in-water emulsion, said cationic emulsion being composed of an organosiloxane in an amount of from 1 to 10 percent by weight based upon the total weight of the cationic oil-in-water emulsion and a cationic emulsifying agent in an amount of from 2 to 10 percent by weight based upon the weight of the organosiloxane and alkaline catalyst in an amount of from one

alkaline molecule per 100 silicon atoms to one alkaline molecule per 50,000 silicon atoms inclusive and the necessary water to give the desired solids content; the organosiloxane being of the unit formula

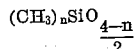


wherein R is a monovalent hydrocarbon radical and  $n$  has an average value of from 1.95 to 2.05 and said alkaline catalyst is selected from the group consisting of (a)  $\text{R}'_4\text{NOH}$  and (b)  $\text{R}'_4\text{NX}$  admixed with Q wherein R' is alkyl, X is a halogen anion and Q is an alkaline compound selected from the group consisting of ammonia, sodium carbonate and organic amines, said cationic oil-in-water emulsion being prepared by polymerizing the organosiloxane in the presence of a cationic emulsifying agent, rendering the emulsion alkaline by the addition of an alkaline compound and allowing the polymerization to proceed until the molecular aggregation of between 10 to 10,000 cs. at  $25^\circ \text{C}$ . is obtained.

3. A method for rinsing hair to improve the appearance, manageability and softness of the hair consisting essentially of submitting the hair to the action of

7

a cationic oil-in-water emulsion, said cationic emulsion being composed of an organosiloxane of the unit formula



wherein  $n$  has an average value of from 1.95 to 2.05 and in an amount of from 1 to 10 percent by weight based upon the total weight of the cationic oil-in-water emulsion and an emulsifying agent of the formula  $\text{R}'_4\text{NX}$  in which  $\text{R}'$  is alkyl, at least one of the  $\text{R}'$ 's has at least 12 carbon atoms and  $\text{X}$  is an acid anion and in an amount of from 2 to 10 percent by weight based upon the weight of the organosiloxane and an alkaline compound selected from the group consisting of ammonia, sodium carbonate and organic amines and in an amount of from one alkaline molecule per 100 silicon atoms to one alkaline molecule per 50,000 alkaline molecules, said cationic oil-in-water emulsion being prepared by polymerizing the organosiloxane in the presence of said emulsifying agent, rendering the emulsion alkaline by the addition of an alkaline

8

compound and allowing the polymerization to proceed until the molecular aggregation of between 10 to 10,000 cs. at 25° C. is obtained and thereafter rendering the emulsion neutral.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

|           |      |             |          |
|-----------|------|-------------|----------|
| 2,750,947 | 6/56 | Gant        | 167—87   |
| 2,826,551 | 3/58 | Geen        | 167—87   |
| 2,840,087 | 6/58 | Hersh       | 167—87   |
| 2,891,920 | 6/59 | Hyde et al. | 260—29.2 |

##### FOREIGN PATENTS

|           |      |                |
|-----------|------|----------------|
| 688,465   | 3/53 | Great Britain. |
| 1,069,982 | 2/54 | France.        |
| 1,088,513 | 9/54 | France.        |

JULIAN S. LEVITT, *Primary Examiner.*

FRANK CACCIAPAGLIA, Jr., *Examiner.*

**UNITED STATES PATENT OFFICE**  
**CERTIFICATE OF CORRECTION**

Patent No. 3,208,911

September 28, 1966

Paul E. Oppliger

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 53, and column 2, line 60, for "10<sub>6</sub> cs." each occurrence, read -- 10<sup>6</sup> cs. --; column 3, lines 14 and 15, strike out "such as methlyheptadecyl benzimidazolines".

Signed and sealed this 25th day of October 1966.

(SEAL)

Attest:

**ERNEST W. SWIDER**

Attesting Officer

**EDWARD J. BRENNER**

Commissioner of Patents