

[54] **METHOD OF EXTINGUISHING FIRES
AND COMPOSITIONS THEREFOR
CONTAINING CATIONIC SILICONE
SURFACTANTS**

[72] Inventors: **Meyer R. Rosen**, Irvington; **Bela Prokai**, Mahopac, both of N.Y.

[73] Assignee: **Union Carbide Corporation**, New York, N.Y.

[22] Filed: **Dec. 22, 1969**

[21] Appl. No.: **887,341**

[52] U.S. Cl.**169/1 A**, 252/3, 252/8.05, 252/307

[51] Int. Cl.**A62c 1/12**, A62d 1/00

[58] Field of Search.....252/3, 8.05, 307, 308, 357; 260/448.2 B, 448.2 N; 169/1 A

[56] **References Cited**

UNITED STATES PATENTS

2,165,997 7/1939 Daimler et al. 252/3

2,514,310 7/1950 Busse et al. 252/3
2,972,598 2/1961 Morehouse.....260/448.2 B
3,258,423 6/1966 Tuve et al. 252/3
3,402,191 9/1968 Morehouse 252/357
3,471,541 10/1969 Morehouse 252/357
3,475,333 10/1969 Meldrum et al. 252/3

Primary Examiner—Robert F. Burnett

Assistant Examiner—D. J. Fritsch

Attorney—Paul A. Rose, Aldo John Cozzi, Eugene C. Trautlein, George A. Skoler and Reynold J. Finnegan

[57] **ABSTRACT**

Cationic siloxanes in the liquid phase of fire extinguishing foams, with or without other materials as foam promoters, stabilizers or special purpose additives, provide rapid extinguishment of flames, are capable of forming vapor-securing films over burning hydrocarbon liquids to prevent reignition upon foam rupture or disintegration and impart unique elastic properties useful in producing high expansion foams and in producing low expansion foams for sprinkler systems.

31 Claims, No Drawings

METHOD OF EXTINGUISHING FIRES AND COMPOSITIONS THEREFOR CONTAINING CATIONIC SILICONE SURFACTANTS

This invention relates to methods of extinguishing fires and to compositions for use therein. The invention also relates to methods and compositions for extinguishing fires of low flash point flammable liquids and for preventing ignition or reignition for extended periods.

The extinguishment of low flash point hydrocarbon liquid and fuel oil fires by the application of an aqueous base foam blanket is well known. The technique involves spreading a continuous, free flowing floating foam over the burning hydrocarbon, thus forming a tough, air excluding blanket. This blanket seals off volatile, combustible vapor from the ambient air and prevents reignition. As the water in the foam drains it cools the hydrocarbon.

The extinguishment of fires by means of foam or water sprinkler systems also is well known. However, heretofore, such sprinkler systems have been highly inefficient because the water or foam rapidly drains off of the burning object.

One class of fire fighting foam which has gained wide acceptance is known as mechanical foam. It is usually generated by the aspiration of a gas (e.g., air) into a stream of water and a surface active agent which promotes and stabilizes the foam.

Another class of fire fighting foam is the chemical foam which is generated by the reaction, to produce carbon dioxide, of an alkali metal carbonate such as sodium bicarbonate with an acid compound such as aluminum sulfate. When combined with a suitable foam stabilizer, such as, licorice, saponin, glue, glycerin, glucose, sodium sulfonate, quillaia bark, and the like, a stable foam is produced.

A type of mechanical foam which is well known in the art consists of hydrolyzed animal or vegetable protein as foam-former, water and sundry additives, such as, buffers, freezing point depressants, additional foam stabilizers, bacteriocides and anti-corrosive agents.

Many types of protein have been used to produce the proteinaceous foam-formers and these include keratins, albumins, globulins, hemoglobulins, seed meals and the like (U.S. Pat. No. 2,361,057; 2,368,623; 2,481,875 and 2,405,438). Typical sources of these proteins include horns, hoofs, hair, feathers, blood, soya bean meal, pea flower, cotton seed meal and peanut cakes. These proteins are usually degraded with a hydrolyzing agent in the form of an alkaline earth metal oxide or hydroxide, such as, magnesium, calcium or barium oxide. The hydrolysis proceeds, for example, as described in U.S. Pat. No. 2,324,951, until a minimum of 25 percent of the nitrogen present is converted to the peptone form.

One type of foam stabilizer commonly used for proteinaceous foams is a salt, e.g., ferrous sulfate, which on dilution or formation of the foam, will hydrolyze to an insoluble hydroxide, e.g., ferrous hydroxide, as described in U.S. Pat. No. 2,361,057. Another type of foam stabilizer is a soluble phosphated inorganic salt containing a fatty alcohol, such as a soluble, phosphated sodium lauryl sulfate as described in U.S. Pat. No. 2,193,541.

Mechanical foam of the hydrolyzed protein type has the advantage of being relatively inexpensive; however, it suffers from several disadvantages. A heavy blanket of foam is required, and the hydrocarbon is subject to reignition if the foam blanket is ruptured by the action of wind or other forces in the presence of an ignition source. Even the footprints of the fire-fighter as he moves through the foam, disrupt the foam body and permit the possibility of reignition.

The use of certain commercial fluorocarbons in combination with the hydrolyzed protein partially overcomes the disadvantages of the hydrolyzed protein system. The resulting foam is compatible with commercial silicone-treated potassium bicarbonate, commercially known as Purple K powder, but still requires a heavy foam blanket which, if ruptured, will allow flammable vapor to escape and reignition to occur.

More recently, mechanical foams have been generated by the use of perfluorocarbon surfactants which are not silicones

in combination with a high molecular weight synthetic polymer. This system, known as "light water" (U.S. Pat. No. 3,258,423), involves the use of relatively more expensive components.

Certain types of silicones have previously been used in compositions for extinguishment and/or prevention of liquid hydrocarbon fires. The addition of a nonionic liquid alkyl silicone polymer to a chemical foam generated by sodium bicarbonate and aluminum sulfate, stabilized with licorice (U.S. Pat. No. 2,790,502) is stated to have the effect of increasing the flash point and fire point by migrating into the surface of the liquid. It is asserted that the composition may be used both as a preventative and extinguishing agent for organic oil fires.

In another application, a nonionic alkyl silicone-kerosene system (U.S. Pat. No. 2,543,672) is added to fuel oil to inhibit foaming. Water is applied to the burning liquid and the heat vaporizes the water to steam. The patent asserts that the presence of the silicone prevents boil-over of the burning fuel by inhibiting foaming which would result from the generation of steam within the fuel body. It is alleged that the steam rises to the surface and acts as a smothering barrier between the flammable vapors and oxygen.

It has been found that the use of nonionic alkyl silicones as disclosed in the two above-mentioned patents in fire fighting does not result in the formation of vapor-securing films and in some cases they act as anti-foams to destroy the fire-smothering foam.

The present invention relates to foams and provides novel methods and foam compositions and concentrates which are effective in extinguishing fires when utilized singly or in combination with other fire extinguishing agents. The present foam compositions display a remarkable effect in their ability to protect newly extinguished flammable surfaces from possible recurrence of fire. In this respect, the novel foams have been found to be especially useful in combating fires in gasoline, benzene and other combustible hydrocarbons having highly flammable vapors. They are also useful in combating fires in other hydrocarbons, which are capable under the heat conditions of the fire to give off considerable flammable vapor, for example, naphtha, toluene, kerosene, jet fuels, diesel oils, etc.

The present invention also relates to compositions and concentrates which form water solutions that are surprisingly pseudo-plastic, rheopectic and elastic in nature. Foams made from such solutions have yield points and hence they tend to adhere to solid surfaces. For example, such solutions when stirred exhibit the unusual property, after cessation of stirring, of slowing, stopping and then "unwinding" in a direction opposite to that of the initial stirring. This unusual property improves the ability of foams made from such solutions to stick to surfaces and permits the use of such solutions in foam form for sprinkler systems which are efficient in extinguishing Class A fires (wood, etc.) as well as liquid hydrocarbon fires. This unique property also permits the production of foams which drain more slowly and thus facilitates the production of high expansion foams, i.e., as high as 1,000, and low expansion foams, i.e., 5 to 10, which are slow draining in character.

The present invention utilizes cationic silicone surfactants in the liquid phase of a fire-fighting foam. These silicone surfactants reduce the surface tension of water in the foam to exceptionally low values and foams containing them are stable in contact with burning surfaces as well as during exposure to the heat generated in a typical fire.

These silicone surfactants, when added in small amounts to heretofore known foam systems and compatible therewith, e.g., hydrolyzed protein foam systems, unexpectedly impart the ability of forming spreading, vapor-securing films which are especially useful in extinguishing burning liquids, e.g., gasoline.

The liquid draining from aqueous foams containing these surfactants has the property of forming a surfactant-water film which spreads over liquid hydrocarbon surfaces and forms a vapor-securing barrier film. This film effectively seals off the

hydrocarbon from radiant energy input from an ignition source, if present. The film also prevents further release of flammable vapor after the flames have been suppressed. It has the property of spreading under the flames and rapidly sealing off any exposed liquid hydrocarbon surface which may occur as a result of mechanical disruption of the foam blanket, as by falling debris, wind, etc.

The formation of a vapor-securing film is an unexpected property of the specific classes of cationic silicone surfactants disclosed herein. In contrast, similar foam-promoting, low surface tension surfactants do not perform satisfactorily. For example, they do not form vapor-securing films under comparable conditions and/or are extremely poor in resistance to radiant heat attack, etc.

The cationic silicones themselves, when used in the relatively higher concentrations, act as the major foam-former and no substantial amounts, if any, of other known foam-formers, such as hydrolyzed protein, licorice, etc., are needed. Alternatively, the known foam-formers can be employed as the primary or major foam-former and the cationic silicone is used in the relatively lower concentrations, i.e., about 0.1 percent or less, for imparting to the foam the capability of forming the spreading, vapor-securing film, if desired.

A most unusual property of the cationic silicones described herein is their ability to form water solutions which, at concentrations as low as 0.5 to 2 wt. percent, or even up to 10 wt. percent, of the silicone, are pseudoplastic, rheopectic and, most interestingly, elastic. These properties are also present in solutions containing 1 to 50 wt. percent of the cationic silicone, 1 to 50 wt. percent of polar solvent and 49 to 89 wt. percent of water. These are believed to be extremely unusual properties for such low molecular weight materials at such low concentrations. The liquid draining from foams formed from such solutions also exhibits these highly unusual properties. This facilitates the production of high expansion foams, i.e., as high as 1,000, and also permits the efficient use of these solutions and foams made from them in sprinkler systems. Also, low expansion foams made from these solutions are more stable, i.e., they drain more slowly than similar foams made with surfactants that do not provide this property.

The cationic silicone surfactants also appear to impart oleophobicity to foams made from them. This is important in subsurface injection of the foam into large fuel storage tanks. The cationic silicone inhibits entrainment of fuel by the foam as it rises through the fuel. At the surface, the foam is effective in providing an oxygen excluding blanket for extinguishing flames. In those systems where the foam picks up too much fuel as it rises through the fuel, upon reaching the surface, the foam quickly burns off without extinguishing the flames.

The concentration of the cationic silicone surfactant employed in this invention is not narrowly critical. The liquid solutions from which foams are made according to this invention form the foam lamella or liquid phase upon mixing with air or other suitable gas. In order to impart to the foam the capability of forming spreading, vapor-securing films, it is highly desirable to use at least about 0.01 percent of the silicone based on the total weight of the liquid phase of the foam. When the silicone surfactant is employed as the major foam-former or -stabilizer, the liquid phase preferably contains from about 0.4 to about 10 percent, more preferably about 0.5 to about 1 percent, of the silicone surfactant based on the total weight of the liquid solution. When employed in systems wherein the major foam-forming action is provided by a known foam-former, e.g., hydrolyzed protein foam systems, less than about 0.4 percent and as little as 0.01 percent of the silicone surfactant on the same weight basis provides the above described advantageous properties.

The rate of drainage of liquid from foams produced according to this invention is largely dependent on the type of fire to be extinguished and the type of delivery system. In extinguishing hydrocarbon liquid fires the production of spreading, vapor-securing films is important. The spreading surfactant-water, vapor-securing film of this invention is supplied by

drainage of liquid from the foam lamella and the rate of drainage is important. In the heretofore known hydrolyzed protein foam systems, and in extinguishing other types of fires, a high rate of drainage may be undesirable since this reduces the water content and the resistance of the foam to radiant heat attack.

In the case of liquid hydrocarbon fires, if the drainage from foams produced by the cationic silicone surfactants is too rapid, the draining aqueous liquid film formed is thicker and the resulting denser surfactant-water film may settle beneath the liquid hydrocarbon surface. Moreover, at excessive drainage rates the foam itself may be caused to collapse prematurely. If the drainage is retarded somewhat, however, a continuous supply of liquid over a longer time period will be made available for film formation and spreading. The rate of drainage should not be too slow or loss of film, due to evaporation and possible solubilization in the liquid hydrocarbon, may exceed the input of film-forming liquid to the surface.

In extinguishing other types of fires, for example, when high expansion foams are used, it is generally desired to have a low rate of drainage in order to extend the life of the foam and to extend the "sticking" properties imparted by the elastic characteristics previously mentioned.

Drainage rates of aqueous foams generated by cationic silicone surfactants can be adjusted as desired and are effectively retarded by employing relatively high concentrations of the silicone surfactants and/or by the addition of a suitable organic or inorganic material, such as, asbestos, bentonite clay, etc., or water-soluble or water-dispersible organic polymers, to the foam liquid. These materials and polymers increase the bulk viscosity and surface plasticity of the foam lamellae. Useful polymers comprise any solid water-soluble or water-dispersible polymer, among which are included carboxymethylcellulose, hydroxyethylcellulose, cationic modified hydroxyethylcellulose, polyoxyethylene, polyvinyl alcohol, sodium polyacrylate, ethylene-maleic anhydride copolymers, and the like. Polymer concentrations in the liquid phase of the foam can be in the range of about 0.03 to 5.0 percent by total weight of the liquid phase.

Foams generated according to this invention by the use of cationic silicone surfactants with or without one or more of the drainage retarding polymers mentioned above can be applied to liquid hydrocarbon fires by either or both of two general methods, surface application or sub-surface injection. In the surface application method, the foam is applied to the burning surface and the flames are smothered as the fluid foam flows across the surface. Foam breakdown at the foam-flame front takes place during foam application, liberating some liquid. This liquid spreads as a film across the burning surface under the flames and acts as a vapor suppressing barrier. The covering of a burning, exposed area by the spreading film is enough to extinguish the flame. This extinguishing action is separate and distinct from the smothering effects of the foam itself. Upon extinguishment, the vapor-securing properties of the film, which is replenished and supplied by the foam, continue in effect. As long as there is liquid remaining in the foam it can drain due to gravitational action and the supply of liquid for film formation is assured. The film exhibits great mobility and travels rapidly to close any ruptures caused by mechanical agitation of the foam-film blanket, thus possessing self-healing properties. The mobility and self-healing properties of the vapor-securing film are obtained throughout the entire range of concentrations of cationic silicone surfactants given above and the foam can be formed and stabilized by any suitable means.

The sub-surface foam injection technique is useful for liquid hydrocarbon tank fires since existing product inlet lines at the tank base can be used rather than installing costly foam lines on the tank side for delivery to the hydrocarbon surface. Upon reaching the surface, the foam blanket and vapor-securing film action is similar to that described for the surface application.

Fire-fighting foams having cell walls are conveniently formed by introduction of a stream of air or other gas into aqueous solutions of the silicone surfactant corresponding to the liquid phase described above. The aqueous solutions can be conveniently made by the use of aqueous concentrates containing the silicon surfactant and, if desired, other additives, e.g., drainage retardant, hydrolyzed protein, licorice, etc. The aqueous silicone surfactant concentrate forms an active foamable solution on dilution with water.

The novel concentrates of this invention contain the silicone surfactant, a drainage retardant and can also contain a polar solvent, such as, isopropanol, ethanol, ethylene glycol and low molecular weight polyethylene glycols to reduce the viscosity and stabilize the drainage retarding polymer against oxidative degradation. They can also contain freezing point depressants, anti-bacterial agents, hydrolyzed proteins, licorice and other special purpose additives. The novel concentrates can contain about 0.01 to about 90 or 99.97 percent silicone surfactant; about 0.03 to about 50 percent drainage retardant; about 0, preferably 1, to about 49 percent of the above-mentioned polar solvent, and about 0, preferably about 1, to about 49 percent water, the percentages being based on the total weight of the concentrate. The concentrate can be diluted with from about 10 to about 1,000 times or more of its weight of water.

When the cationic silicone surfactants are used in accordance with this invention, they are most effective in a pH range of greater than about 6 to about 10, preferably about 6.5 to about 8.0. Any suitable buffers or pH adjusting materials can be used which are not reactive with the materials employed in the system. Suitable pH adjusting materials are the mineral acids, such as, hydrochloric acid, sulfuric acid and any suitable organic acid. From the standpoint of avoiding excessive degradation of silicone surfactant, it appears desirable to avoid pH's which are deep in the acid or basic ranges.

The ratio of foam volume to liquid weight in the foam is defined as the foam expansion. Foam expansion is adjusted by mechanically controlling the volume of air or other gas mixed with the foam solution. Generally speaking, foam expansions between about 4 and about 11 are most useful for producing low expansion foams of this invention. Foam expansion is also important in controlling the rate of liquid drainage and the foam fluidity. High expansion foams can also be made, for example, up to 1,000 or higher.

Excessively low expansion foams, for example, below about 4, may be thin and watery and may be extremely poor in their resistance to heat. Higher expansion foams, for example, about 15, have high apparent viscosities and may not be fluid enough to satisfactorily spread across burning liquid hydrocarbon surfaces. As the expansion of a foam is increased by incorporation of more air into the system, the rate of drainage decreases. The molecular weight, type and concentration of drainage retarding polymer also affects drainage rates and thus the optimum foam expansion varies in accordance therewith. The optimum expansion for a given foam solution, corresponding to optimum foam fluidity and drainage rate will be that which gives minimum extinguishment time and lowest drainage rate to obtain longest film duration for the type of fire to be extinguished.

Air, nitrogen, carbon dioxide, Ucon-12 or other suitable gaseous media can be used to expand and form the foam from the water-silicone surfactant concentrate.

The silicone surfactants used herein for use in foams for extinguishing hydrocarbon liquid fires, preferably have only limited, if any, solubility in liquid hydrocarbons with which they would be expected to come into contact. The solubility can be varied, for example, by changing the nature of the oleophilic group attached to the silicone backbone and/or solubility can be decreased by increasing the ratio of oleophilic to oleophobic portions of the silicone surfactant. The lower the solubility in the hydrocarbon, the longer is the effective life of the vapor-securing film provided the surfactant still adequately lowers surface tension.

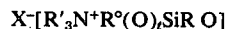
Many variations are possible in the constitution of the foam-forming concentrate and a wide variety of special purpose additives, i.e., bactericides, anti-freeze agents, anti-corrosive agents, etc., can be added. However, it is preferable to select the ingredients of the foam producing concentrate so that they are substantially mutually compatible.

Cationic silicone surfactants useful in the present invention include siloxanes or siloxane mixtures having the average formula:



wherein n is an integer of at least 1 and preferably varies from 1 to 3.

In this formula, B is a cationic siloxy unit illustrated by the formula:



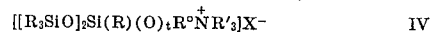
wherein R is selected from the class consisting of hydrogen and a monovalent hydrocarbon group free of aliphatic unsaturation having one to 18 carbon atoms; R'' is a divalent organic group having two to 18 carbon atoms, preferably two to eight, is free of aliphatic unsaturation, and is selected from the class consisting of divalent hydrocarbon groups, preferably alkylene groups, hydroxyl-substituted divalent hydrocarbon groups, preferably hydroxy-substituted alkylene groups, and $-R''OR''-$ groups wherein R'' is selected from the class consisting of divalent hydrocarbon, preferably alkylene, and hydroxy-substituted hydrocarbon, preferably hydroxy-substituted alkylene; R' is selected from the class consisting of a monovalent hydrocarbon group, free of aliphatic unsaturation, preferably alkyl, having one to 18 carbon atoms, when taken individually and when two R' groups are taken together with N, a divalent group containing a five to six member heterocyclic ring comprising carbon, nitrogen and hydrogen in which N is bonded to the R'' group and the remaining R' group such as morpholinium, $>N^+(CH_2CH_2)_2O$, piperidinium, $>N^+C_5H_{10}$, pyrrolidium, piperazinium, and the like; X is any inorganic anion having one to three valences, such as, chlorine, bromine, iodine, aryl sulfonate having six to 18 carbon atoms, nitrate, nitrite and borate anions, when taken individually, sulfate and sulfite anions when two X groups are taken together and phosphate when three X groups are taken together. Preferably X is selected from the class consisting of bromine, iodine, chlorine and aryl sulfonate as described above, when taken individually, and sulfate when two X groups are taken together. More preferably, X is bromine, iodine or chlorine, and t is an integer of 0 to 1.

In formula I, the A's are siloxy units of the formula:



wherein Z is a monovalent hydrocarbon group having one to 18 carbon atoms. Typical of the units represented by formula III are trimethylsiloxy, triphenylsiloxy, triphenylethylsiloxy, triethylsiloxy, tritolylsiloxy and the like.

Preferably, the cationic silicone surfactants represented by formula I are linear as shown by the following formula:



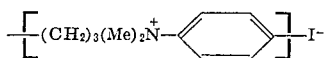
wherein R, R'' , R' , X and t are as defined above.

Typical monovalent hydrocarbon groups represented by R, R' and Z are alkyl or cycloaliphatic groups, such as, methyl, ethyl, propyl, cyclopentyl, butyl, amyl, octyl, cyclohexyl, isopropyl, tert-butyl, octadecyl, isooctyl and the like, aryl groups, such as, phenyl, biphenyl, naphthyl and the like, aralkyl groups, such as, benzyl, beta-phenylethyl, beta-phenylpropyl, alkaryl groups such as tolyl, and the like.

The groups R, R' and Z and the integers t and y can be each the same or different throughout the same unit. The siloxane surfactant can contain two or more different units of formula II and/or formula III in the same molecule or all units of formula II and/or III may be the same throughout the same molecule.

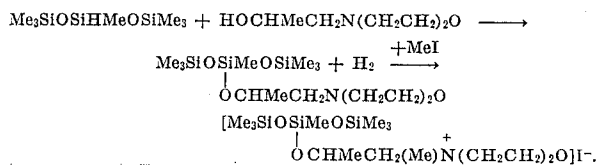
Typical divalent groups as represented by R^o in the above formulas include ethylene, 1,3-propylene, 1,2-propylene, 1,4-butylene, 1,3-butylene, 1,5-pentylene, 1,4-pentylene and 1,6-hexylene, cycloalkylene including cyclohexylene, cyclopentylene, and the like, arylene including phenylene, tolylene, xylylene, naphthylene, —C₆H₄CH₂C₆H₄—, benzylidene, 5,6-dimethyl-1,3-phenylene, 2,4-dimethyl-1,3-phenylene anthrylene and the like; hydroxyl-substituted divalent hydrocarbon groups such as hydroxyalkylene groups including hydroxymethylene, hydroxyethylene, 2-hydroxy-1,3-propylene, 3-hydroxy-1,2-propylene, 2-hydroxy-n-butylene, 2-hydroxy-1,3-butylene and the like, hydroxycycloalkylene including 2-hydroxy-1,3-cyclopentylene, 2-hydroxy-1,4-cyclohexylene and the like, hydroxyarylene groups including 2-hydroxy-1,4-phenylene, 3-hydroxy-1,4-tolylene, 2-hydroxy-1,4-xylylene, 3-hydroxy-1,2-naphthylene, 6-hydroxy-1,2-anthrylene and the like; and divalent groups of formula —R''OR''— wherein R'' is selected from the class consisting of divalent hydrocarbon groups such as those listed above and hydroxyl-substituted divalent hydrocarbon groups such as those listed above, including by way of example, 1,3-propyleneoxy-1,3-propylene, 1,3-propyleneoxy-1,4-butylene, 1,3-propyleneoxy-1,2-butylene, 1,3-propyleneoxy-2-hydroxy-1,3-propylene, 1,2-propyleneoxy-3-hydroxy-1,4-butylene and the like. Typical alkyleneoxyalkylene groups represented by R^o in the above formulas include ethyleneoxyethylene, 1,2-propyleneoxy-1,2-propylene and the like. The groups, radicals and integers set forth in the above formulas may be respectively the same or different in the same molecule and, where more than one such group, radical or integer appears in each unit, it may be the same or different in the same unit.

Typical —(O)R^oN⁺R'₃ X⁻ groups in the above formulas (IV) and (II) include —[O(CH₂)₂(Me)N⁺C₅H₁₀] I⁻, —[O(CH₂)₂N⁺Me₃] I⁻, —[OCHMeCH₂N⁺Me₃] I⁻, —[O(CH₂)₂N⁺Et₂Me] I⁻, —[OCHMeCH₂N⁺Et₂Me] I⁻, —[O(CH₂)₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[OCHMeCH₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[OCHMeCH₂OCHMeCH₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[OCHMeCH₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[O(CH₂)₂O(CH₂)₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[(CH₂)₃N⁺Me₃] I⁻, —[(CH₂)₃N⁺Et₂Me] I⁻,

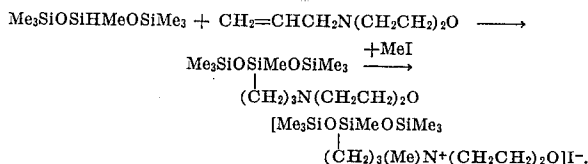


—[(CH₂)₃OCHMeCH₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[(CH₂)₃(Me)N⁺C₅H₁₀] I⁻, —[(CH₂)₃(Me)N⁺(CH₂CH₂)₂O] I⁻, —[(CH₂)₃OCH₂CH(OH)CH₂(Me)N⁺(CH₂CH₂)₂O] I⁻, —[(CH₂)₂CHMe(Me)N⁺(CH₂CH₂)₂O] I⁻, —[(CH₂)₃N⁺Et₂Me]₂SO₄⁻, —[(CH₂)₂CHMeN⁺(CH₂CH₂)₂O]NO₃⁻, —[OCHMeCH₂(Me)N⁺(CH₂CH₂)₂O]CH₃C₆H₅SO₃⁻, —[(CH₂)₃(Me)N⁺C₅H₁₀]₃PO₄⁻, and —[O(CH₂)₂(Me)N⁺(CH₂CH₂)₂O]BO₂⁻.

Cationic polysiloxane surfactants belonging to the hydrolyzable class, i.e., those of the above formulas (IV) and (II) wherein $\tau=1$, are prepared by the stannous octoate catalyzed reaction of a hydrosiloxane, e.g., R₃SiOSiHROSiR₃, with an alcohol containing a tertiary nitrogen and subsequent reaction with a hydrocarbyl halide, e.g., methyl iodide. For example:



Cationic polysiloxane surfactants belonging to the non-hydrolyzable class, i.e., those of formulas (IV) and (II) wherein $\tau=0$, are prepared by the platinum-catalyzed addition of a hydrosiloxane, e.g., R₃SiOSiHROSiR₃, to an alkenyl amine, e.g., a tertiary allyl amine, followed by reaction with a hydrocarbyl halide, e.g., methyl iodide. For example:

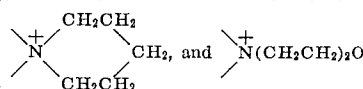


These reactions are readily carried out by mixing the initial reactants together with the catalyst. The mixture is then heated to elevated temperature, e.g., about 100° to about 200° C. and the reaction is carried out under a nitrogen blanket. Completion of the reaction is determined by testing with AgNO₃ for any remaining hydrosiloxane. After completion, the reaction mixture is cooled and, if need be, neutralized as with sodium bicarbonate. The resulting reaction product can be filtered and subjected to vacuum and moderate temperature, e.g., 30° to 50° C., to remove volatiles by evaporation such as by rotary evaporation. The reactants are advantageously mixed on a mole for mole basis and, if desired, suitable solvents can be used.

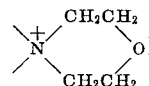
The reaction with the hydrocarbyl halide does not require a special catalyst and need not be carried out in a solvent, although it is advantageous to dissolve both the siloxane and the halide in about 40 to about 100 wt. percent polar solvent, e.g., alcohols or ethers. Atmospheric or super-atmospheric pressures can be used. The reactants preferably are mixed on a mole for mole basis. Moderate temperatures, e.g., 40° to 80° C., can be used. All reactants and solvent can be mixed at once and maintained at the reaction temperature or they may be added in any desired order. The product can be separated in any convenient manner, e.g., vacuum rotary evaporation. Purification, as by washing with inert solvents, can be carried out, if desired.

Cationic siloxanes and methods for making them are disclosed in U.S. Pat. application Ser. No. 887,428 entitled "Cationic Siloxanes" filed concurrently herewith by Bela Prokai. Cationic siloxanes are also disclosed in U.S. Pat. Nos. 3,402,191; 3,278,465; 2,972,598, and others and British Pat. No. 1,153,824 and others. The disclosures of these applications and patents are incorporated herein by reference.

The following examples are presented wherein, unless otherwise indicated, Me means methyl, percentages and parts are by weight, temperatures are in degrees Centigrade, viscosities are in centipoises at 25° C., >N⁺C₅H₁₀ designates the piperidinium group,



designates the morpholinium group



Various tests used in these examples are described below.

examples are described below.

A. Time For Foam Breakdown On Gasoline

Thirty cc of regular gasoline (Esso) is placed in a 100 cc petri dish. Fifty grams of a 1 percent by weight surfactant solution in tap water is placed in a Waring Blender. The solution is blended for 30 seconds at 5,000 rpm. Within the next 30 seconds, the foam is scooped into the petri dish and leveled with a spatula. This point in time is called zero. The dish is allowed to set at room temperature until the first opening in the foam blanket occurs and gasoline is exposed. This time is called time for foam breakdown on gasoline. It measures the resistance of the foam to breakdown as a result of contact with gasoline liquid and vapor.

B. Time That Film Lasts On Gasoline

The time at which the first opening in the foam blanket (produced according to method A) occurs as described in the previous test is taken as time zero. A lighted match is held about one-half inch above the exposed gasoline surface. No immediate ignition demonstrates the presence of a vapor-securig film. At frequent intervals the resistance to ignition is tested in the same way. The time until first ignition occurs is denoted as the "time film lasted on gasoline".

C. Foam Stability Test (Quarter Time)

The solution is blended 30 seconds as described in test A above and scooped into a 200 cc drainage tray. As the foam drains, the liquid is collected in a graduate and volume versus time recorded. Time zero is taken as 30 seconds after blending stops. The total weight of foam is determined and the time for one quarter of this weight of liquid to drain is the quarter-time. Expansion is the foam volume (standardized 200 cc) divided by the weight of liquid in the foam in grams.

D. Elastic Properties

A 1 percent surfactant solution is gently swirled in a 4-ounce bottle. If elastic properties are present, the solution swirls slowly to a stop (taking as reference any bubbles in the solution), then reverses in direction. Test results given in the examples include the durability of such elastic properties measured in days.

E. Sea Water Compatibility

The surfactant solution of the desired concentration is prepared and diluted to 50 g with ASTM D-1141-52 sea salt solution. The solution is shaken in a bottle and observation of the foam volume is made.

Also, in the examples, surface tension is given in dynes per centimeter, expansion is the ratio of foam volume (e.g., in cubic centimeters) to the weight (e.g., in grams) of liquid in the foam and quarter time is the time in minutes for one quarter of the liquid by weight to drain from a foam.

EXAMPLES 1-14

In these examples several cationic surfactants as identified in Table 1 below were tested using the above-described methods A, B and D. The results are listed in Table 1.

EXAMPLES 15-40

These examples illustrate the effects of the cationic silicone surfactants on hydrolyzed protein concentrates and foam systems produced from such concentrates. In Examples 15-27 (Table 2), the hydrolyzed protein concentrate used was Mearl-foam 5 sold by Mearl Corporation. The hydrolyzed protein used in Examples 28-40 (Table 3) was National Aer-O-Foam, 6 percent Regular, sold by National Foam System, Inc. Both concentrates contained 50 percent hydrolyzed protein solids in water. The amounts and types of silicone surfactants designated in Tables 2 and 3 were thoroughly mixed with the concentrate. Two controls with no added surfactant were also run. The properties of the resulting concentrates and controls are given in Tables 2 and 3.

The concentrates and controls were each diluted with tap water at the ratio of 1 weight part of concentrate or control to 16 weight parts of water and beaten with air to form foams. The properties of the resulting solutions and foams are given in Tables 2 and 3. All solutions were clear except Example 22 which was cloudy.

TABLE 2

Properties of Protein Foam Systems

Exam- ple No.	Surfac- tant No.	% Sur- factant Solids	pH	Sur- face Ten- sion	Sur- face Ten- sion	Foam Solution Quarter Time	Expan- sion
15	6% Pro- tein Control	0.0	6.9	43.5	51.2	17.5	6.4
35	16	0.1	6.8	38.8	37.2	12.5	6.9
	17	0.11	6.8	35.4	36.1	6.7	6.7
	18	0.15	6.8	33.8	31.0	6.3	6.9
	19	0.11	6.75	29.7	24.2	6.3	6.7
	20	0.1	6.75	34.3	35.5	6.0	7.0
	21	0.22	6.75	32.2	29.6	4.1	6.7
	22	1.02	6.8	23.9	24.1	3.3	7.1
40	23	1.03	6.8	26.9	27.3	1.8	5.0
	24	1.02	6.8	26.6	27.5	~1.7	4.8
	25	1.0	6.8	28.2	26.1	~1.4	4.8
	26	1.03	6.8	26.8	26.5	~1.4	4.7
	27	1.02	6.8	27.3	27.5	~1.4	4.8

TABLE 1

Example number	Surfactant number	Surfactant structure	A. Time for foam break- down on gasoline (minutes)	B. Time that film lasts on gasoline (minutes)	D. Elastic properties (days)
1.....	1	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NMe}_3]^+\text{I}^-$	7	4 hours.....	Yes (8).
2.....	2	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NMe}_3]^+\text{Cl}^-$	About 1	>4 hours.....	No (7).
3.....	3	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NMe}_3]^+\text{Br}^-$	25	About 18 hours...	Do.
4.....	4	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{Me})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]^+\text{Br}^-$	14	37.....	No (1).
5*.....	5	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{Me})\text{NHC}_6\text{H}_{11}]^+\text{I}^-$	About 1	0.....	No (6).
6.....	6	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NEt}_3]^+\text{I}^-$	24	3.....	Yes (11).
7.....	7	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3\text{NEt}_3]^+\text{I}^-$	16	3.....	Yes (13).
8.....	8	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{Me})\text{NC}_6\text{H}_{10}]^+\text{I}^-$	5	About 4 hours ¹ ...	
9.....	9	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{Et})\text{NC}_6\text{H}_{10}]^+\text{I}^-$	16	2.....	Yes (1).
10.....	10	$[(\text{Me}_3\text{SiO})_2\text{MeSiOCHMeCH}_2\text{NMe}_3]^+\text{I}^-$	15	>15.....	Small amount. No (7).
11**.....	11	$[(\text{Me}_3\text{SiO})_2\text{MeSiO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2(\text{Me})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]^+\text{I}^-$	1	0.....	Yes (1).
12.....	12	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_2\text{CHMe}(\text{Me})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]^+\text{I}^-$	7	0.5.....	No (1).
13.....	13	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_2\text{OCHMeCH}_2(\text{Me})\text{N}(\text{CH}_2\text{CH}_2)_2\text{O}]^+\text{I}^-$	>48	>3 hours ¹	Yes (5).
14.....	14	$[(\text{Me}_3\text{SiO})_2\text{MeSi}(\text{CH}_2)_3(\text{Me})\text{N}(\text{C}_6\text{H}_4)]^+\text{I}^-$	10	3.....	No.

¹ Excellent resealing properties.

*Does not illustrate the invention; presented for comparison.

**Apparently hydrolyzed on standing and thus did not provide better results.

TABLE 3

Properties of Protein Foam Systems

Exam- ple No.	Foam Concentrate		pH	Foam Solution			Expan- sion
	Surfac- tant No.	% factant Solids		Sur- face Ten- sion	Sur- face Ten- sion	Quarter Time	
28	6% Pro- tein Control	0.0	7.5	40.9	51.9	25.0	6.9
29	6	0.050	7.42	35.1	38.7	16.5	7.2
30	7	0.054	7.42	34.6	38.5	16.3	7.1
31	8	0.056	7.50	34.6	38.5	15.5	7.2
32	13	0.052	7.40	31.4	31.4	15.5	7.1
33	1	0.052	7.50	35.3	39.8	14.6	7.1
34	3	0.054	7.45	34.7	39.6	13.8	7.1
35	7	0.104	7.45	33.0	36.4	14.3	7.2
36	8	0.099	7.40	33.0	36.9	14.3	7.2
37	13	0.105	7.45	29.3	29.0	13.4	7.3
38	6	0.104	7.42	32.8	36.7	12.1	7.0
39	1	0.101	7.50	33.3	37.3	12.0	7.1
40	3	0.102	7.50	32.7	37.2	10.0	7.2

EXAMPLE 41

Surfactant No. 1 was mixed with tap water to provide a solution having a concentration of 0.75 wt. percent surfactant. The solution was then foamed with air to provide a foam having an expansion of 8.0 cc/g and a quarter-time of 4.3 minutes.

The resulting foam was placed on 5 cc gasoline. The time until the foam had broken down sufficiently to expose the gasoline was 7 minutes. On 30 cc gasoline it was found to be 6 minutes and 25 seconds. No large bubbles formed at the foam-gasoline interface. Such bubbles result from evaporating gasoline and can rise through the foam to the surface and can burst and ignite at the surface. The absence of such bubbles indicates that the surfactant containing solution forms a tough film on the gasoline.

Foam prepared as described above was gently delivered to the surface of room temperature gasoline in a dish. At time zero the flame (about one-half inch long) of a propane torch was held at the edge of the dish about 1 inch above the foam to determine how long the foam acted as an effective barrier to the flammable vapors. This is defined as the resistance-to-ignition time and was found to be 20 seconds. At the onset of re-ignition, the time required for the flames to completely destroy the foam-film blanket and for the gasoline to burn freely, defined as the burnback time, was found to be 1 minute. A vapor-securing film of the surfactant solution over the gasoline was evident.

EXAMPLE 42

Surfactant No. 1 was mixed with sea water to provide a solution having a concentration of 0.66 percent surfactant (see Method E). The solution was then foamed with air to provide a stable foam. When tap water was used in place of sea water, a more stable foam was obtained.

EXAMPLE 43

An aqueous solution was prepared from tap water to contain 0.72 percent solids of Surfactant No. 1 and 0.23 percent solids of a polyethylene oxide polymer, a 1 percent aqueous solution of which has a viscosity of 150 cps at 25° C., (Union Carbide Corporation POLYOX WSRN 3000). Ignition resistance time was measured in the manner described in Example 41 and was found to be 1 minutes. The burnback time was measured in the manner described in Example 41 and was found to be 2 minutes and 35 seconds.

In systems utilizing the hydrolyzed protein or other known foam stabilizer as the major foaming and stabilizing agent, the hydrolyzed protein or other known stabilizer is preferably used in those amounts conventionally used in previous hydrolyzed protein systems. Other known stabilizers include powdered licorice extract, glue, saponin, glycerin, glucose,

sodium sulfonate and quillaia bark and, when each is used in place of the hydrolyzed protein of Examples 15-40 on a weight for weight basis, results similar to those of Examples 15-40 are obtained. The known foam stabilizers, especially the hydrolyzed protein stabilizers, impart additional durability or persistency to the foam. Similarly, the drainage retardant polymers impart durability or persistency.

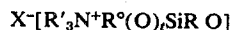
It is preferred that the drainage retarding organic polymer employed herein be such that a 1 weight percent aqueous solution thereof has a viscosity of about 2 to about 10,000 cps at 25° C.

What is claimed is:

1. A process for extinguishing a burning combustible, which comprises (1) providing on the surface of the combustible a self-healing, vapor-securing film of an aqueous liquid containing a silicone surfactant that is at least partially soluble therein and reduces the surface tension thereof, said surfactant having the formula:

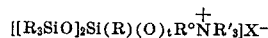


wherein n is an integer of 1 to 3, A is a siloxy unit of the formula: $Z_3SiO_{1/2}$ wherein Z is a monovalent hydrocarbon group free of aliphatic unsaturation and having one to 18 carbon atoms, and B is a cationic siloxy unit of the formula:



wherein R is selected from the class consisting of hydrogen and monovalent hydrocarbon groups free of aliphatic unsaturation having one to 18 carbon atoms; R'' is a divalent organic group having two to 18 carbon atoms, is free of aliphatic unsaturation, and is selected from the class consisting of divalent hydrocarbon groups, hydroxyl-substituted divalent hydrocarbon groups, and $-R''OR''$ -groups wherein R'' is selected from the class consisting of divalent hydrocarbon groups and hydroxyl-substituted divalent hydrocarbon groups, R' is selected from the class consisting of monovalent hydrocarbon groups free of aliphatic unsaturation and having one to 18 carbon atoms when taken individually and, when two R' groups are taken together with N of said formula, a divalent group containing a five to six member heterocyclic ring in which N is bonded to said R'' group and the remaining R' group; X is an inorganic anion, and t is an integer of 0 to 1; and (2) providing an aqueous foam in contact with and immediately above the film of aqueous liquid, wherein the cell walls of the aqueous foam comprise an aqueous liquid containing said silicone surfactant and said film is formed by drainage of said liquid from said foam.

2. Process as claimed in claim 1 wherein said silicone surfactant has the formula:



wherein R , R'' , R' , X and t are as defined in claim 1.

3. Process as claimed in claim 2 wherein said silicone surfactant has the formula given in claim 2 wherein R is monovalent hydrocarbon; R'' is selected from the class consisting of alkylene, hydroxy-substituted alkylene, alkyleneoxyalkylene and hydroxy-substituted alkyleneoxyalkylene; R' is selected from the class consisting of alkyl when taken individually and morpholinium and piperidinium when two R' groups are taken with N of said formula; X is selected from the class consisting of chloride, iodine and bromine anions when taken individually an sulfate anion when two X groups are taken together; and t is an integer of 0 to 1.

4. Process as claimed in claim 3 wherein the aqueous liquid in the cell wall consists essentially of water and said silicone surfactant as the major foaming and foam stabilizing agent.

5. Process as claimed in claim 3 wherein the aqueous liquid consists essentially of water, said silicone surfactant and a foam former.

6. Process as claimed in claim 5 wherein the foam former is a partially hydrolyzed protein.

7. Process as claimed in claim 6 wherein said surfactant is present in the amount of about 0.01 to about 0.4 percent based on the total weight of said aqueous liquid.

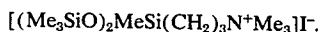
8. Process as claimed in claim 5 wherein said aqueous liquid comprises water and a mixture of a major amount of said foam former and a minor amount of said silicone surfactant.

9. Process as claimed in claim 5 wherein said aqueous liquid comprises water and a mixture of a minor amount of said foam former and a major amount of said silicone surfactant.

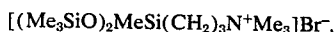
10. Process as claimed in claim 3 wherein said silicone surfactant is the major foaming and foam-stabilizing agent and is present in amounts of about 0.4 to about 10 percent based on the total weight of said aqueous liquid.

11. Process as claimed in claim 6 wherein said silicone surfactant is present in amounts of about 0.5 to about 1 percent based on the total weight of said aqueous liquid.

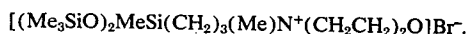
12. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



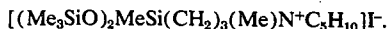
13. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



14. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



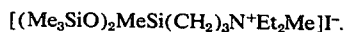
15. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



16. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



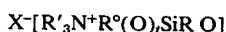
17. Process as claimed in claim 3 wherein said silicone surfactant has the average formula:



18. A concentrate for the production of a fire-fighting foam having cell walls comprised of an aqueous liquid containing said concentrate, comprising, about 0 to about 49 percent water, about 0.01 to about 99.97 percent of a silicone surfactant having the formula:

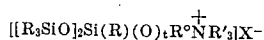
AB_nA

wherein n is an integer of 1 to 3, A is a siloxy unit of the formula: $\text{Z}_3\text{SiO}_{1/2}$ wherein Z is a monovalent hydrocarbon group free of aliphatic unsaturation and having one to 18 carbon atoms, and B is a cationic siloxy unit of the formula:



wherein R is selected from the class consisting of hydrogen and monovalent hydrocarbon groups free of aliphatic unsaturation having one to 18 carbon atoms; R^0 is a divalent organic group having two to 18 carbon atoms, is free of aliphatic unsaturation, and is selected from the class consisting of divalent hydrocarbon groups, hydroxyl-substituted divalent hydrocarbon groups, and $-\text{R}''\text{OR}''$ -groups wherein R'' is selected from the class consisting of divalent hydrocarbon groups and hydroxyl-substituted divalent hydrocarbon groups, R' is selected from the class consisting of monovalent hydrocarbon groups free of aliphatic unsaturation and having one to 18 carbon atoms when taken individually and, when two R' groups are taken together with N of said formula, a divalent group containing a five to six member heterocyclic ring in which N is bonded to said R^0 group and the remaining R' group; X is an inorganic anion, and t is an integer of 0 to 1; about 0.03 to about 50 percent of a normally solid organic water-soluble polymer capable of retarding drainage of liquid from said cell walls, and about 0 to about 49 percent of a polar solvent, all of said percentages being based on the total weight of said concentrate.

19. Concentrate as claimed in claim 18 wherein said surfactant has the formula:



wherein R is monovalent hydrocarbon; R^0 is selected from the class consisting of alkylene, hydroxy-substituted alkylene, al-

kyleneoxyalkylene and hydroxy-substituted alkyleneoxyalkylene; R' is selected from the class consisting of alkyl when taken individually and, when two R' groups are taken together with N of said formula, a divalent group containing a five to six member heterocyclic ring in which N is bonded to said R^0 group and the remaining R' group; X is an inorganic anion, and t is an integer of 0 to 1; R, R^0 and R' each containing no more than 18 carbon atoms and being free of aliphatic unsaturation.

20. Concentrate as claimed in claim 19 wherein said water-soluble polymer is polyoxyethylene glycol.

21. Concentrate as claimed in claim 19 wherein said water-soluble polymer is a cationic modified hydroxyethylcellulose.

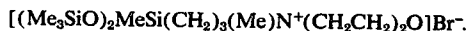
22. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:



23. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:



24. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:



25. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:



26. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:



27. Concentrate as claimed in claim 19 wherein the amount of said silicone surfactant is about 0.01 to about 98.97 percent, the amount of said water-soluble polymer is about 0.03 to about 50 percent, the amount of water is about 1 to about 49 percent and the amount of polar solvent is 1 to about 49 percent.

28. An aqueous, fire-extinguishing foam-forming composition comprising an aqueous liquid containing about 0.01 to about 10 percent of a silicone surfactant having the formula:

AB_nA

wherein n is an integer of 1 to 3, A is a siloxy unit of the formula: $\text{Z}_3\text{SiO}_{1/2}$ wherein Z is a monovalent hydrocarbon group free of aliphatic unsaturation and having one to 18 carbon atoms, and B is a cationic siloxy unit of the formula:



wherein R is selected from the class consisting of hydrogen and monovalent hydrocarbon groups free of aliphatic unsaturation having one to 18 carbon atoms; R^0 is a divalent organic group having two to 18 carbon atoms, is free of aliphatic unsaturation, and is selected from the class consisting of divalent hydrocarbon groups, hydroxyl-substituted divalent hydrocarbon groups, and $-\text{R}''\text{OR}''$ -groups wherein R'' is selected from the class consisting of divalent hydrocarbon groups and hydroxyl-substituted divalent hydrocarbon groups, R' is selected from the class consisting of monovalent hydrocarbon groups free of aliphatic unsaturation and having one to 18 carbon atoms when taken individually and, when two R' groups are taken together with N of said formula, a divalent group containing a five to six member heterocyclic ring in which N is bonded to said R^0 group and the remaining R' group; X is an inorganic anion, and t is an integer of 0 to 1; and about 0.03 to about 5 percent of a water-soluble polymer, said percentages being based on the weight of said liquid.

29. Composition as claimed in claim 28 wherein said water-soluble polymer is polyoxyethylene glycol.

30. Composition as claimed in claim 28 wherein said water-soluble polymer is cationic modified hydroxyethylcellulose.

31. Concentrate as claimed in claim 19 wherein said surfactant has the average formula:

