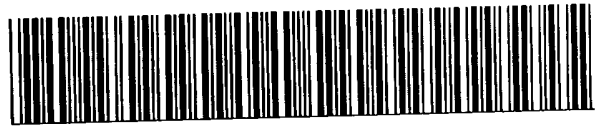


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(57) Abstract

This invention relates to water-soluble fluorochemical foam stabilizers and film formers derived from polyamines, perfluoroalkyl group containing esters or acid halides and hydrophilic and hydrophobic group containing compounds which react with primary, secondary and tertiary amino groups. The novel foam stabilizers and film formers are useful as additives for aqueous film forming foam fire-fighting agents improving the foam stability against polar solvents and enhancing the fire-fighting performance.

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FLUOROCHEMICAL FOAM STABILIZERS AND FILM FORMERS.

BACKGROUND OF INVENTION

The instant invention related to novel water soluble fluorochemical foam stabilizers and film formers useful as additives to aqueous film forming foam agents improving the stability of foams of such agents when in contact with polar solvents and fuels, improving the fire performance of such foams and allowing the formulation of aqueous film forming agents having Newtonian properties.

Fire fighting foam concentrates which produce aqueous film forming foams are known a) as AFFF agents (for Aqueous Film Forming Foam) if they have the capability of extinguishing non-polar solvent or fuel fires and b) as AR-AFFF agents (for Alcohol Resistant AFFF agent) if they have the capability of extinguishing polar as well as non-polar solvent or fuel fires. Aqueous film forming foams are the most efficient fire fighting agents because they act in the following two ways as outlined in US 4,472,286:

- a) As aqueous foams they are used as primary fire extinguishing agents and
- b) As aqueous film formers they act as vapor suppressors, augmenting the fire-extinguishing efficiency of the foam and preventing reignition of fuel of solvent vapors.

It is the second property which makes AFFF and AR-AFFF agents far superior to other known fire fighting agents. With AFFF and AR-AFFF agents, the vapor sealing action on non-polar solvents and fuels is achieved by the spreading of the aqueous agent solution draining from the foam onto the non-polar solvent and fuel surfaces, while with AR-AFFF agents, the vapor sealing action on polar

solvents and fuels is achieved by the precipitation of a polymer film from a polymer solution draining from the foam onto the polar solvent surface and the spreading of the aqueous film forming solution, also draining from the AR-AFFF foam, over the surface of the precipitated polymer film.

The criterion necessary to attain spontaneous spreading of two immiscible liquids has been taught by Harkins et al, *Journal of American Chemistry*, 44, 2665 (1922).

The measure of the tendency for spontaneous spreading of an aqueous solution over the surface of non-polar solvents such as hydrocarbons is defined by the spreading coefficient (SC) and can be expressed as follows:

$$SC_{a/b} = \gamma_b - \gamma_a - \gamma_j, \text{ where}$$

$SC_{a/b}$ = Spreading coefficient

γ_b = Surface tension of the lower hydrocarbon fuel phase,

γ_a = Surface tension of the upper aqueous phase,

γ_j = Interfacial tension between the aqueous upper phase and the lower hydrocarbon phase.

If the SC is positive, an aqueous solution should spread and film formation on top of the hydrocarbon surface should occur. The more positive the SC, the greater the spreading tendency will be.

For example, if a hydrocarbon fuel has a surface tension of 20 dynes/cm and an aqueous solution has a surface tension of 16 dynes/cm and the interfacial tension between the two immiscible liquids is 1.0 dyne/cm, then the spreading coefficient (SC) will be +3 ($SC = 20 - 16 - 1 = +3$) and therefore film formation will occur.

Today's AFFF and AR-AFFF agents contain one or more fluorochemical surfactants providing the desired low surface tension of 15 to 18 dynes/cm, one or more hydrocarbon surfactants, providing the desired interfacial tension of 1 to 5 dynes/cm as well as the desired foam properties such as foam expansion, foam fluidity and foam drainage, fluorochemical synergists to improve the efficiency of fluorochemical surfactants, foam stabilizers, solvents, electrolytes, pH buffers, corrosion inhibitors and the like. In addition to the above components in AFFF agents, AR-AFFF agents contain one or more water-soluble polymers which

precipitate on contact with a polar solvent or fuel, providing a protecting polymer film at the interface between fuel and the aqueous film forming foam. Many US patents describe the composition of AFFF agents as summarized in U.S. Pat. No. 4,999,119. Additional AFFF agent compositions are also described in U.S. Pat. Nos. 4,420,434; 4,472,286; 5,085,786 and 5,218,021.

Compositions of AR-AFFF agents using thixotropic polysaccharide gums as water-soluble polymers which precipitate on contact with polar solvents or fuels and which were found to be the most efficient polymeric film formers are described in U.S. Pat. Nos. 3,957,657; 4,060,489; 4,149,599; 4,306,979; 4,387,032; 4,644,267; 4,060,132 and 4,999,119.

Unlike regular AFFF agents foams which collapse within seconds upon contact with polar solvents and fuels, AR-AFFF agent foams based on thixotropic polysaccharides have foam stabilities ranging from about a minute up to 10 minutes before collapsing. While the development of AR-AFFF agents based on thixotropic gums has been a significant progress since AR-AFFF agents can be used to fight both polar and non-polar solvent fires, they have nevertheless shown to have a number of deficiencies.

In order for AR-AFFF agents to be efficient in fighting polar solvent fires, it was found that AR-AFFF agents for 6 and 3% proportioning with fresh or sea water require from 1 to 1.5% of thixotropic polysaccharide to be efficient film formers providing the required foam stability and therefore fire fighting efficiency.

At these polysaccharide levels, AR-AFFF agents are thixotropic gel like materials with viscosities as high as 5000 centipoise which only upon application of shear will turn into fluid and readily flowable agents which can be proportioned with water. In addition, polysaccharides as natural products are readily biodegradable and oxidizable and upon aging, AR-AFFF agents were found to form solid blocks of gum on the surface of AR-AFFF agents. Furthermore, polysaccharide gums are not soluble in solvents used as antifreeze, and it is therefore not possible to produce freeze-protected AR-AFFF agents protected to temperature much below zero °C.

In U.S. Pat. No. 4,424,133 AR-AFFF agents are described using polysaccharide gums in combination with protein hydrolysates and U.S. Pat. No. 4,859,349 discloses the use of complexes of anionic polysaccharides and cationic

fluorochemical surfactants.

U.S. Pat. No. 4,303,534 describes foam fire fighting compositions comprising fluorochemical and hydrocarbon surfactants, hydrolized protein and a water soluble high molecular weight compound having several repeating units containing a fluoroalkyl group and a water solubilizable group having a fluorine content of not less than 10% and a molecular weight of not less than 5000, useful for fighting polar solvent fires.

U.S. Pat. No. 4,563,287 describes a non-foaming cooking oil fire extinguishing composition comprising a water soluble high molecular weight compound as described in U.S. Pat No. 4,303,534 having a fluorine content of not less than 15%.

It has now been surprisingly found that novel water soluble oligomeric and polymeric additives derived from oligomeric and polymeric amines, esters or halides of perfluoroalkyl group containing acids and optionally and preferably hydrophilic group containing compounds and optionally hydrophobic group containing compounds capable to react with primary, secondary or tertiary amino groups are useful additives to aqueous film forming agents of both the AFFF and AR-AFFF type acting as foam stabilizers and film formers, improving the performance of such agents. Depending on the structure and molecular weight of the instant additives, they also act as foaming agents.

Fluoroamide-amino polymers derived from polyethyleneimines and perfluoroalkyl esters are described in U.S. Pat. No. 3,769,307 as oil repellent finishes for cellulosic textiles.

Such fluoroamide-amino polymers were found to be useful as foam stabilizers and film formers; however, they were found to be considerably less effective than foam stabilizers and film formers derived from polyamines, where a part of the primary and secondary amines were reacted with R_f -group containing esters or acid halides and essentially all of the remaining primary and secondary amino groups were reacted with hydrophilic group and optionally with hydrophobic, non-fluorochemical group containing reactants.

More specifically, the instant additives, referred to as Foam Stabilizers or FS-additives, act similarly as polysaccharides act in AR-AFFF agents. The FS-

additives are, like polysaccharides soluble in water, but insoluble in polar solvents so they will precipitate from an aqueous film forming foam containing the instant FS-additives and form a liquid or solid film at the polar solvent/foam interface and prevent the further collapse and destruction of the aqueous film forming foam. Because the instant FS-additives contain perfluoroalkyl groups, they also improve the burnback resistance of aqueous film forming foams the same way as water soluble R_f -group containing oligomers and polymers act which are derived from perfluoroalkyl group containing mercaptans and hydrophilic monomers such as acryl amide, as described in U.S. Pat. No. 4,460,480.

These performance properties make the instant FS-additives useful in several ways as additives to aqueous film forming foam agents:

As additives to polysaccharide based AR-AFFF agents, they will improve the polar solvent foam stability without increasing the viscosity and without affecting or only marginally affecting other agent properties.

The FS-additives can also be used as partial replacements of polysaccharide in classical AR-AFFF agents, yielding lower viscosity AR-AFFF agents, still having some of the beneficial effects of the polysaccharide additive, such as long foam drainage times, and much better polar solvent foam stability than classical AR-AFFF agents.

Furthermore, and most importantly, the instant FS-additives can be used as additives to AFFF agents, yielding Newtonian AR-AFFF agents having as low a viscosity as regular AFFF agents and non-thixotropic properties. Newtonian AR-AFFF agents yield foams which are more fluid than non-Newtonian AR-AFFF agents containing polysaccharides, show faster control and extinguishment times and longer foam lives. If used on non-polar solvents, Newtonian AR-AFFF agents have increased burnback resistance when compared with the corresponding AFFF agent not containing the instant FS-additive.

Finally, the instant FS-additives can be used as additives to protein foams and fluoroprotein foams yielding improved burnback resistance and improved foam stability against polar solvents.

DETAILED DISCLOSURE

The present invention pertains to novel water soluble fluorochemical foam stabilizers and film formers useful as additives to aqueous film forming foam agents, improving the foam stability on polar solvents and therefore improving the extinguishment and the burnback resistance of these agents.

The present invention, furthermore, pertains to so-called alcohol resistant AFFF agents (AR-AFFF agents) having a reduced or no polysaccharide content and, therefore, significantly reduced viscosity, making it possible to produce AR-AFFF agents which are Newtonian or non-thixotropic and which can be produced in higher concentrations than today's AR-AFFF agents for 3% proportioning.

The novel additives, referred to as previously indicated as Foam Stabilizers or FS-additives, are water soluble oligomers and polymers derived from polyamines containing one or more Segment A, optionally and preferably one or more Segment B and optionally one or more Segment C.

Segment A are segments of formula Ia and Ib containing an oleophobic and hydrophobic perfluoroalkyl group.



wherein

R_f is independently a straight or branched perfluoroalkyl group of 4 to 20 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

E is either zero or independently a divalent linking group and can be a straight or a branched alkylene group of 1 to 16 carbon atoms or said alkylene group interrupted by one to three groups selected from the group consisting of $-NHR_1-$, $-O-$, $-S-$, $-SO_2-$, $-COO-$, $-OOC-$, $-CONR_1-$, $-NR_1CO-$, $-SO_2NR_1-$, $-NR_1SO_2-$ or terminated at the R_f -end with $-CONR_1-$ OR $-SO_2NR_1-$, where R_1 is attached to the carbon or sulfur atom and wherein R_1 is independently hydrogen or alkyl of 1 to 6 carbon atoms.

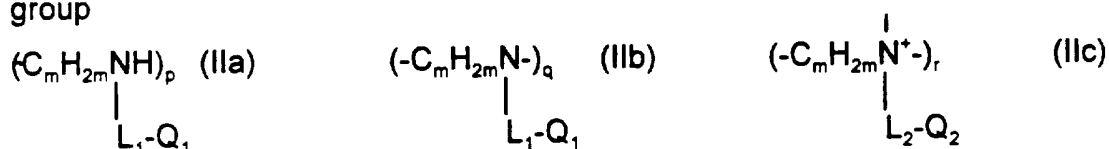
W is $-CO-$ or $-SO_2-$;

m is 2 to 10 and

p and q are 0 to 500 and p+q are equal or larger than 1.

Preferably, R_1 is a straight perfluoroalkyl group with 6 to 12 carbon atoms, E is zero or alkylene with 1 to 6 carbon atoms if W is $-\text{CO}-$ or $-\text{SO}_2-$ and $-\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{SCH}_2-$ or $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, if W is $-\text{CO}-$; m is 2 and p and q are 1 to 100.

Segment B are segments of formula IIa, IIb and IIc containing a hydrophilic group



wherein

L_1 is a divalent linking group and can be a straight or branched saturated or unsaturated hydrocarbon group of 1 to 16 carbon atoms or said hydrocarbon group interrupted by one to three groups selected from $-\text{NHR}_1-$, $-\text{O}-$, $-\text{S}-$, $-\text{CONR}_1-$, $-\text{NR}_1\text{CO}-$, $-\text{SO}_2\text{NR}_1-$, $-\text{NR}_1\text{SO}_2$ or terminated with $-\text{CO}-$ or $-\text{SO}_2-$ where the linking group L_1 is attached to the nitrogen in formula IIa or IIb;

L_2 is alkylene with 1 to 4 carbons;

Q_1 is a hydrophilic group and can be $-\text{COOH}$, $-\text{SO}_3\text{H}$ and salts thereof; $-\text{CONH}_2$, $-\text{CONHCH}_2\text{OH}$ or $(\text{OCH}_2\text{CH}_2)_n\text{OH}$;

Q_2 is $-\text{COO}^-$;

m is 2 to 10;

n is 1 to 10 and

p and q are 1 to 500.

Preferably, L_1 is $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$ and $-\text{CH}_2\text{CH}_2\text{CONHC}(\text{CH}_3)_2\text{CH}_2-$; and L_2 is $-\text{CH}_2-$; Q_1 is $-\text{COOH}$ and $-\text{SO}_3\text{H}$ or a salt thereof and m is 2 and p, q and r are 1 to 100.

Segment C are segments of formula IIIa and IIIb containing a hydrophobic group



wherein

L_3 is zero, -CO- or -SO₂-;

Q_3 is a straight or branched hydrocarbon group with 6 to 18 carbon atoms;

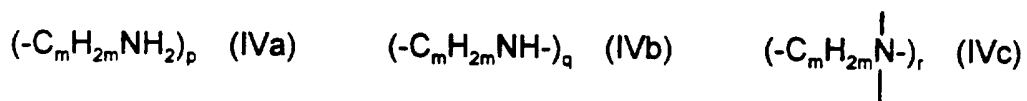
m is 2 to 10 and

p and q are 0 to 100.

Preferably, L_3 is zero or -CO-; Q_3 is straight alkyl with 8 to 18 carbons, m is 2 and p and q is 0 to 50.

The instant FS-additives can readily be derived in quantitative or near quantitative yield from polyamines containing segments of formula IVa, IVb and IVc and esters or acid halides of perfluoroalkyl groups containing carboxylic and sulfonic acids of formula V and VI, and reactants of formula VIIa, VIIb and VIII.

Polyamines containing segments of formula IVa, IVb and IVc



suitable for the synthesis of the instant FS-additives must have at least a combined total of three primary or secondary amino groups.

Suitable polyamines are commercially available aliphatic polyamines as described in Kirk Othmer, *Concise Encyclopedia of Chemical Technology*, John Wiley and Son, p. 350-351, (1985) and include:

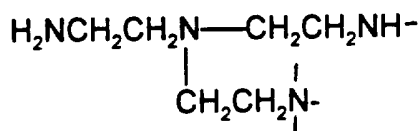
diethylenetriamine (DETA)	$H_2NCH_2CH_2NHCH_2CH_2NH_2$
triethylenetetramine (TETA)	$H_2N(CH_2CH_2NH)_2CH_2CH_2NH_2$
tetraethylenepentamine (TEPA)	$H_2N(CH_2CH_2NH)_3CH_2CH_2NH_2$
pentaethylenehexamine (PEHA)	$H_2N(CH_2CH_2NH)_4CH_2CH_2NH_2$
aminoethylpiperazine (AEP)	$NH_2CH_2CH_2N(CH_2CH_2)_2NH_2$
iminobispropylamine (IBPA)	$H_2N(CH_2)_3NH(CH_2)_3NH_2$

Higher molecular weight polyamines can be derived from the above amines, as well as from ethylene diamine, propylene diamine, 1,3-diamino propane and hexamethylene diamine, by reaction with difunctional halohydrins or with diesters and with divinyl compounds as described in U.S. Pat. No. 2,977,245. Preferred

polyamines are so-called polyethyleneimines or alkyl substituted polyethyleneimines which are derived by the homopolymerization of ethyleneimine and its derivatives using acid catalysts such as HCl, BF₃ and the like.

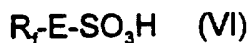
Examples of such monomers yielding polyethyleneimines useful for the synthesis of the instant additives are ethyleneimine; 1,2-propyleneimine, 1,2-butyleneimine, 2,2-dimethylethyleneimine; 2,3-butyleneimine and 2,2-dimethyl-3-n-propylethyleneimine as described in the "Journal of American Chemical Society," Vol. 57, p. 2328 (1935) and "Journal of Organic Chemistry," Vol. 9, p. 500 (1944).

Most important of the above polyimines are polyethyleneimines (PEIs), which are available commercially with molecular weights ranging from 300 to 70,000 and contain approximately 25% primary amino groups, 50% secondary amino groups and 25% tertiary amino groups. The units forming PEI are (-CH₂CH₂NH₂), (-CH₂CH₂NH-) and (-CH₂CH₂-N-). The polymer structure of PEI can also be described as a highly branched polyamine containing polymer segments such as:

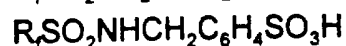
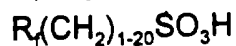
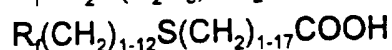
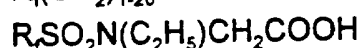
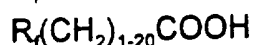


Preferred polyethyleneimines can have molecular weights ranging from 600 to 70,000 and depending on the specific performance properties desired, blends of polyethyleneimines with different average molecular weights can also be utilized.

Suitable perfluoroalkyl carboxylic and sulfonic acids of type V and VI



and esters and acid halides thereof wherein R_f and E are as defined previously are well known and extensively described in the patent literature as for instance listed in U.S. Pat Nos. 4,472,286 and 5,085,786 and include for example



Preferred R_f -esters and R_f -acid halides used for the synthesis of the instant FS-additives are the ones either commercially available or which can be derived in high yields from commercially available R_f -precursors. Commercially available R_f -acid halides are R_f -carboxylic acid and sulfonic acid fluorides produced via electrofluorination and R_f -acids obtained via oxidation of R_f -ethyl iodides. R_f -esters which are obtained in very high yield from R_f -ethyl iodides and commercially available mercapto esters or by the addition of commercially available R_f -ethyl mercaptans to acrylic esters, using in both instances bases as catalysts as shown in the equations below:



or



wherein R is lower alkyl and R_f is as defined previously. Instead of the above mercapto-esters, diesters such as $HS(CH_2)_{1 \text{ or } 2}COO-CH_2CH_2-OCO(CH_2)_{1 \text{ or } 2}SH$ can also be utilized as described in the experimental part.

Reactants of formula VII are compounds with hydrophilic group as well as a group reacting readily with primary and secondary amino groups and optionally with tertiary amino groups present in polyamines containing segments of formula IVa, IVb and IVc.

The reaction of primary and secondary amines with aldehydes and ketones, alkyl halides, isocyanates and thioisocyanates, activated double bond sites, epoxy compounds, cyanamide and guanidine or urea and the like, acids and anhydrides and acyl halides, is well known to the one skilled in the art.

Similarly, it is well known that tertiary amino groups can be converted into betaines via carboxalkylation with halogen carboxylic acids and salts thereof or into sulfobetaines via sulfalkylation with sultones such as propane sultone or butane sultones.

Of the above possibilities to introduce hydrophilic groups to obtain segments of formula IIa, IIb and IIc the following reactants were found to be the preferable ones;

Hydrophilic group containing alkyl halides of formula VIIa



wherein

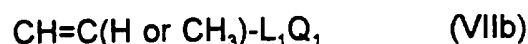
X is halogen and preferably Cl,

L₁ is alkylene with 1 to 4 carbons and preferably -CH₂- and

Q₁ is a salt of -COOH and preferably -COONa

will yield segments of formula IIa, IIb and IIc, the most preferred reactant VIIa being monochloro sodium acetate.

Hydrophilic group containing activated double bond compounds such as maleic anhydride and acrylates and methacrylates of formula VIIb



wherein

L₁ is zero or a bivalent linking group and

Q₁ is -COOH and -SO₃H and salts thereof, -CONH₂, -CONHCH₂OH or -(OCH₂CH₂)_nOH and

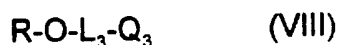
n is 1 to 10

will yield segments of formula IIa and IIb. The most preferable reactants being acrylic acid, maleic anhydride and acrylamide.

Furthermore, it is possible to obtain segments of formula IIa and IIb wherein -L₁-Q₁ is -COCH₂CH₂COOH and salts thereof by reaction of the primary and secondary amino groups with anhydrides such as succinic anhydride or to obtain formula IIa and IIb segments wherein -L₁-Q₁ is -COCH=CHCOOH and salts thereof by the reaction with maleic anhydride.

Reactants of formula VIII are compounds with a non-fluorochemical hydrophobic group as well as a group reacting with primary and secondary amino groups as outlined for reactants of formula VIIa and VIIb.

However, because of commercial availability, the preferred reactants of formula VIII are lower alkyl esters of longchain alkanoic acids,



wherein

R is alkyl with 1 to 4 carbons

L₃ is -CO- and

Q₃ is straight or branched alkyl with 12 to 18 carbons.

The synthesis of the instant FS-additives is carried out by using well known reaction conditions, solvents and reactants as described.

The preferred synthesis procedure consists of reacting in a first step one mole of a polyamine with a select number of moles of an R_F-ester as defined or with a blend of an R_F-ester and a fatty acid ester, if it is desired to incorporate a non-fluorochemical hydrophobic group into the FS-additive to be synthesized.

This first step is carried out by heating the reactants in a solvent such as isopropanol in the absence or the presence of a catalyst such as sodium ethoxide and sodium borohydride to 80 to 110° C for several hours under nitrogen and good stirring conditions, until IR-analysis shows that the ester-bond has completely disappeared and the amide-formation is complete. After conversion is completed, the isopropanol and the alcohol formed is distilled off and the resulting polyamine-amide adduct, a brownish viscous liquid is charged slowly into an aqueous solution containing a select number of moles of the hydrophilic group containing reactant of formula VIIa or VIIb keeping reaction temperature at 40 to 70° C until addition is completed, followed by heating the reaction mixture for several hours to about 70-80°C. Then a 50% sodium hydroxide solution is added in amounts to bring the pH to about 7.5. The resulting solution with a solids content ranging from 30 to 40% can be used as an FS-additive without any further purification.

Alternatively, one can add the aqueous solution of the hydrophilic group containing reactant slowly into the addition product (step 1) of the polyamine and the R_F-ester.

Since it is known how many primary, secondary and tertiary amino groups are present per mole of polyamine, one also knows, how many moles of reactants can be added and be added in such a ratio of perfluoroalkyl group, hydrophilic and hydrophobic group containing reactants, that the end product will be water soluble, which means having a solubility of at least 0.1% in water at 25° C. In

order to determine the optimum composition of the instant water soluble FS-additive, different FS-additives have to be evaluated as additives in select AFFF and AR-AFFF agents.

EXPERIMENTAL PART

The following examples are illustrative of the various representative embodiments of this invention and are not to be interpreted as limiting in scope of the appended claims.

In these examples, references are made to specifications used by the industry to evaluate the performance and efficiency of the instant foam stabilizers. More specifically, the examples refer to the following specifications and laboratory test methods:

1. Surface Tension and Interfacial Tension: According to ASTM C-1331-56.
2. Laboratory Film Spreading and Burnback Test: This test is carried out to determine film formation and film speed of AFFF premixes on cyclohexane as well as film life.

A 100 x 20 mm pyrex petri dish is placed over a dark, wet surface, so that good visual observation is possible. 50 ml of cyclohexane solvent is added to the petri dish. A 0.5 inch long stainless steel wood screw, pointing upwards, is placed in the center of the dish. The timer is started and simultaneously 3 ml of AFFF premix are added dropwise from a capillary pipette in one-second intervals onto top of screw.

When the surface of the solvent is completely covered with the film, the time of seal is recorded. The timer is left running and the screw is removed carefully so as not to disturb the film layer. With a lighter, the surface is tested for breakup of the seal. If the seal is broken, the solvent will ignite. The flames are extinguished by placing a cardboard over the dish. The timer is stopped and the time of breakup is recorded.

3. Laboratory Foam Expansion and Drain Time Test: 100 ml of an AFFF premix to be tested is prepared with either tap or artificial seawater (ASTM D1141). 100 ml of AFFF premix is poured into a Waring blender. At medium

speed, the AFFF solution is blended for 60 seconds. The generated foam is poured into a graduated 1000 ml cylinder, and a spatula is used to remove any residual foam in the blender cup. The foam height is recorded and the foam expansion ratio is calculated by dividing foam volume (ml) by foam weight (g).

The time which passes between the time the blender was stopped and the drain in the graduated cylinder reaches (a) 25.0 ml and (b) 50 ml is recorded. These times are called 1/4 and 1/2 drain times.

4. **Laboratory IPA Foam Stability Test:** This test is carried out to determine the stability of foam generated from AFFF and AR-AFFF agents in contact with hot isopropanol. Alternatively, this test can also be carried out with other polar solvents, such as acetone.

Virgin IPA, heated to 70° C is poured into a 150 mm wide and 75 mm high pyrex dish to an IPA level of approximately one inch. To the hot IPA is immediately poured all of the foam generated from 100 ml of a 3% AFFF or AR-AFFF agent premix, by blending the premix solution for 60 seconds on medium speed in a Waring blender. The time which passes between the time the foam is poured onto the hot IPA and the time when 50% of the surface area is visible is called the 50% foam collapse time and the time required until 100% of the surface area is visible is called the 100% foam collapse time.

5. **Modified UL 162 Fire Test:** This test is carried out to determine the efficiency of aqueous film forming foams to control and extinguish either isopropanol or acetone fires on a scale suitable for developmental agents.

15 liters of 99% isopropanol or acetone is placed into a round pan that is 2.69 ft² in area and 4 1/2" deep, and ignited. After one minute of free burning a foam discharge delivering 0.269 gpm's of solution is directed onto the far wall of the fire pan in a solid stream application for two minutes with a Type II Fixed Nozzle producing a foam quality that conforms to UL 162 5th edition paragraphs 15-15.9. One minute after the three minute foam application, a jet (5/32" diameter) of propane gas is ignited and discharged over the center of the foam blanket at the rate of 100 cc/m. metered by a full view Rotameter, Model 8900D as manufactured by Brooks Instrument Div. Emerson Electric Co., King of Prussia, PA or equivalent.

The impingement of the propane flame commences two inches above the

top of the tank and shoots downwardly over the foam blanket.

The propane flame is removed 30 seconds after the foam under the propane flame has collapsed and the fuel surface under the flame is visible. The burnback test is continued until 20% of the surface area of the test pan is on fire.

In this test, the following is measured or timed: Air, agent premix and initial fuel temperature; foam expansion and quarter drain time (tested separately with same nozzle as used in fire test), time required to cover 25, 50 and 75% of pan surface with foam; time required to achieve 90% and 98% control of the fire and total extinguishment time. Furthermore, the time required from start of the burnback test until the fuel surface is exposed under the flame and time required until 20% of surface area is reinvolved in flames is measured.

In the following examples, the following commercial raw materials were used for the synthesis of intermediates and of the instant foam stabilizers:

Perfluoroalkylethyl iodides with perfluoroalkyl groups having from 6 to 12 carbon atoms are available from Atochem under the Foralkyl name, (Foralkyl EI 6, EI 8, EI 6N, EI 8N and EI 10N); from DuPont under the Zonyl name (Zonyl TELB, TELB-L and TELB-N) and Hoechst-Celanese under the Fluowet name (Fluowet EI-600, EI-612 and EI-812).

Perfluoroalkylethyl mercaptans with R_f -groups as present in the above perfluoroalkylethyl iodides are available from Atochem under the Foralkyl name (Foralkyl EM 6, EM 8, EM 6N, EM 8N and EM 10N).

Thioglycolates and mercaptopropionates, such as n-butyl thioglycolate and glycol dimercaptpropionate are available from the Evans Chemetics unit of Hampshire Chemical Corporation.

Esters of perfluorocarboxylic acids such as methyl perfluorooctanoate, and methyl perfluorononanoate are available from PCR, Inc., and perfluoro alkane sulfonyl fluorides such as perfluorooctane sulfonyl fluoride are available from the 3M Company.

Polyethylenemines with molecular weights ranging from 300 to 70,000 are available from Nippon Shokubai Co. under the Epomin name (Epomin SP-003, SP-006, SP-018, SP-200 and P-1000).

Polyamines such as diethylenetriamine (DETA), triethylenetetramine

(TETA), tetraethylenepentamine (TEPA), pentaethylenehexamine (PEHA), iminobispropylamine (IBPA) are commodity chemicals and available from a number of companies.

In order to show the efficiency of the instant foam stabilizers and their impact when added to AFFF and AR-AFFF agents, commercial AFFF and AR-AFFF agents by the leading US agent producers were selected as model agents, namely Ansulite 3% AFFF and Ansulite 3 x 3 AR-AFFF agents produced by Ansul Fire Protection; Aer-O-Lite 3% AFFF and Universal Gold 3 x 3 AR-AFFF agents produced by National Foam Inc., and Light Water FC-203CS 3% AFFF and Light Water FC-603F 3 x 3 AR-AFFF agents produced by the 3M Company. Also used were developmental agents produced by the Dynax Corporation.

The following examples 1 to 6 show the synthesis of R_f -esters which were used as intermediates for the synthesis of the instant foam stabilizers. The reaction of iodides with mercaptans yielding sulfides as well as the addition of mercaptans to unsaturated esters using base catalysts is well known to the one skilled in the art giving yields which are almost quantitative, making the use of crude R_f -esters possible without any further purification. In Table 1, the structures of R_f -esters A-1 through A-6 are presented, as well as the R_f -distribution in these esters and in the R_f -ethyl iodides and R_f -ethyl mercaptan raw materials.

Also listed in Table 1 are R_f -esters and a R_f -sulfonyl fluoride which are available commercially.

Example 1

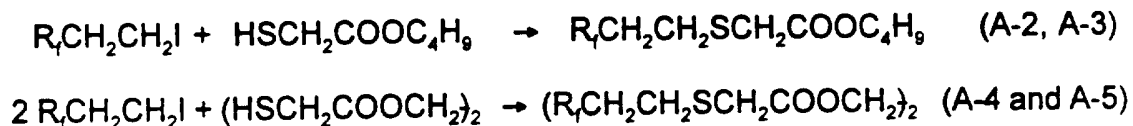


To a 3-neck flask equipped with stirrer, thermometer, dropping funnel and reflux condenser were charged 474 gm (1.0 mole) of $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{I}$, 163 gm (1.1 mole) of n-butyl thioglycolate, 37 gm (0.37 mole) of triethylamine and 120 gm of butyl acetate. While stirring, the reaction mixture was heated to 55° C, allowed to exotherm to 70° and kept at 70-75° C for 3 hours. After this heating period, another 74 gm (0.74 moles) of triethylamine were added over a two-hour period while the reaction temperature was kept at 70 to 75° C. Upon completion of the

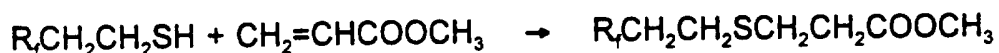
addition of the triethylamine, the temperature was raised to 100° C and kept overnight (12 hours) at this temperature. GC analysis showed, that the content of $C_6F_{13}CH_2CH_2I$ in the reaction mixture had dropped to less than 1.0%. The reaction mixture was cooled to 50° C and 200 ml of deionized water was added. After stirring for 30 minutes and letting the reaction mixture stand for another 30 minutes, the organic layer was separated from the aqueous layer. The organic layer was once more washed with 200 ml of deionized water. After separation of the aqueous from the organic layer, the organic layer was transferred to a distillation flask and under vacuum of 25 to 100 mg Hg, the volatiles, butyl acetate, small amounts of $C_6F_{13}CH=CH_2$ byproduct, unreacted $C_6F_{13}CH_2CH_2I$, triethylamine and water were distilled off by raising the distillation batch temperature to 130° C, until distillation did come to a halt. A total of 493 gm (99.6% yield) of butyl perfluorohexylethylthioglycolate was obtained as a slightly off-white viscous liquid, which was used without any further purification for the reaction with oligomeric and polymeric amines of this invention.

Examples 2 to 5

Using the synthesis method as described in Example 1, the following perfluoroalkylethylthioglycolate esters A-2, A-3, A-4 and A-5 were synthesized from the following perfluoroalkylethyl iodides having an R_f -distribution as shown in Table 1, and butyl thioglycolate and glycol dimercaptopropionate:



Example 6



To a 3-neck flask equipped with stirrer, dropping funnel, thermometer and reflux condenser were added 63.6 g (0.74 moles) of methyl acrylate and 7.0 g (0.07 moles) of triethylamine. At room temperature and under stirring, a total of 377.6 g (0.716 moles) of perfluoroalkylethyl mercaptan, having a R_f -distribution as

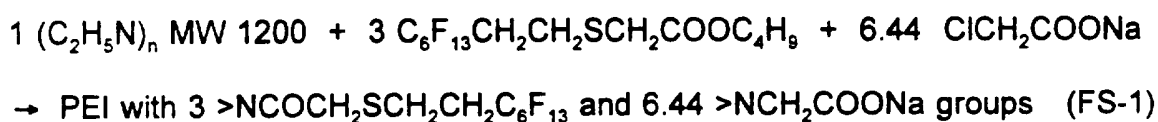
Table 1

Example	A-#	Formula	R _r -Distribution, %				
			C ₆ F ₁₃	C ₈ F ₁₇	C ₁₀ F ₂₁	≥C ₁₂ F ₂₅	
1	A-1	R _r CH ₂ CH ₂ SCH ₂ COOC ₄ F ₉	98.0	2.0	---	---	
2	A-2	"	38-46	28-34	13-17	10 max.	
3	A-3	"	10-20	50-56	18-22	12 max.	
4	A-4	(R _r CH ₂ CH ₂ SCH ₂ COOCH ₂) ₂	38-46	28-34	13-17	10 max.	
5	A-5	"	10-20	50-56	18-22	12 max.	
6	A-6	R _r CH ₂ CH ₂ SCH ₂ CH ₂ COOCH ₃	<1.0	62	25.7	8.6	
---	A-7	C ₇ F ₁₅ COOCH ₃	---	---	---	---	
---	A-8	C ₆ F ₁₇ COOCH ₃	---	---	---	---	
---	A-9	C ₆ F ₁₇ SO ₂ F	---	---	---	---	

shown in Table 1, were added over a period of one hour, during which the exotherm raised the batch temperature to 58° C. The conversion after completion of addition as determined by GC-analysis was approximately 70%. After the reaction mixture was kept at 60° C overnight, GC-analysis showed 100% conversion. The product (456 g, 98.5% yield) was a white, semi-solid compound at room temperature and was used for the reaction with oligomeric and polymeric amines of this invention without any further purification.

The following examples 7 to 20 show the synthesis of select FS-additives derived from commercially available polyamines, while examples 21 to 40 show the laboratory evaluations of AFFF and AR-AFFF agent premixes containing such select FS-additives. Examples 41 and 42 show fire tests carried out with polysaccharide-free AR-AFFF agents containing FS-additives and using tap and sea water for the preparation of agent premixes and isopropanol and acetone as polar solvent fuels.

Example 7



To a 3-neck flask equipped with stirrer, thermometer and reflux condenser were charged 200 g (0.166 mole) of polyethyleneimine (Epomin P012) with an average mole weight of 1200; 247 g (0.5 mole) of n-butyl perfluorohexylethylthioglycolate (A-1) and 110 g of isopropanol. The reactants were mixed and when homogeneous, 6.5 g of a 20% solution of sodium ethoxide in ethanol and 1.3 g of sodium borohydride were added to the reaction mixture. Upon inertion of the reactor with nitrogen, the reaction mixture was heated to 105 to 115° C and was kept at this temperature for 4 hours by refluxing the isopropyl alcohol during the first one hour period and by distilling off the isopropyl alcohol during the remaining three-hour period. An IR taken after the four-hour period showed that the amide formation was completed and the ester band at 1725-1735 cm^{-1} had disappeared. Vacuum was applied and residual volatiles were

distilled off at 105° C and a vacuum of 100 mm Hg.

The resulting brown viscous liquid was cooled to 80-90° C and over a 30-minute period charged into a flask containing a solution of 375 g (3.22 mole) of sodium chloroacetate in 900 g of water kept at a temperature of 50° C, controlling the exotherm by cooling the flask so that a temperature between 45 and 55° C was maintained during the addition. The 3-neck flask which did contain the viscous R_r-ester polyethylenimine adduct was rinsed with 150 g of water and this rinse was added to the flask with the sodium chloroacetate reaction mixture. After addition of this rinse out, the reaction mixture was kept at 65 to 70° C for four hours. Two hours into this holding period, 24.9 g of a 50% sodium hydroxide solution was added to raise the pH to 7.5. A total of 1845 g (96% yield) of a brown solution with an actives content of 35% was obtained which was used without any further purification.

Example 8

1 (C₂H₅N)_n MW 70,000 + 85 R_rCH₂CH₂SCH₂COOC₄H₉ (A-2) + 1154 ClCH₂COONa

→ PEI with 85 >NCOCH₂SCH₂CH₂R_r and 1154 >NCH₂COONa groups (FS-2)

To a 3-neck flask equipped with a stirrer, thermometer and reflux condenser were charged 13 g (0.0227 moles) of butyl perfluoroalkyl-ethylthioglycolate A-2, 61.9 g (0.00027 moles) of a 30% aqueous solution of polyethyleneimine (Epomin P-1000) with an average molecular weight of 70,000 and 80 g of isopropanol. The reaction mixture was heated to 100° C and kept at reflux overnight for a total of 18 hours. IR analysis showed only trace amounts of ester groups. A total of 100 ml of IPA/water were distilled off and a total of 70.2 g of a yellowish solution was obtained. 200 g of water and 100 g of propylene glycol were added, followed by the addition of 34 g (0.3 moles) of sodium chloroacetate at 40° C. The reaction mixture was kept at 75-80° C for 4 hours. A foaming mass was obtained. Addition of 100 g of butyl cellosolve did not brake the foam. Upon standing for 3 days, the foam had collapsed and a total of 445 g of a brown foam stabilizer solution with an actives content of 12.3% was obtained which was used without any further purification.

Table 2

Example	Foam Stabilizer Nr.	Mol. Weight of PEI ¹⁾	R _r -Ester	Hydrophile	Mole Ratios of Reactants	% Actives in Solution
7	FS-1	1,200	A-1	CICH ₂ COONa	1:3:19	34.7
8	FS-2	70,000	A-2	"	1:85:1154	12.3
9	FS-3	1,200	"	"	1:2:20	36.4
10	FS-4	"	A-6	"	1:2:20	40.0
11	FS-5	"	A-2	"	1:1.5:21	35.4
12	FS-6	1,800	A-1	"	1:3:28	36.9
13	FS-7	"	"	CH ₂ =CHCOONa	1:3:28	43.8
14	FS-8	10,000	"	CICH ₂ COONa	1:8:167	20.3

¹⁾ Polyethyleneimines (PEIs) used are the following Epomines (SP and P Series), having the following molecular weights and numbers of primary, secondary and tertiary amino groups:

Epomin Nr.	MW	-NH ₂	-NH-	-N<	Total N
SP-012	1,200	7	14	7	28
SP-018	1,800	10.5	21	10.5	42
SP-200	10,000	58	116	58	232
SP-1000	70,000	406	813	406	1,625

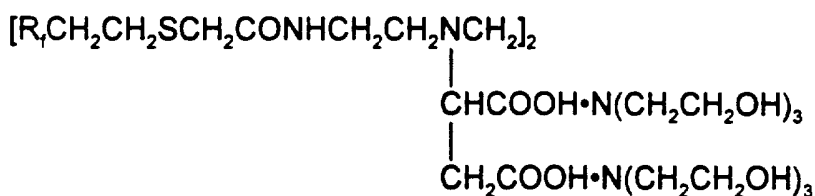
Example 9 to 14

Using the synthesis procedure and the catalysts as described in Example 7, Epomin polyethyleneimines were reacted with R_F-esters (step 1) and then either sodium chloroacetate or acrylic acid (step 2) in mole ratios as indicated in Table 2 yielding foam stabilizers B-3 to B-8. In these reactions, the polyethylenimine/R_F-ester adduct was mixed in one step with the aqueous sodium chloroacetate solution, rather than added over a period of time, since controlling the exotherm on a small synthesis scale was no problem. Because foaming in step 2 was a problem, propylene glycol was added to break the foam which was only marginally successful and did lead to more diluted foam stabilizer solutions as indicated in Table 2. All foam stabilizer solutions obtained with active contents as shown in Table 2 were light to dark brown in color.

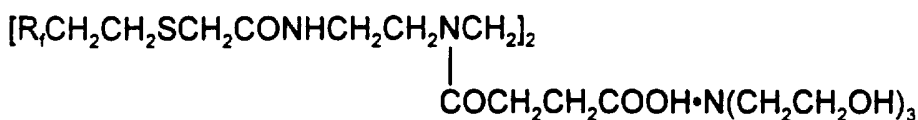
Example 15 to 17

Using the synthesis procedure as described in Example 7, but using in step 2 propylene glycol as solvent and triethanolamine as a catalyst and solubilizer, foam stabilizers were prepared from polyamines, R_F-esters and hydrophiles as shown in Table 3, having the following idealized structures:

Example 15 (FS-9):



Example 16 (FS-10):



Example 17 (FS-11):

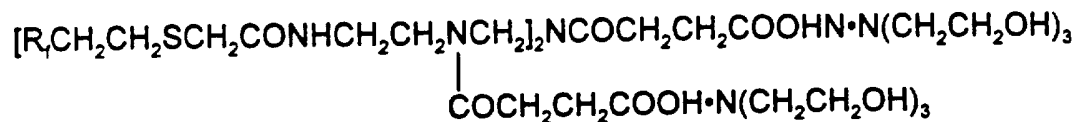


Table 3

Ex.	Polyamine	R _r Ester	Hydro- phile	Mole Ratio ¹⁾	% Solids in Solution
15	H ₂ N(CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	A-4	MA ²⁾	1:1:2	28.6%
16	H ₂ N(CH ₂ CH ₂ NH) ₂ CH ₂ CH ₂ NH ₂	A-5	SA ³⁾	1:1:1.9	36.9%
17	H ₂ N(CH ₂ CH ₂ NH) ₃ CH ₂ CH ₂ NH ₂	A-4	SA	1:1:3	38.8%

1) Mole Ratio of Polyamine to R_r-Ester to Hydrophile.

2) MA = Maleic anhydride.

3) SA = Succinic anhydride.

Examples 18 to 20

Using synthesis methods as described for examples 7 through 17, foam stabilizers can be derived from esters of perfluorocarboxylic acids A-7, A-8 and acid sulfonyl fluoride A-9, polyamines and hydrophiles such as sodium chloroacetate, maleic anhydride, and succinic anhydride having structures as shown below:

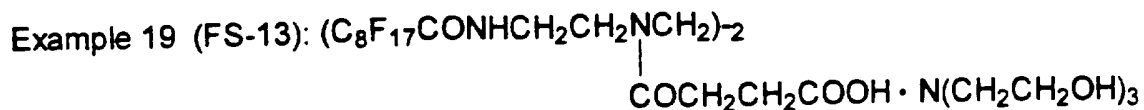
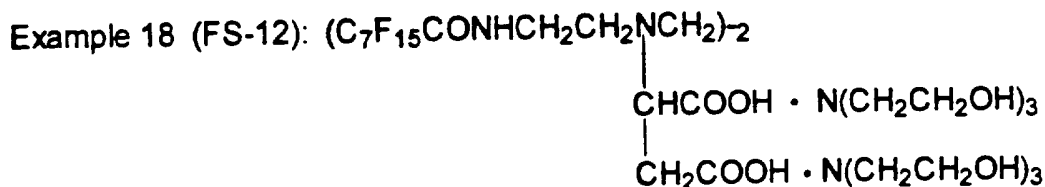


Table 4

Example	Foam Stabilizer Number	IPA Foam Stabilizer Collapse Time in Minutes/Seconds			
		Ansulite 3x3		LightWater FC-603F	
		50%	100%	50%	100%
21	None	2:46	3:05	6:21	7:32
22	FS-1	28:40	>30:00	27:31	28:05
23	FS-3	19:18	28:59	24:23	>30:00
24	FS-4	18:29	21:04	18:11	21:33
25	FS-6	11:31	14:03	26:15	29:55
26	FS-7	9:00	11:29	22:27	25:29
27	FS-8	--- ¹⁾	--	--- ¹⁾	---
28	FS-9	9:59	13:53	10:36	21:26
29	FS-10	25:16	>30:00	14:26	21:45
30	FS-11	10:55	13:37	12:51	16:45

¹⁾ Precipitate formed, not evaluated.

Examples 31-35

In order to show how the instant foam stabilizers can improve the IPA foam stability of AR-AFFF agents as a function of the amount of foam stabilizer added, agent premixes were prepared by blending 3 parts of Universal Gold 3% AR-AFFF agent with 0.25 to 1.0 parts of a solution containing 3% by weight of FS-3 foam stabilizer solids. The IPA foam stability tests carried out with these premixes gave results as shown in Table 5, indicating 50% foam collapse time increased from 37 seconds to 27 minutes.

Table 5

Example	AR-AFFF Premixes	IPA Collapse Time Minutes	
		50%	100%
31	Universal Gold 3%	0:37	0:51
32	Universal Gold + 0.25% FS-3	8:19	12:54
33	Universal Gold + 0.50% "	14:57	28:26
34	Universal Gold + 0.75% "	22:63	42:20
35	Universal Gold + 100% "	27:19	53:41

Examples 36 to 40

In order to demonstrate that AR-AFFF agents with lower polysaccharide contents and lower viscosity can be prepared with the help of the instant foam stabilizers, the following was carried out:

It was established that Universal Gold 3%, a 3x3 AR-AFFF agent and Aer-O-Lite 3%, a 3% AFFF agent, both produced by National Foam, Inc., were compatible when mixed in ratios from 80/20 to 40/60 of Aerowater Gold 3% to Aer-O-Lite 3% yielding agents with Brookfield viscosities as shown in Table 6.

It was found that addition of small amounts of foam stabilizers (0.25 to 1.0% FS-Solids) did not affect the above viscosities. Agent premixes were prepared by blending 3 parts of the above agent compositions and 3 parts of a solution containing 0.75% solids of foam stabilizer FS-3, with 94 parts of tap water.

As shown in Table 6, these premixes were evaluated and did yield the following results:

Most importantly, the IPA collapse times were significantly increased when compared with the IPA collapse time of Universal Gold 3% alone. However, IPA collapse times were increased less the higher the amount of Aer-O-Lite was in the agent blend and the lower the content of Universal Gold 3%. Foam drainage times decreased with amounts of Aer-O-Lite 3% greater than 20% while surface and interfacial tensions increased slightly with increasing

amounts of Aer-O-Lite 3% in the premix.

Table 6 Laboratory Evaluation of Agent Premixes

Examples	36	37	38	39	40
Universal Gold 3% (AR-AFFF)	100	100	80	60	40
Aer-O-Lite 3% AFFF	—	—	20	40	60
Foam Stabilizer FS-3 ¹⁾	No	Yes	Yes	Yes	Yes
Surface Tension, dynes/cm	17.1	17.3	17.5	17.6	17.7
Interfacial Tension, dynes/cm	2.1	2.2	2.2	2.3	2.4
Foam Expansion	7.1	7.1	6.7	7.5	9.0
25% Drain Time, Minutes	12:02	11:11	13:22	10:52	8:58
50% Drain Time, Minutes	15:28	15:37	17:54	13:18	12:15
IPA 50% Collapse Time, Minutes	0:37	22:38	7:15	2:19	0:15
IPA 100% Collapse Time, Minutes	0:51	42:20	14:58	6:44	1:25
Viscosity, cps, Brookfield ²⁾	2880	2880	2227	1420	748

¹⁾ 0.75% Solids FS-3 in agent concentrate, 0.015% Solids in agent premix.

²⁾ Brookfield LVT, 30 RPM, Spindle 3.

Examples 41 and 42

A Dynax 3% AFFF agent (DX-1) with a fluorine content of 0.7% and performance properties as shown in Table 7 was reformulated in such a way that in addition to all components present in DX-1, 1.4% solids of foam stabilizer FS-1 and 1.15% solids of foam stabilizer FS-2 were incorporated into the 3% concentrate. The comparative laboratory evaluations in Table 7 show that incorporation of the foam stabilizers did only very marginally affect surface and interfacial tensions, did slightly decrease the film speed, but more importantly did increase both foam expansion and drain times and most importantly did provide excellent IPA foam resistance as the very long 50% and 100% IPA collapse times show in both tap and sea water.

In order to show the efficiency of this "Newtonian" 3x3 AR-AFFF agent, modified UL 162 2.69 sq. ft. fire tests were carried out with tap and sea water

on IPA and acetone fires.

As the test results in Table 8 show, excellent fire control and extinguishment times were obtained on both IPA and acetone fires.

Table 7 Laboratory Evaluations of DX-1 and DX-2 Agents

Examples	41		42	
	Dynax 3% AFFF DX-1		Dynax 3x3 AR-AFFF DX-2	
Properties of AFFF and AR-AFFF Premixes	Tap	Sea	Tap	Sea
Surface Tension, dynes/cm	17.1	17.6	18.3	18.2
Interfacial Tension, dynes/cm	1.6	1.4	1.8	1.6
Foam Expansion Ratio	5.2	5.2	6.3	6.0
¼ Drain Time, min./sec.	4:58	4:07	7:39	8:05
½ Drain Time, min./sec.	6:23	5:07	10:38	11:01
Seal Time, min./sec.	0:04	0:04	0:12	0:10
Seal Breakup, min./sec.	>30:00	>30:00	>30:00	>30:00
IPA 50% Collapse min./sec.	0:12	0:12	97:05	19:51
IPA 100% Collapse min./sec.	0:12	0:12	188:00	53:51

Table 8 Comparative Modified UL 162 Fire Tests

	85° F (°C) 70°F (°C) 80°F (°C)	Tap Water Premix		Sea Water Premix	
		IPA	Acetone	IPA	Acetone
Air Temperature		9.47	9.47	8.21	8.21
Agent Premix Temperature		3:12	3:12	3:30	3:30
Initial Fuel Temperature		0:09	0:03	0:06	0:04
Foam Expansion Ratio		0:21	0:11	0:20	0:08
Quarter Drain Time	min./sec.	0:33	0:16	0:36	0:16
25% Coverage	min./sec.	0:39	0:31	0:46	0:32
50% Coverage	min./sec.	0:55	0:42	0:52	0:38
75% Coverage	min./sec.	1:00	0:51	0:57	0:47
90% Control	min./sec.	2:50	4:15	3:35	4:55
98% Control	min./sec.	4:00	5:25	5:07	5:50
Extinguishment					
Fuel Exposed					
20% Burnback					

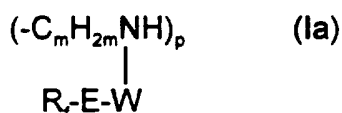
What is claimed is:

1. A water soluble foam stabilizer and film former comprising an oligomer or polymer derived from a polyamine with a molecular weight from 100 to 100,000 with 3 to 2200 nitrogens and a minimum of 3 primary or secondary amino groups, containing segments with

- a) an oleophobic and hydrophobic perfluoroalkyl group,
- b) a hydrophilic group other than an amino group,
- c) optionally a non-perfluoroalkyl hydrophobic group and
- d) optionally unreacted primary, secondary and tertiary amino groups of the polyamine starting material.

2. A water soluble foam stabilizer and film former according to claim 1, containing

- a) segments of formula Ia and Ib



wherein

R_f is independently a straight or branched perfluoroalkyl group of 4 to 20 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

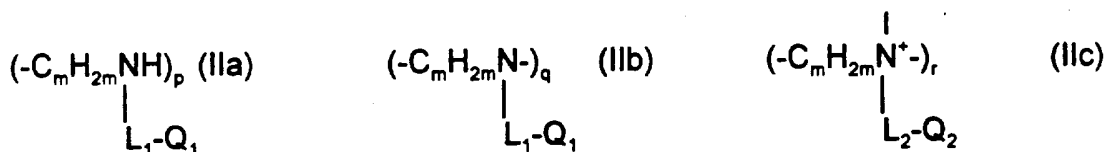
E is either zero or independently a divalent linking group and can be a straight or a branched alkylene group of 1 to 16 carbon atoms or said alkylene group interrupted by one to three groups selected from the group consisting of -NHR₁-, -O-, -S-, -SO₂-, -COO-, -OOC-, -CONR₁-, -NR₁CO-, -SO₂NR₁-, -NR₁SO₂- or terminated at the R_f-end with -CONR₁- OR -SO₂NR₁-, where R_f is attached to the carbon or sulfur atom and wherein R₁ is independently hydrogen or alkyl of 1 to 6 carbon atoms.

W is -CO- or -SO₂-,

m is 2 to 10 and

p and q are 0 to 500 and p+q are equal or larger than 1,

b) segments of formula IIa and IIb and IIc,



wherein

L_1 is a divalent linking group and can be a straight or branched saturated or unsaturated hydrocarbon group of 1 to 16 carbon atoms or said hydrocarbon group interrupted by one to three groups selected from $-NHR_1-$, $-O-$, $-S-$, $-CONR_1-$, $-NR_1CO-$, $-SO_2NR_1-$, $-NR_1SO_2$ or terminated with $-CO-$ or $-SO_2-$ where the linking group L_1 is attached to the nitrogen in formula IIa or IIb,

L_2 is alkylene with 1 to 4 carbons,

Q_1 is a hydrophilic group and can be $-COOH$, $-SO_3H$ and salts thereof; $-CONH_2$, $-CONHCH_2OH$ or $(OCH_2CH_2)_nOH$,

Q_2 is $-COO^-$,

m is 2 to 10,

n is 1 to 10,

p and q are 0 to 500 and

r is 0 to 500.

c) optionally segments of formula IIIa and IIIb



wherein

L_3 is zero, $-CO-$ or $-SO_2-$,

Q_3 is a straight or branched hydrocarbon group with 6 to 18 carbon atoms,

m is 2 to 10 and

p and q are 0 to 100

3. A water soluble foam stabilizer and film former according to claim 1 containing

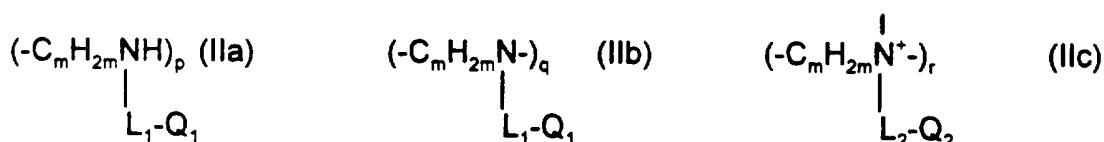
a) segments of formula Ia and Ib



wherein

R_f is a straight or branched perfluoroalkyl group of 6 to 12 carbons,
 E is zero, $-CH_2CH_2SCH_2-$, $-CH_2CH_2SCH_2CH_2-$, or $-CH_2CH_2OCH_2CH_2-$,
 W is $-CO-$,
 m is 2 and
 p and q are 0 to 100 and p + q are equal or larger than 1.

b) segments of formula IIa, IIb and IIc



wherein

L_1 is $-CH_2-$ and $-CH_2CH_2-$,
 L_2 is $-CH_2-$,
 Q_1 is $-COOH$ and $-COONa$,
 Q_2 is $-COO^-$,
 p and q are 1 to 100 and
 r is 0 to 100.

4. A water soluble foam stabilizer and film former according to claim 1, wherein the foam stabilizer and film former is derived from

diethylenetriamine (DETA)
 triethylenetetramine (TETA)
 tetraethylenepentamine (TEPA)
 pentaethylenehexamine (PEHA)
 aminoethylpiperazine (AEP)
 iminobispropylamine (IBPA)

5. A water soluble foam stabilizer and film former according to claim 1, wherein the foam stabilizer and film former is derived from polyethyleneimines with average molecular weights ranging from 300 to 70,000.

6. A method to improve the foam stability, polymeric film forming properties and fire fighting performance of polar solvent type aqueous film forming foam agents (AR-AFFF agents) based on fluorochemical surfactants, hydrocarbon surfactants, solvents, water and polysaccharide gums as polymeric film formers and optionally polymeric thickeners, fluorochemical synergists, electrolytes, pH buffers, corrosion inhibitors and the like by the addition of an effective amount of a foam stabilizer and film former derived from a polyamine with a molecular weight from 100 to 100,000 and 3 to 2200 nitrogens and a minimum of 3 primary or secondary amino groups containing segments with

- a) an oleophobic and hydrophobic perfluoroalkyl group,
- b) optionally a hydrophilic group other than an amino group,
- c) optionally a non-perfluoroalkyl hydrophobic group and
- d) optionally unreacted primary, secondary or tertiary amino groups of the polyamine starting material.

7. A method according to claim 6, wherein the water soluble foam stabilizer and film former is based on oligomers and polymers containing

- a) segments of formula Ia and Ib,



wherein

R_r is independently a straight or branched perfluoroalkyl group of 4 to 20 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

E is either zero or independently a divalent linking group and can be a straight or a branched alkylene group of 1 to 16 carbon atoms or said alkylene group interrupted by one to three groups selected from the group consisting of -NHR₁-, -O-, -S-, -SO₂-, -COO-, -OOC-, -CONR₁-, -NR₁CO-, -SO₂NR₁-, -NR₁SO₂-

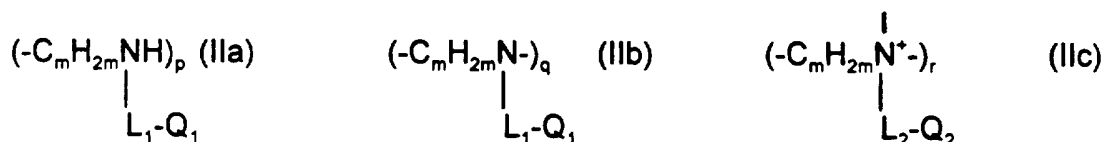
or terminated at the R_f -end with $-\text{CONR}_f-$ or $-\text{SO}_2\text{NR}_f-$, where R_f is attached to the carbon or sulfur atom and wherein R_f is independently hydrogen or alkyl of 1 to 6 carbon atoms.

W is $-\text{CO}-$ or $-\text{SO}_2-$,

m is 2 to 10 and

p and q are 0 to 500 and $p+q$ are equal or larger than 1,

b) segments of formula IIa, IIb and IIc,



wherein

L_1 is a divalent linking group and can be a straight or branched saturated or unsaturated hydrocarbon group of 1 to 16 carbon atoms or said hydrocarbon group interrupted by one to three groups selected from $-\text{NHR}_1-$, $-\text{O}-$, $-\text{S}-$, $-\text{CONR}_1-$, $-\text{NR}_1\text{CO}-$, $-\text{SO}_2\text{NR}_1-$, $-\text{NR}_1\text{SO}_2-$ or terminated with $-\text{CO}-$ or $-\text{SO}_2-$ where the linking group L_1 is attached to the nitrogen in formula IIa or IIb;

L_2 is alkylene with 1 to 4 carbons,

Q_1 is a hydrophilic group and can be $-\text{COOH}$, $-\text{SO}_3\text{H}$ and salts thereof, $-\text{CONH}_2$, $-\text{CONHCH}_2\text{OH}$ or $-(\text{OCH}_2\text{CH}_2)_n\text{OH}$,

Q_2 is $-\text{COO}^-$,

m is 2 to 10,

n is 1 to 10,

p and q are 0 to 500 and

r is 0 to 500,

c) segments of formula IIIa and IIIb



wherein

L_3 is zero, -CO- or -SO₂-,

Q_3 is a straight or branched hydrocarbon group with 6 to 18 carbon atoms,

m is 2 to 10 and

p and q are 0 to 100.

8. A method according to claim 6, wherein the water soluble foam stabilizer and film former is based on oligomers and polymers containing

a) segments of formula Ia and Ib,



wherein

R_f is a straight or branched perfluoroalkyl group of 6 to 12 carbons,

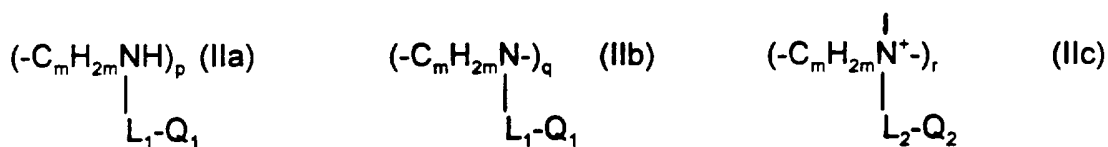
E is zero, -CH₂CH₂SCH₂-, -CH₂CH₂SCH₂CH₂-, or -CH₂CH₂OCH₂CH₂-,

W is -CO-,

m is 2 and

p and q are 0 to 100 and $p + q$ are equal or larger than 1,

b) segments of formula IIa, IIb and IIc



wherein

L_1 is -CH₂- and -CH₂CH₂-,

L_2 is -CH₂-,

Q_1 is -COOH and -COONa,

Q_2 is -COO⁻,

p and q are 0 to 100 and

r is 0 to 100.

9. A method according to claim 6, wherein the water soluble foam stabilizer and film former is derived from

- diethylenetriamine (DETA)
- triethylenetetramine (TETA)
- tetraethylenepentamine (TEPA)
- pentaethylenehexamine (PEHA)
- aminoethylpiperazine (AEP)
- iminobispropylamine (IBPA)

10. A method according to claim 6, wherein the foam stabilizer and film former is derived from polyethyleneimines with average molecular weights ranging from 300 to 70,000.

11. A method to convert aqueous film forming foam agents (AFFF agents) based on fluorochemical surfactants, hydrocarbon surfactants, solvents and water and optionally polymeric thickeners, fluorochemical synergists, electrolytes, pH buffers, corrosion inhibitors and the like useful to fight non-polar solvent and fuel fires into non-thixotropic polar solvent type aqueous film forming foam agents (AR-AFFF agents) capable of fighting both polar and non-polar solvent fires by the addition of an effective amount of a water soluble foam stabilizer and film former derived from a polyamine with a molecular weight from 100 to 100,000 with 3 to 2200 nitrogens and a minimum of 3 primary or secondary amino groups, containing segments with

- a) an oleophobic and hydrophobic perfluoroalkyl group,
- b) optionally a hydrophilic group other than an amino group,
- c) optionally a non-perfluoroalkyl hydrophobic group and
- d) optionally unreacted primary, secondary or tertiary amino groups of the polyamine starting material.

12. A method according to claim 11, wherein the water soluble foam stabilizer and film former is based on oligomers and polymers containing

- a) segments of formula Ia and Ib,



wherein

R_f is independently a straight or branched perfluoroalkyl group of 4 to 20 carbon atoms or said perfluoroalkyl substituted by perfluoroalkoxy of 2 to 6 carbon atoms,

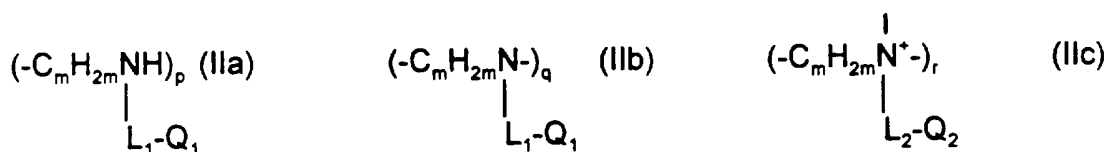
E is either zero or independently a divalent linking group and can be a straight or a branched alkylene group of 1 to 16 carbon atoms or said alkylene group interrupted by one to three groups selected from the group consisting of $-NHR_1-$, $-O-$, $-S-$, $-SO_2-$, $-COO-$, $-OOC-$, $-CONR_1-$, $-NR_1CO-$, $-SO_2NR_1-$, $-NR_1SO_2-$ or terminated at the R_f -end with $-CONR_1-$ or $-SO_2NR_1-$, where R_f is attached to the carbon or sulfur atom and wherein R_f is independently hydrogen or alkyl of 1 to 6 carbon atoms.

W is $-CO-$ or $-SO_2-$,

m is 2 to 10 and

p and q are 0 to 500 and $p+q$ are equal or larger than 1,

b) segments of formula IIa, IIb and IIc,



wherein

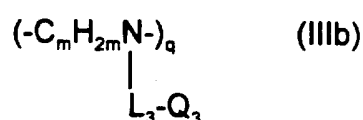
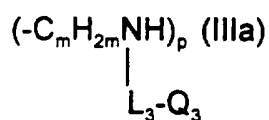
L_1 is a divalent linking group and can be a straight or branched saturated or unsaturated hydrocarbon group of 1 to 16 carbon atoms or said hydrocarbon group interrupted by one to three groups selected from $-NHR_1-$, $-O-$, $-S-$, $-CONR_1-$, $-NR_1CO-$, $-SO_2NR_1-$, $-NR_1SO_2-$ or terminated with $-CO-$ or $-SO_2-$ where the linking group L_1 is attached to the nitrogen in formula IIa or IIb,

L_2 is alkylene with 1 to 4 carbons,

Q_1 is a hydrophilic group and can be $-COOH$, $-SO_3H$ and salts thereof; $-CONH_2$, $-CONHCH_2OH$ or $(OCH_2CH_2)_nOH$,

Q_2 is $-\text{COO}^-$,
 m is 2 to 10,
 n is 1 to 10,
 p and q are 0 to 500 and
 r is 0 to 500,

c) segments of formula IIIa and IIIb



wherein

L_3 is zero, $-\text{CO}-$ or $-\text{SO}_2-$,

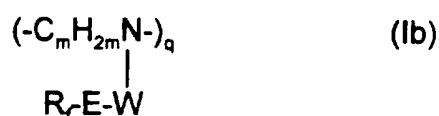
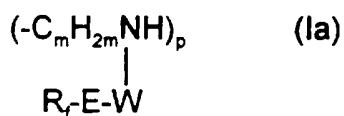
Q_3 is a straight or branched hydrocarbon group with 6 to 18 carbon atoms,

m is 2 to 10 and

p and q are 0 to 100.

13. A method according to claim 11 wherein the water soluble foam stabilizer and film former is based on oligomers and polymers containing

a) segments of formula Ia and Ib,



wherein

R_r is a straight or branched perfluoroalkyl group of 6 to 12 carbons,

E is zero, $-\text{CH}_2\text{CH}_2\text{SCH}_2-$, $-\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2-$, or $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$,

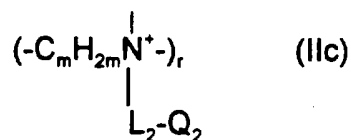
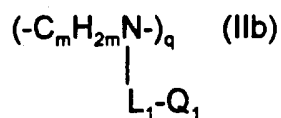
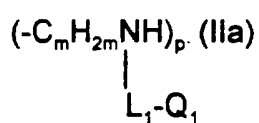
W is $-\text{CO}-$,

m is 2 and

p and q are 0 to 100 and $p + q$ are equal or larger than 1,

b) segments of formula IIa, IIb and IIc

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wherein

L_1 is $-CH_2-$ and $-CH_2CH_2-$,

L_2 is $-CH_2-$,

Q_1 is $-COOH$ and $-COONa$,

Q_2 is $-COO^-$,

p and q are 0 to 100 and

r is 0 to 100.

14. A method according to claim 11, wherein the water soluble foam stabilizer and film former is derived from

diethylenetriamine (DETA)

triethylenetetramine (TETA)

tetraethylenepentamine (TEPA)

pentaethylenehexamine (PEHA)

aminoethylpiperazine (AEP)

iminobispropylamine (IBPA)

15. A method according to claim 11, wherein the foam stabilizer and film former is derived from polyethyleneimines with average molecular weights ranging from 300 to 70,000.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/10805

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A62D 1/04; C07C 229/00, 315/00
US CL : 252/8.05; 562/556, 561

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/8.05; 562/556, 561

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 2,764,602 (AHLBRECHT) 25 September 1956, see entire document.	1-15
A	US, A, 4,420,434 (FALK) 13 December 1983, see entire document.	1-15
A	US, A, 4,536,298 (KAMEI ET AL.) 20 August 1985, see entire document.	1-15
A	US, A, 5,085,786 (ALM ET AL.) 04 February 1992, see entire document.	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

<p>* Special categories of cited documents:</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*T*</p> <p>*X*</p> <p>*Y*</p> <p>*Z*</p>	<p>later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>document member of the same patent family</p>
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Date of the actual completion of the international search 09 NOVEMBER 1995	Date of mailing of the international search report 17 NOV 1995
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