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(54) Fire extinguishing composition

Feuerlöschende Zusammensetzung

Composition extinctrice d’incendie

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(56) References cited:
WO-A-96/05889 US-A- 4 536 298

- **DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; retrieved from STN-INTERNATIONAL, accession no. 102: 206152 CA XP002183659 & JP 59 230566 A (DAINIPPON INK AND CHEMICALS) 25 December 1984 (1984-12-25)**

Remarks:
The file contains technical information submitted after the application was filed and not included in this specification

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a fire extinguishing composition comprising polyethyleneimine or a derivative thereof, and more particularly to a fire extinguishing composition which is superior in terms of rapid extinguishing performance, flame resistance, fuel resistance, and reignition prevention performance.

2. Description of the Background Art

[0002] Generally, in the case of fires involving polar solvents such as alcohols, ketones, esters, ethers and amines, even if fire extinguishing is attempted with a typical petroleum fire extinguishing composition, the foam disappears soon after contacting the combustion surface, and the fire is unable to be extinguished. As a result, the following types of compositions have been proposed as polar solvent fire extinguishing compositions:

(1) protein hydrolysates to which a metallic soap has been added,
(2) synthetic surfactants to which a metallic soap has been added,
(3) protein hydrolysates to which a fluorine based surfactant has been added (a fluorinated protein), and
(4) fluorine based surfactants to which a water soluble high molecular weight material has been added to form a thixotropic liquid.

[0003] Of these compositions, fire extinguishing compositions of type (4) above are aqueous film forming foam compositions based on a fluorine based surfactant, to which a water soluble high molecular weight material (such as a polysaccharide) has been added to give thixotropic properties. On contact with a polar solvent, foams which consist of this type of composition lose water at the combustion interface, and the remaining water soluble high molecular weight material, incorporating air bubbles, forms a gel-like mat across the solvent surface, preventing direct contact between the upper part of foam and the solvent, and covering the entire combustion surface. It is believed that the fire is then extinguished by cooling and smothering effects. Compared with the fire extinguishing compositions of types (1), (2) and (3) above, compositions of type (4) offer better foam development on the combustion surface, and also offer an improved fire extinguishing effect.

[0004] However, assuming the mechanism above, wherein the gel-like mat of the water soluble high molecular weight material protects the foam from the solvent, fire extinguishing compositions of the type (4) above will display poor fire extinguishing effect on solvents such as alcohols (such as isopropyl alcohol and t-butanol) or propylene oxide which have large heats of combustion or are highly volatile, and so depending on the type of solvent, the dilution ratio of the composition concentrate may need to be increased, which makes handling somewhat troublesome. Moreover, because fire extinguishing compositions of the type (4) described above rely on smothering utilizing the covering effect of the gel-like mat, good effects are displayed in so-called soft running methods where the foam is poured gently onto the surface of the fuel along the side wall of a tank such as in a foam chamber, but in methods where the foam is shot directly onto the solvent surface from the foam discharge nozzle of a chemical fire engine or the like, a method which represents the most common fire fighting strategy, the surface of the fuel is disturbed, meaning the gel-like mat can sink and the fuel surface can reappear above the mat and reignite, and consequently problems still remain over the performance of these type (4) compositions in actual fire fighting situations.

[0005] Furthermore, these fire extinguishing compositions incorporate large amounts of water soluble high molecular weight material, and so the composition concentrate is extremely viscous (at least 1200 mm^2/s), and moreover the viscosity value varies considerably with temperature. Consequently, considerable care needs to be taken with the fire extinguishing equipment (such as mixers and piping), and there are handling concerns associated with the practical application of these types of compositions to existing equipment. Furthermore, conventionally these type of fire extinguishing compositions have been prone to forming a thin membrane (skin) on the surface of the liquid and on the walls of the tank during storage, and moreover producing sedimentation on the bottom of the tank, and problems have also arisen over the life of the product with concerns that they do not cope with extended storage. In addition, these types of fire extinguishing compositions also have a relatively high freezing point of approximately 0°C, and because they are not reversible in terms of freezing and remelting, use or storage of such compositions in cold regions requires special considerations.

[0006] An example of a fire extinguishing composition which displays superior fuel resistance, flame resistance (for example, reignition sealing) and heat resistance when compared with conventional compositions was disclosed by the present applicants in Japanese Unexamined Patent Application, First Publication No. Sho-59-230566, and comprises a surfactant with an anionic hydrophilic group and a cationic water soluble high molecular weight compound, mixed with a third constituent comprising a polybasic acid compound of 3 to 24 carbon atoms.

[0007] However, although this fire extinguishing composition is able to be used for extinguishing both polar solvent fires and non-polar solvents, the time required to extinguish a fire is relatively long, and the composition could not be claimed to offer rapid fire extinguishing performance. In addition, the composition also has problems in terms of flame resistance, and reignition prevention. Furthermore, in actual fire fighting activity, when the fire extinguishing composition concentrate was diluted with either fresh water or sea water, problems arose in terms of the extended stability of the diluted solution, with cloudiness developing in the diluted solution.

[0008] Similarly, in US 4,536,298, the present applicant disclosed a fire extinguishing composition which comprises a surfactant and a cationic water-soluble polymeric substance, wherein the surfactant is a fluorine-containing aminosulfonate-type surface-active agent. Optionally, the composition also contains a polybasic acid compound.

[0009] WO 96/05889 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.

BRIEF SUMMARY OF THE INVENTION

[0010] An object of the present invention is to provide a fire extinguishing composition which when compared with conventional fire extinguishing compositions displays superior rapid fire extinguishing performance, flame resistance, fuel resistance and reignition prevention performance, for both non-polar solvent fires and polar solvent fires, as well as displaying superior stability as a diluted solution.

[0011] In order to achieve the above object, the present invention is a fire extinguishing composition which comprises a cationic polyamine based high molecular weight compound (A) which has primary, secondary, and tertiary cationic groups within the molecular structure, a surfactant with an anionic hydrophilic group (B) and a polybasic acid compound (C) **characterized in that** said primary cationic groups account for no more than 40% by weight of the total cationic groups within the molecule.

[0012] Moreover, the present invention provides a method for extinguishing fire, comprising the steps of providing a fire extinguishing composition according to the present invention; and applying the composition to a fire.

[0013] The fire extinguishing composition of the present invention forms a foam which is extremely stable with respect to polar solvents, and yet also forms an aqueous film on the surface of non-polar solvents such as petroleum, and offers flame resistance and fuel resistance properties which display markedly improved rapid fire extinguishing performance and reignition prevention.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0014]

FIG. 1 is a nuclear magnetic resonance spectrum of a polyethyleneimine.

FIG. 2 is a diagram showing the chemical structures corresponding with the peak numbers on the nuclear magnetic resonance spectrum shown in FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The cationic polyamine based high molecular weight compound (A) used in the present invention refers to a high molecular weight compound which incorporates cationic groups such as amino groups, ammonium groups, pyridinium groups or quaternary ammonium groups, and is a water soluble high molecular weight compound with a solubility in conventional water of at least 0.1 % by weight.

[0016] The cationic groups described above comprise primary, secondary and tertiary groups, and the cationic groups can exist on either the main chain or a side chain of the polyamine based high molecular weight compound.

[0017] There are no particular restrictions on the relative proportions of primary, secondary and tertiary cationic groups, although in the present invention, for the reasons outlined below, primary cationic groups must account for no more than 40% by weight of the total cationic groups.

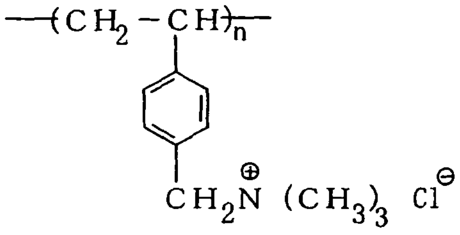
[0018] The degree of polymerization of the water soluble high molecular weight compound is regulated by the water solubility of the compound, and from the oligomer region, degrees of polymerization of at least several tens of thousands, namely weight average molecular weights of 1,000 to 1,000,000 are typical, with values of 4,000 to 300,000 being preferred, and degrees of polymerization of 50,000 to 100,000 being the most desirable in terms of producing a composition with the most superior fire extinguishing performance, flame resistance and fuel resistance with respect to polar solvents.

[0019] Specific examples of the cationic polyamine based high molecular weight compound (A) include those detailed below, although it should be noted that the present invention is in no way limited by these specific examples.

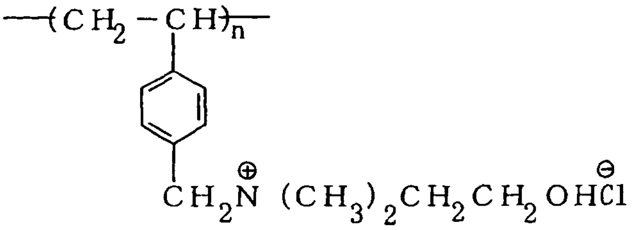
A-I	polyethyleneimine
A-II	N-substituted polyethyleneimine Examples of the N-substituted group include $-C_nH_{2n+1}$, $-CONHC_nH_{2n+1}$, $-COC_nH_{2n+1}$, and $-(CH_2CH_2O)_n-H$ (where n represents an integer of 1 to 6).
A-III	condensation products of melamine and formaldehyde
A-IV	condensation products of guanidine and formaldehyde

[0020] In the fire extinguishing composition of the present invention, additional cationic polyamine based high molecular weight compounds may be used in conjunction with the cationic polyamine based high molecular weight compound (A) used as the essential constituent. Examples of these compatible cationic polyamine based high molecular weight compounds include:

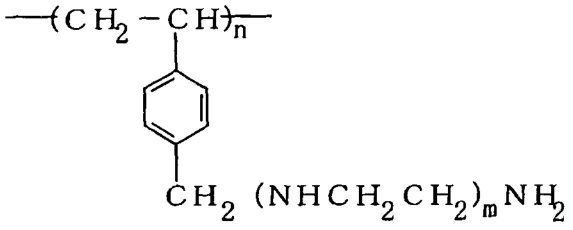
A-V



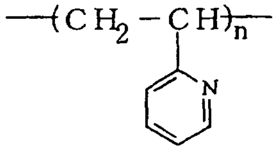
A-VI



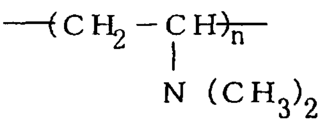
A-VII



A-VIII

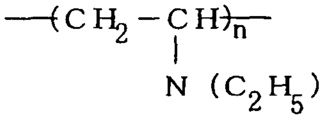


A-IX



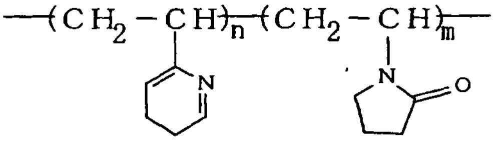
$$-\!\left(CH_2-\underset{N(CH_3)_2}{CH}\right)_n\!-$$

A-X



$$-\!(CH_2-\underset{\displaystyle N(C_2H_5)_2}{\underset{|}{C}}H)_n\!-$$

A-XI



[0021] A fire extinguishing composition of the present invention must not only display the type of performance required of a foam type fire extinguishing composition with rapid fire extinguishing performance, flame resistance, and an ability to retain a layer of foam on the liquid surface of both non-water soluble hazardous materials and water soluble hazardous materials, namely fuel resistance, but must also satisfy certain basic properties of specific gravity, pour point, viscosity, hydrogen ion concentration, sedimentation, and corrosiveness and the like as stipulated in the national certification regulations, which are based on a ministerial ordinance (Ministry of Home Affairs Ordinance No. 26) brought into effect on December 9, 1975 and defining the technical specifications relating to foam type fire extinguishing compositions. Consequently, in order to reach compatibility between fire extinguishing performance and basic performance, it is necessary to mix the main constituent of the fire extinguishing composition with a variety of other additives such as additional foam stabilizers, freezing point depressants, rust prevention agents, and pH regulators and the like.

[0022] A variety of cationic polyamine based high molecular weight compounds, such as those described above, can be used as the main constituent of a fire extinguishing composition which complies with the above requirements, but as mentioned above, it is a requirement that primary cationic groups within the compound account for no more than 40% by weight of the total cationic groups.

[0023] If a cationic polyamine based high molecular weight compound in which the proportion of primary cationic groups exceeds 40% by weight is used, then not only does sedimentation occur in an aqueous solution produced by mixing 3 to 6 parts by weight of the foam fire extinguishing composition concentrate with 97 to 94 parts of fresh water or sea water, which raises a dilution stability problem in that the composition does not satisfy one of the technical specifications of the Ministry of Home Affairs Ordinance No. 26, but furthermore, sedimentation can block the tips of the various types of nozzles used in actual fire fighting activity, resulting in unexpected situations which inhibit effective fire fighting.

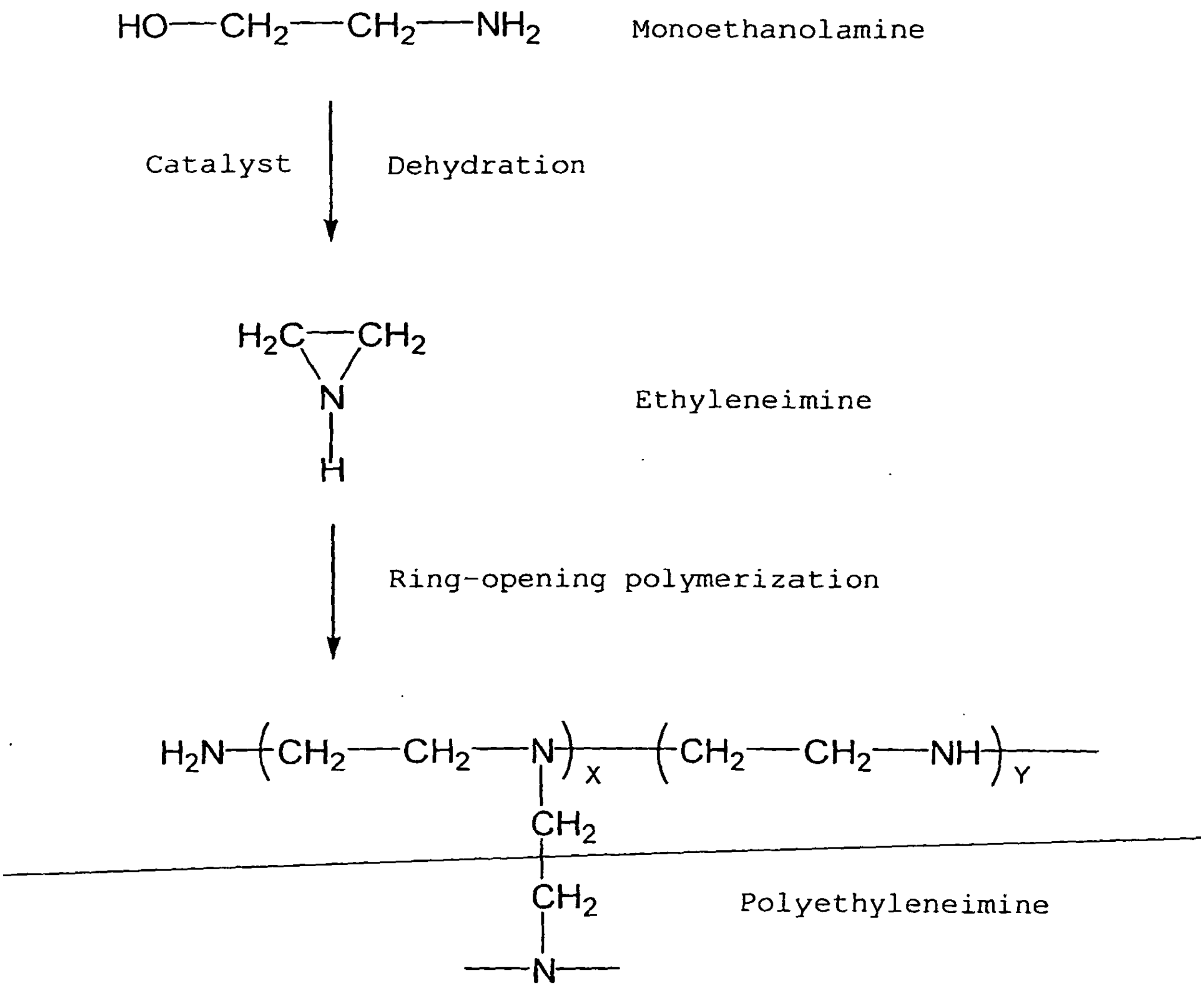
[0024] Moreover, in terms of fire extinguishing performance, using a compound in which the proportion of primary cationic groups accounts for no more than 40% by weight of the total number of cationic groups results in even superior performance in terms of rapid fire extinguishing performance, flame resistance, fuel resistance, and reignition prevention performance.

[0025] Cationic polyamine based high molecular weight compounds in which the proportion of primary cationic groups accounts for no more than 40% by weight of the total number of cationic groups, and the secondary cationic groups account for at least 35% by weight of the total cationic groups, display even more superior effects in terms of fire extinguishing performance and dilution stability, and are consequently preferred.

[0026] Furthermore, in selecting a suitable cationic polyamine based high molecular weight compound, consideration of compatibility with additives such as additional foam stabilizers, freezing point depressants, rust prevention agents, and pH regulators, as well as consideration of other factors such as cost merit, safety with regards to both personnel and the environment, and the availability of the raw materials, results in polyethyleneimine or partially modified polyethyleneimine being used in preference.

[0027] Identification of the relative proportions of primary, secondary and tertiary cationic groups within the cationic polyamine based high molecular weight compound can be determined by using nuclear magnetic resonance spectroscopy to record a ^{13}C-NMR spectrum, and then using the spectral peaks, chemical shift values, and integration curves to calculate the relative weight proportions of primary, secondary and tertiary cationic groups ($-NH_2$, -NH-, -N= in the case of polyethyleneimine) within the molecule.

[0028] There are no particular restrictions on the method of manufacturing the cationic polyamine based high molecular weight compound according to the present invention, although a typical method of manufacturing polyethyleneimine comprises synthesizing ethyleneimine by a direct cyclodehydration of gaseous mono ethanolamine in the presence of a solid acid-base catalyst, and then subjecting the ethyleneimine produced by this method to a ring-opening polymerization in the presence of an acid catalyst to form polyethyleneimine. Reaction kinetics mean that polyethyleneimine manufactured in this manner will not be a perfectly linear macromolecule, but will rather be a high molecular weight compound with a branched structure comprising primary, secondary and tertiary amine groups, as shown in the chemical equation below. Furthermore, the acid catalyst used in the ring-opening polymerization of ethyleneimine may utilize any of the mineral acid, inorganic or organometallic based Lewis acids, although the branched structure will vary depending on the catalyst used, as will the ratio of primary, secondary and tertiary amines within the produced molecule.



[0029] Furthermore, in order to improve fuel resistance,
a surfactant (B) with an anionic hydrophilic group is also included in the fire extinguishing composition of the present invention. A surfactant with an anionic hydrophilic group undergoes an electrostatic interaction with the cationic polyamine based high molecular weight compound (A), and the surfactant in the present invention is a compound with at least one anionic hydrophilic group within each molecule.

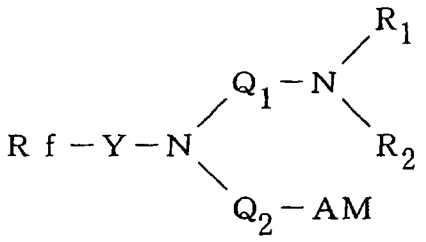
[0030] Preferred anionic hydrophilic groups include groups such as $-COOH$, $-SO_3H$, $-OSO_3H$, and $-OP(OH)_2$, with $-SO_3H$ being particularly desirable. Furthermore, in terms of counter ions for the cationic groups, compounds with organic or inorganic anionic groups may also be used.

[0031] The hydrophilic group of the surfactant may incorporate one or more of the same, or different anionic groups, or alternatively, an amphoteric ion type surfactant which incorporates a cationic hydrophilic group and/or a nonionic group in addition to the anionic hydrophilic group, is also possible. Of these various options, amphoteric ion type surfactants are preferred for compatibility reasons.

[0032] Examples of the hydrophobic group of the surfactant include aliphatic hydrocarbon groups of 6 or more carbon atoms, dihydrocarbyl siloxane chains, or fluorinated aliphatic groups of 3 to 20 carbon atoms and preferably 6 to 16 carbon atoms. Of these hydrophobic groups, fluorinated aliphatic groups are particularly desirable as they offer improved fuel resistance. Furthermore, the surfactant may also comprise a mixture of different surfactants with different hydrophobic groups.

[0033] The surfactants with an anionic hydrophilic group (B) used in the fire extinguishing composition of the present invention can be broadly classified into: (B-1) fluorine containing amino acid type amphoteric surfactants, (B-2) fluorine containing aminosulfonate type surfactants, (B-3) fluorine containing aminocarboxylate type surfactants, (B-4) fluorine containing trianion type amphoteric surfactants, (B-5) fluorine containing tricarboxylic acid type amphoteric surfactants, (B-6) fluorine containing sulfobetaine type amphoteric surfactants, (B-7) fluorine containing aminosulfate type surfactants, (B-8) fluorine containing sulfatobetaine type surfactants, (B-9) fluorine containing sulfobetaine type surfactants, (B-10) fluorine containing amine oxide type surfactants, and (B-11) other surfactants.

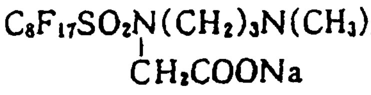
[0034] The fluorine containing amino acid type amphoteric surfactants B-1 are compounds represented by the general formula (B-1):



(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, Y represents either $-SO_2-$ or -CO-, and Q_1 and Q_2 represent organic bivalent linking groups such as aliphatic hydrocarbon groups, aliphatic hydrocarbon groups substituted with hydroxyl groups, aromatic hydrocarbon groups, substituted aromatic hydrocarbon groups, or combinations thereof, with preferred groups including straight chain alkylene groups of 1 to 6 carbon atoms, the 2-hydroxypropan-1,3-diyl group, the 2-methoxypropan-1,3-diyl group, the 2-ethoxypropan-1,3-diyl group, and the 2-propoxypropan-1,3-diyl group. R_1 and R_2 represent hydrogen atoms, aliphatic hydrocarbon groups of 1 to 12 carbon atoms, or aliphatic hydrocarbon groups which have been substituted with hydrophilic groups, or R_1 and R_2 may be linked together forming a ring with the adjacent nitrogen atom. A represents an anionic hydrophilic group such as $-COO^-$, $-SO_3^-$, $-OSO_3^-$, or $-OP(OH)O^-$. M represents a hydrogen atom, an alkali metal, an alkali earth metal, an ammonium group, or an organic cationic group.)

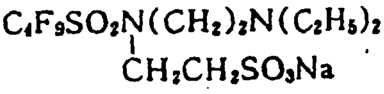
[0035] Specific examples of this (B-1) compound are shown below, although the present invention is not limited to the specific examples shown.

B－1－a



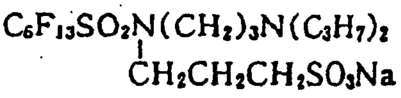
$$\mathrm{C_8F_{17}SO_2\underset{\overset{|}{CH_2COONa}}{N}(CH_2)_3N(CH_3)_2}$$

B－1－b



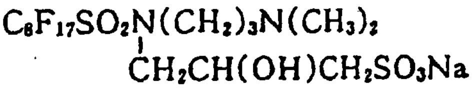
$$\mathrm{C_4F_9SO_2\underset{\overset{|}{CH_2CH_2SO_3Na}}{N}(CH_2)_2N(C_2H_5)_2}$$

B－1－c



$$\mathrm{C_6F_{13}SO_2\underset{\overset{|}{CH_2CH_2CH_2SO_3Na}}{N}(CH_2)_3N(C_3H_7)_2}$$

B－1－d

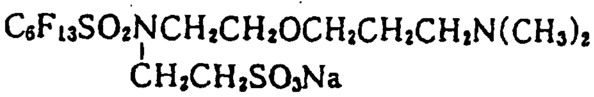


$$\mathrm{C_8F_{17}SO_2\underset{\overset{|}{CH_2CH(OH)CH_2SO_3Na}}{N}(CH_2)_3N(CH_3)_2}$$

B − 1 − e

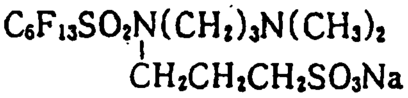
$C_6F_{13}SO_2\underset{CH_2CH_2COONa}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$

B − 1 − f



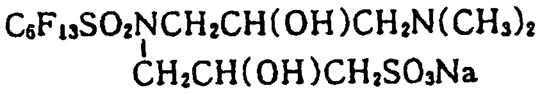
$C_6F_{13}SO_2\underset{CH_2CH_2SO_3Na}{\underset{|}{N}}CH_2CH_2OCH_2CH_2CH_2N(CH_3)_2$

B − 1 − g



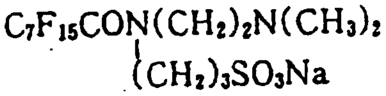
$C_6F_{13}SO_2\underset{CH_2CH_2CH_2SO_3Na}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$

B − 1 − h



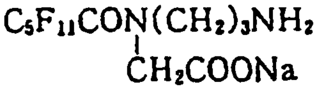
$C_6F_{13}SO_2\underset{CH_2CH(OH)CH_2SO_3Na}{\underset{|}{N}}CH_2CH(OH)CH_2N(CH_3)_2$

B − 1 − i



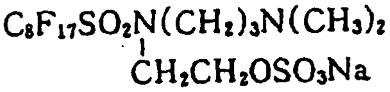
$C_7F_{15}CO\underset{(CH_2)_3SO_3Na}{\underset{|}{N}}(CH_2)_2N(CH_3)_2$

B − 1 − j



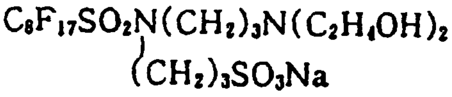
$C_5F_{11}CO\underset{CH_2COONa}{\underset{|}{N}}(CH_2)_3NH_2$

B − 1 − k



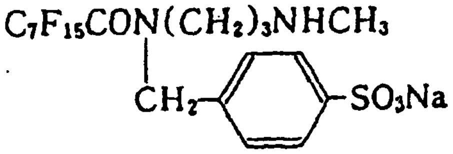
$C_8F_{17}SO_2\underset{CH_2CH_2OSO_3Na}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$

B − 1 − l



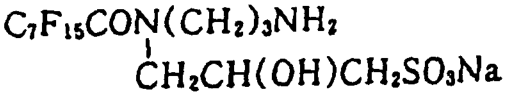
$C_8F_{17}SO_2\underset{(CH_2)_3SO_3Na}{\underset{|}{N}}(CH_2)_3N(C_2H_4OH)_2$

B − 1 − m



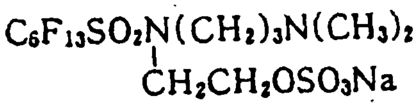
$C_7F_{15}CO\underset{CH_2-\langle\bigcirc\rangle-SO_3Na}{\underset{|}{N}}(CH_2)_3NHCH_3$

B − 1 − n



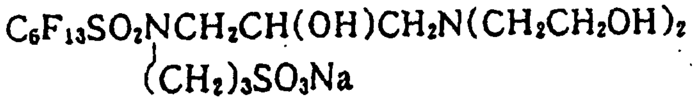
$C_7F_{15}CO\underset{CH_2CH(OH)CH_2SO_3Na}{\underset{|}{N}}(CH_2)_3NH_2$

B − 1 − o



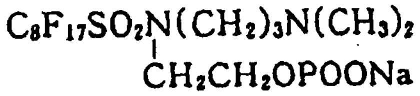
$C_6F_{13}SO_2\underset{CH_2CH_2OSO_3Na}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$

B－1－p



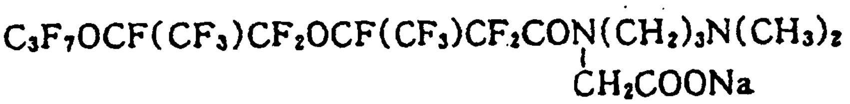
$$C_6F_{13}SO_2\underset{(CH_2)_3SO_3Na}{\underset{|}{N}}CH_2CH(OH)CH_2N(CH_2CH_2OH)_2$$

B－1－q



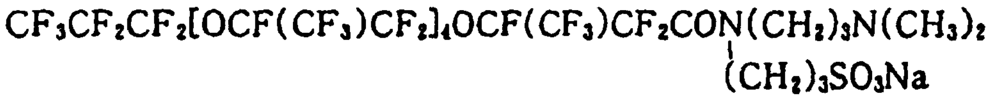
$$C_8F_{17}SO_2\underset{CH_2CH_2OPOONa}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$$

B－1－r



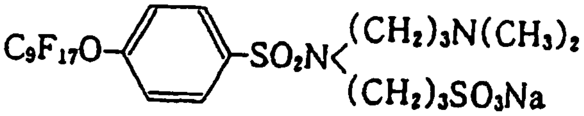
$$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2CO\underset{CH_2COONa}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$$

B－1－s

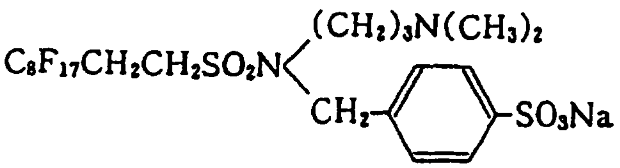


$$CF_3CF_2CF_2[OCF(CF_3)CF_2]_4OCF(CF_3)CF_2CO\underset{(CH_2)_3SO_3Na}{\underset{|}{N}}(CH_2)_3N(CH_3)_2$$

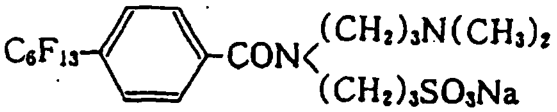
B－1－t



B－1－u



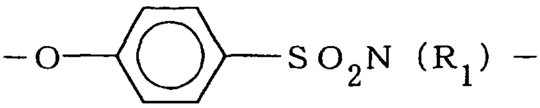
B－1－v



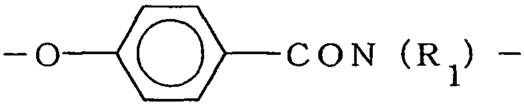
[0036] The fluorine containing aminosulfonate type surfactants (B-2) are compounds represented by the general formula (B-2):

$$Rf\text{-}Z\text{-}Q_1\text{-}N(R)\text{-}Q_2\text{-}SO_2M$$

(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, Z represents a bivalent linking group such as $-SO_2N(R_1)-$, $-CON(R_1)-$,
$-(CH_2CH_2)_iSO_2N(R_1)-$, or compounds covered by the general formula

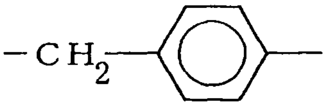


or the general formula



(where R_1 is a hydrogen atom or an alkyl group of 1 to 12 carbon atoms, and i is an integer from 1 to 10), and Q_1 represents a straight chain alkylene group of 1 to 6 carbon atoms, the 2-hydroxypropan-1,3-diyl group, the 2-ethoxypropan-1,3-diyl group, or the 2-propoxypropan-1,3-diyl group.

[0037] R represents a hydrogen atom, an alkyl group of 1 to 3 carbon atoms, a hydroxyalkyl group, $-Q_2SO_3M$, or $-(CH_2)_kCOOM$ (where k is an integer of 1 to 4), Q_2 represents a straight chain alkylene group of 1 to 5 carbon atoms, the 2-hydroxypropan-1,3-diyl group, the 2-ethoxypropan-1,3-diyl group, the 2-propoxypropan-1,3-diyl group, or a bivalent linking group represented by the general formula below.



M represents a hydrogen atom, an alkali metal, an alkali earth metal, or a cationic atom or group of atoms represented by the formula below.

$$-N(H)_m(R_4)_{4-m}$$

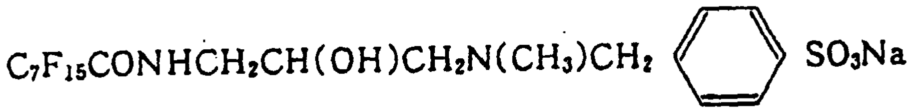
(In the formula, R_4 represents an alkyl group of 1 to 3 carbon atoms, or a hydroxyalkyl group, and m is an integer of 0 to 4.))

[0038] Specific examples of this (B-2) compound are shown below, although the present invention is not limited by the specific examples shown.

[0039]

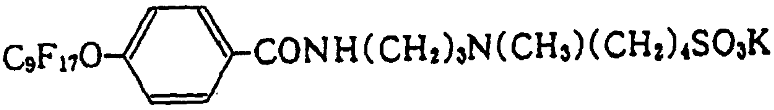
B-2-a	$C_8F_{17}SO_2NH(CH_2)_3N(CH_3)(CH_2)_3SO_3Na$
B-2-b	$C_8F_{17}SO_2NH(CH_2)_3N(CH_2CH_2OH)(CH_2)_3SO_3Na$
B-2-c	$C_6F_{13}SO_2N(CH_3)(CH_2)_3N(C_2H_5)CH_2CH(OH)CH_2SO_3K$
B-2-d	$C_7F_{15}CONH(CH_2)_2N(CH_3)(CH_2)_3SO_3Na$

B-2-e

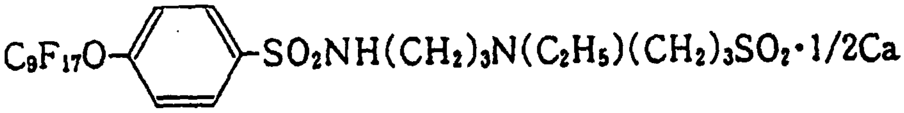


B-2-f	$C_8F_{17}CH_2CH_2SO_2NH(CH_2)_3N(CH_3)(CH_2)_3SO_3Na$

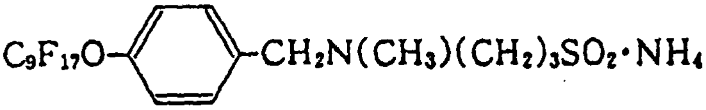
B-2-g



B-2-h

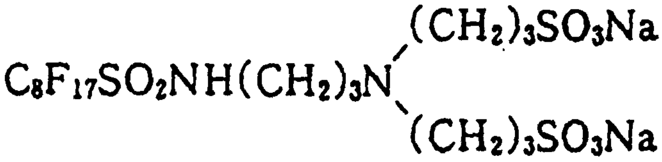


B-2-i

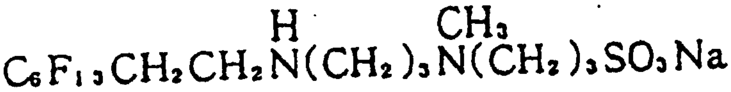


B-2-j	$C_8F_{17}(OCH_2CH_2)_2N(CH_3)(CH_2)_3SO_3.N(C_2H_5)_4$
B-2-k	$C_7F_{15}CH_2CH_2SCH_2COO(CH_2)_2N(CH_3)(CH_2)_2SO_3Na$
B-2-l	$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2CONH(CH_2)_3N(CH_3)(CH_2)_3SO_3Na$
B-2-m	$CF_3CF_2CF_2[OCF(CF_3)CF_2]_4OCF(CF_3)CF_2CONH(CH_2)_3N(CH_3)(CH_2)_2SO_3K$

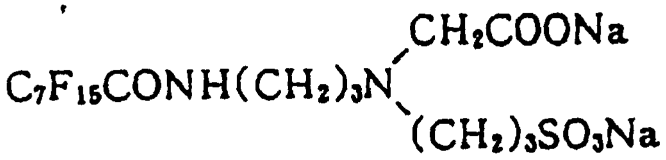
B-2-n



B-2-o

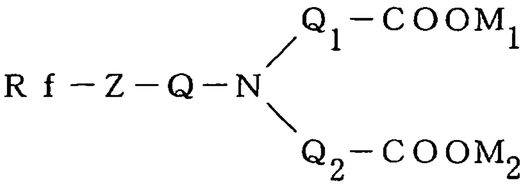


$C_6F_{13}CH_2CH_2\overset{H}{N}(CH_2)_3\overset{CH_3}{N}(CH_2)_3SO_3Na$

B-2-p 

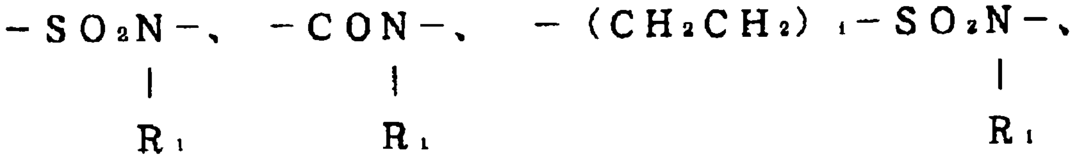
$$C_7F_{15}CONH(CH_2)_3N\left\langle\begin{array}{l}CH_2COONa\\(CH_2)_3SO_3Na\end{array}\right.$$

[0040] The fluorine containing aminocarboxylate type surfactants (B-3) are compounds represented by the general formula (B-3):

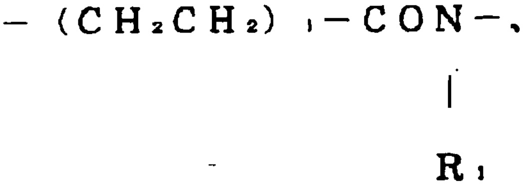


$$Rf-Z-Q-N\left\langle\begin{array}{l}Q_1-COOM_1\\Q_2-COOM_2\end{array}\right.$$

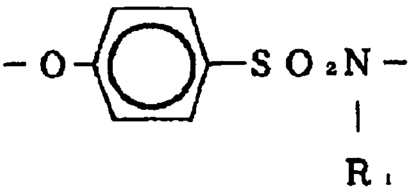
(In the formula, Rf represents a polyfluoroalkyl group, a polyfluoroalkenyl group, a polyfluorocyclohexyl group, a polyfluorocyclohexyl alkyl group or a polyfluorocyclohexyl alkenyl group of 3 to 20 carbon atoms which may also incorporate oxygen atoms, and Z represents a linking group of one of the formulae below.



$$-SO_2\underset{\underset{R_1}{|}}{N}-,\quad -CO\underset{\underset{R_1}{|}}{N}-,\quad -(CH_2CH_2)_l-SO_2\underset{\underset{R_1}{|}}{N}-,$$

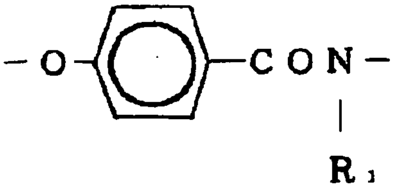


$$-(CH_2CH_2)_l-CO\underset{\underset{R_1}{|}}{N}-,$$

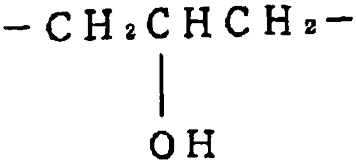


$$-O-C_6H_4-SO_2\underset{\underset{R_1}{|}}{N}-$$

or



(In the formulae, R_1 represents an alkyl group, an alkenyl group or an aromatic ring containing monovalent group incorporating of 1 to 18 carbon atoms, and i represents an integer of 1 to 3.) Q represents a bivalent linking group of one of the formula below.



$$-CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2-$$

$$-(CH_2)_l- \ , \ -(CH_2)_m-O-(CH_2)_n-$$

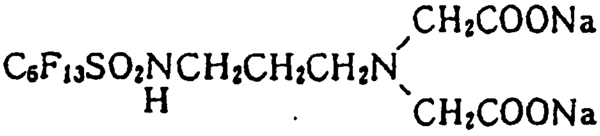
or

$$-(CH_2)_p-O-(CH_2)_2-O-(CH_2)_q-$$

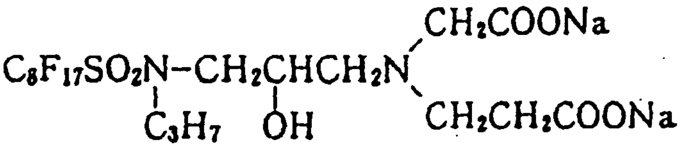
(In the formulae, l represents an integer of 1 to 6, m and n each represent an integer of 2 to 6, and p and q each represent the number 2 or 3 respectively.) Q_1 and Q_2 each represent a alkylene group of 1 to 3 carbon atoms. M_1 and M_2 each represent a hydrogen atom or an inorganic or an organic cation.)

[0041] Specific examples of this (B-3) compound are shown below, although the present invention is not limited by the specific examples shown.

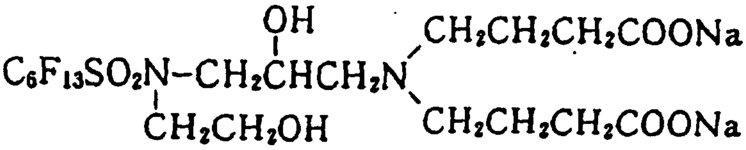
B − 3 − a



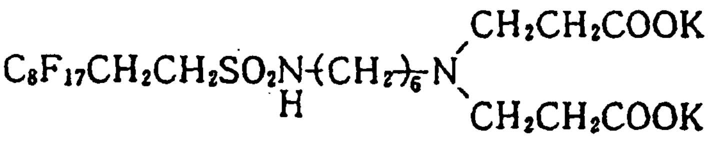
B − 3 − b



B − 3 − c

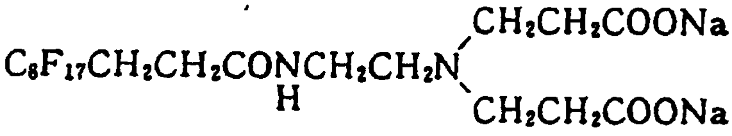


B − 3 − d



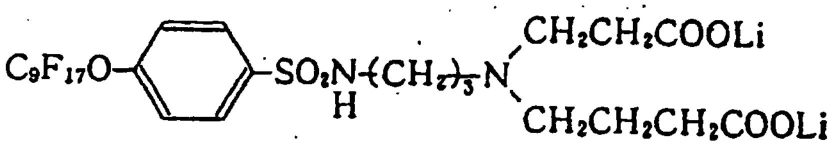
$$C_8F_{17}CH_2CH_2SO_2\underset{H}{N}(CH_2)_6N\begin{array}{l}CH_2CH_2COOK\\CH_2CH_2COOK\end{array}$$

B − 3 − e

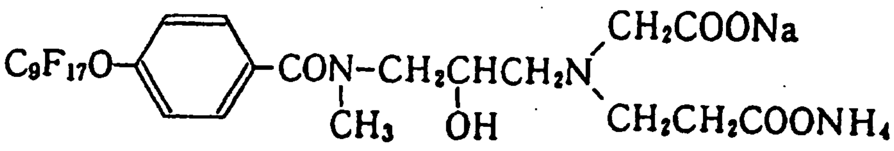


$$C_8F_{17}CH_2CH_2CO\underset{H}{N}CH_2CH_2N\begin{array}{l}CH_2CH_2COONa\\CH_2CH_2COONa\end{array}$$

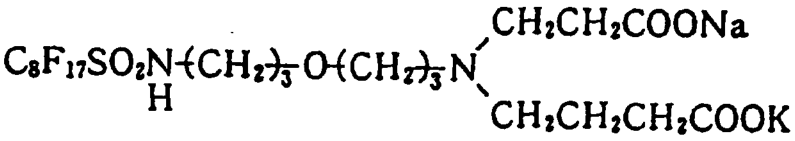
B − 3 − f



B − 3 − g

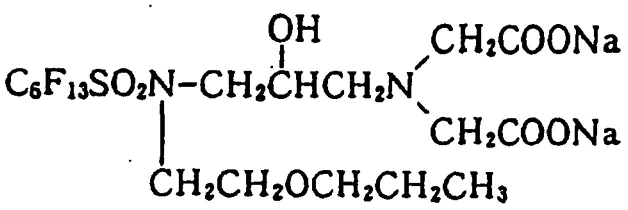


B − 3 − h



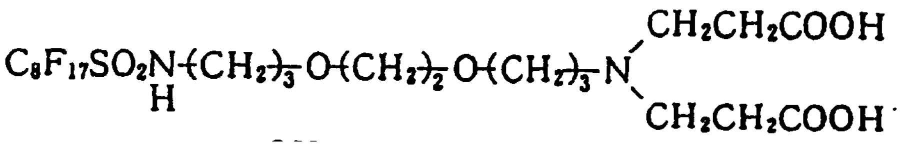
$$C_8F_{17}SO_2\underset{H}{N}(CH_2)_3O(CH_2)_3N\begin{array}{l}CH_2CH_2COONa\\CH_2CH_2CH_2COOK\end{array}$$

B − 3 − i



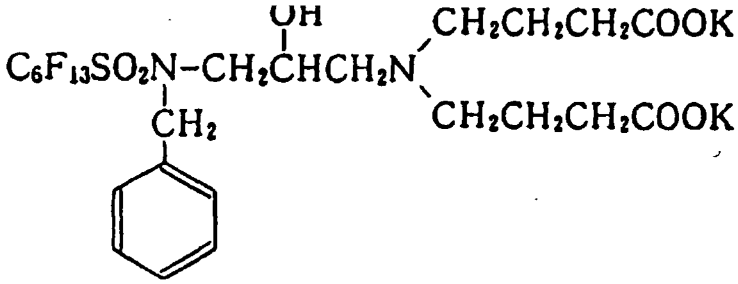
$$C_6F_{13}SO_2\underset{CH_2CH_2OCH_2CH_2CH_3}{N}-CH_2\overset{OH}{C}HCH_2N\begin{array}{l}CH_2COONa\\CH_2COONa\end{array}$$

B − 3 − j

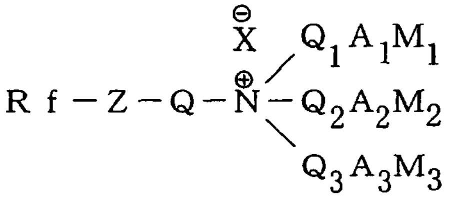


$$C_8F_{17}SO_2\underset{H}{N}(CH_2)_3O(CH_2)_2O(CH_2)_3N\begin{array}{l}CH_2CH_2COOH\\CH_2CH_2COOH\end{array}$$

B − 3 − k

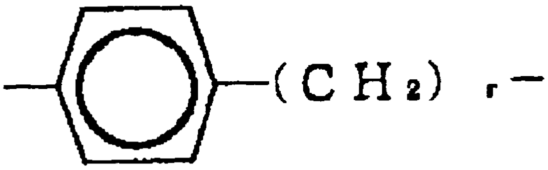


[0042] The fluorine containing trianion type amphoteric surfactants (B-4) are compounds represented by the general formula (B-4):



$$Rf-Z-Q-\overset{\oplus}{N}\overset{\ominus}{X}\begin{cases}Q_1A_1M_1\\Q_2A_2M_2\\Q_3A_3M_3\end{cases}$$

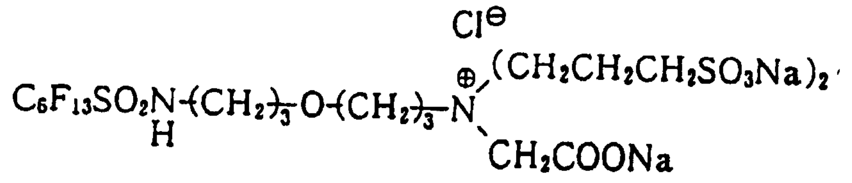
(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, Z represents a bivalent linking group, Q represents a straight chain alkylene group of 1 to 6 carbon atoms, the 2-hydroxypropan-1,3-diyl group, $-(CH_2)_m-O-(CH_2)_n-$ (where m and n are each integers from 2 to 6) or $-(CH_2)_p-O-(CH_2)_2-O-(CH_2)_q-$ (where p and q each represent the number 2 or 3 respectively). Q_1, Q_2 and Q_3 represent bivalent groups such as aliphatic hydrocarbon groups of 1 to 8 carbon atoms, aliphatic hydrocarbon groups of 1 to 8 carbon atoms with substituted hydroxyl groups, or bivalent groups represented by the general formula



(where in the formula, r represents either the number 1 or the number 2), A_1 represents an anionic atom grouping of $-SO_3^-$ or $-OSO_3^-$, A_2 and A_3 also represents an anionic atom grouping of $-SO_3^-$ or $-OSO_3^-$, $-COO^-$, or $-OP(=O)(OH)O^-$, M_1, M_2 and M_3 each represent a hydrogen atom or an inorganic or an organic cation, and X^- represents an inorganic or an organic anion such as OH^-, Cl^-, Br^-, I^-, ClO_4^-, $1/2SO_4^{2-}$, $CH_3SO_4^-$, NO_3^-, CH_3COO^- or the phosphate ion.)

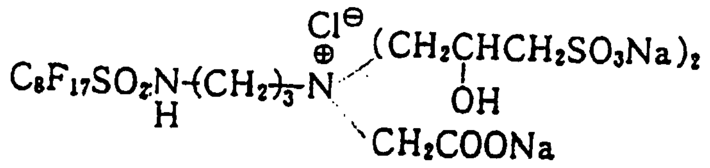
[0043] Specific examples of this (B-4) compound are shown below, although the present invention is not limited by the specific examples shown.

B − 4 − a



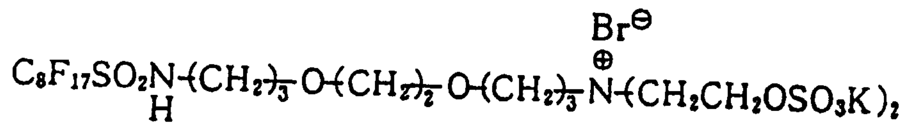
$$C_6F_{13}SO_2\underset{H}{N}\text{+}(CH_2)_3\text{-}O\text{+}(CH_2)_3\text{-}\overset{\oplus}{N}\begin{matrix}(CH_2CH_2CH_2SO_3Na)_2 \\ CH_2COONa\end{matrix}\quad Cl^{\ominus}$$

B − 4 − b



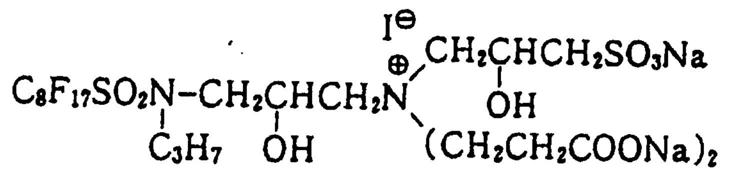
$$C_8F_{17}SO_2\underset{H}{N}\text{+}(CH_2)_3\text{-}\overset{\oplus}{N}\begin{matrix}(CH_2\underset{OH}{CH}CH_2SO_3Na)_2 \\ CH_2COONa\end{matrix}\quad Cl^{\ominus}$$

B − 4 − c



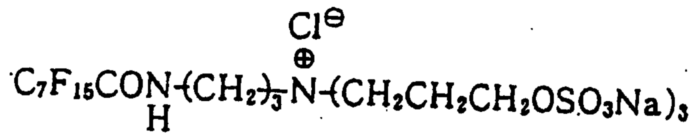
$$C_8F_{17}SO_2\underset{H}{N}\text{+}(CH_2)_3\text{-}O\text{+}(CH_2)_2\text{-}O\text{+}(CH_2)_3\text{-}\overset{\oplus}{N}\text{+}(CH_2CH_2OSO_3K)_2\quad Br^{\ominus}$$

B − 4 − d



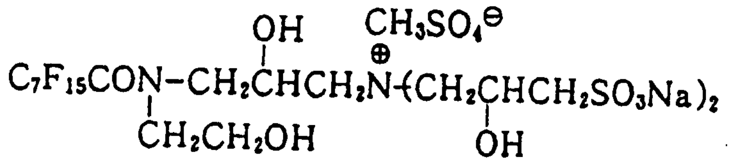
$$C_8F_{17}SO_2\underset{C_3H_7}{N}-CH_2\underset{OH}{CH}CH_2\overset{\oplus}{N}\begin{matrix}CH_2\underset{OH}{CH}CH_2SO_3Na \\ (CH_2CH_2COONa)_2\end{matrix}\quad I^{\ominus}$$

B − 4 − e



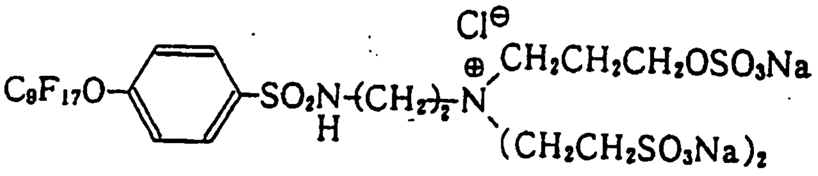
$$C_7F_{15}CO\underset{H}{N}\text{+}(CH_2)_3\text{-}\overset{\oplus}{N}\text{+}(CH_2CH_2CH_2OSO_3Na)_3\quad Cl^{\ominus}$$

B−4−f

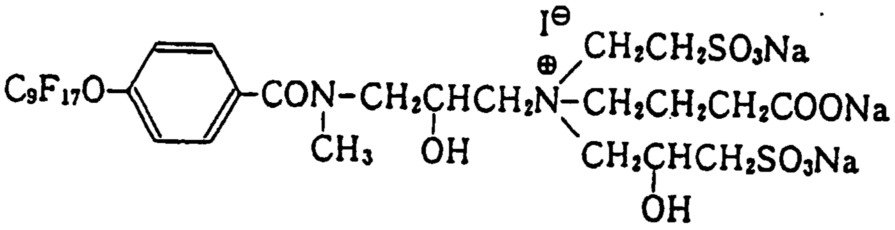


$$C_7F_{15}CO\underset{\displaystyle CH_2CH_2OH}{N}-CH_2\overset{\displaystyle OH}{C}HCH_2\overset{\oplus}{N}\!\left(CH_2\underset{\displaystyle OH}{C}HCH_2SO_3Na\right)_2 \quad CH_3SO_4^{\ominus}$$

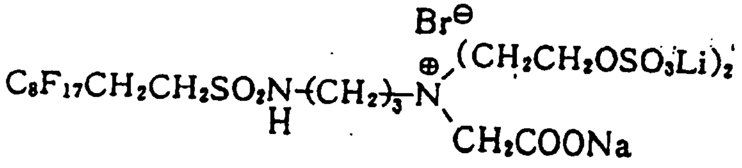
B−4−g



B−4−h

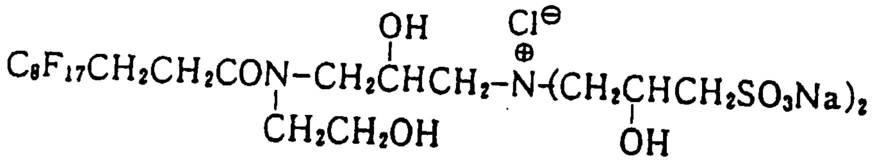


B−4−i



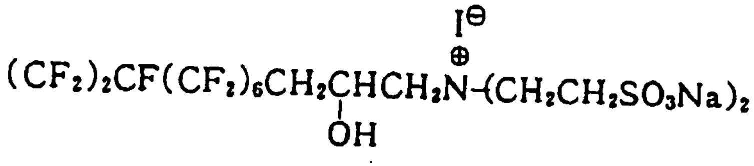
$$C_8F_{17}CH_2CH_2SO_2\underset{\displaystyle H}{N}\!-\!\left(CH_2\right)_3\!-\!\overset{\oplus}{N}\begin{matrix}(CH_2CH_2OSO_3Li)_2\\ CH_2COONa\end{matrix} \quad Br^{\ominus}$$

B-4-j



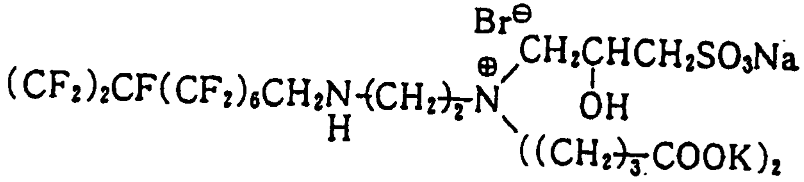
$C_8F_{17}CH_2CH_2CO\underset{CH_2CH_2OH}{N}-CH_2\overset{OH}{C}HCH_2-\overset{Cl^{\ominus}}{\overset{\oplus}{N}}(CH_2\underset{OH}{C}HCH_2SO_3Na)_2$

B-4-k



$(CF_2)_2CF(CF_2)_6CH_2\underset{OH}{C}HCH_2\overset{I^{\ominus}}{\overset{\oplus}{N}}(CH_2CH_2SO_3Na)_2$

B-4-l

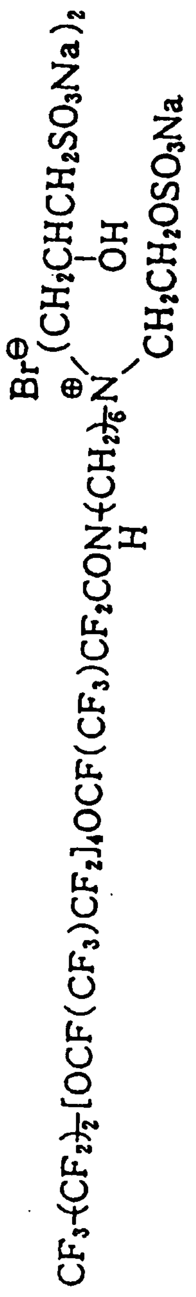


$(CF_2)_2CF(CF_2)_6CH_2\underset{H}{N}(CH_2)_2\overset{Br^{\ominus}}{\overset{\oplus}{N}}\begin{array}{l} CH_2\underset{OH}{C}HCH_2SO_3Na \\ ((CH_2)_3COOK)_2 \end{array}$

B-4-m

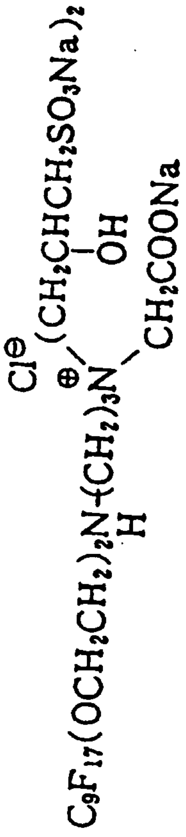
$C_3F_7OCF(CF_2)CF_2OCF(CF_3)CF_2CO\underset{H}{N}(CH_2)_2\overset{I^{\ominus}}{\overset{\oplus}{N}}(CH_2CH_2OSO_3Li)_2$

B-4-n



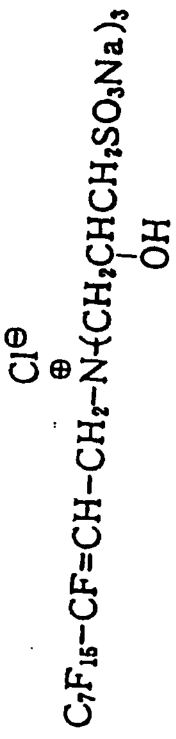
$$CF_3\text{-}(CF_2)_2\text{-}[OCF(CF_3)CF_2]_4OCF(CF_3)CF_2CO\underset{H}{N}\text{-}(CH_2)_6\text{-}\overset{\oplus}{N}\begin{matrix}(CH_2\underset{OH}{CH}CH_2SO_3Na)_2 \\ CH_2CH_2OSO_3Na\end{matrix}\ Br^{\ominus}$$

B-4-o



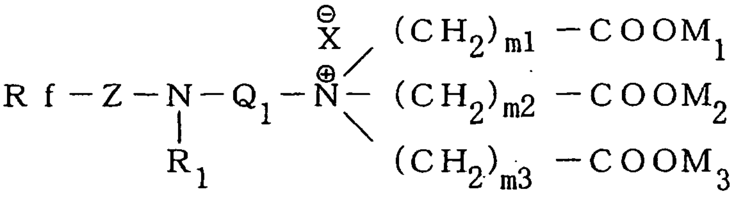
$$C_9F_{17}(OCH_2CH_2)_2\underset{H}{N}\text{-}(CH_2)_3\overset{\oplus}{N}\begin{matrix}(CH_2\underset{OH}{CH}CH_2SO_3Na)_2 \\ CH_2COONa\end{matrix}\ Cl^{\ominus}$$

B-4-p



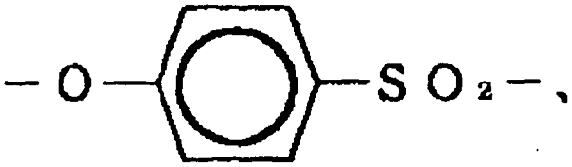
$$C_7F_{15}\text{-}CF{=}CH\text{-}CH_2\text{-}\overset{\oplus}{N}\text{-}(CH_2\underset{OH}{CH}CH_2SO_3Na)_3\ Cl^{\ominus}$$

[0044] The fluorine containing tricarboxylic acid type amphoteric surfactants (B-5) are compounds represented by the general formula (B-5) :

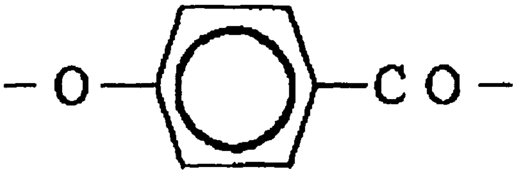


$$Rf-Z-\underset{R_1}{N}-Q_1-\overset{\ominus}{X}\,\overset{\oplus}{N}\begin{cases}(CH_2)_{m1}-COOM_1\\(CH_2)_{m2}-COOM_2\\(CH_2)_{m3}-COOM_3\end{cases}$$

(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, and Z represents -SO_2-, -CO-, -$(CH_2)_l$-SO_2-, -$(CH_2)_l$-CO- (where l represents an integer from 1 to 6), or a bivalent group represented by either the formula



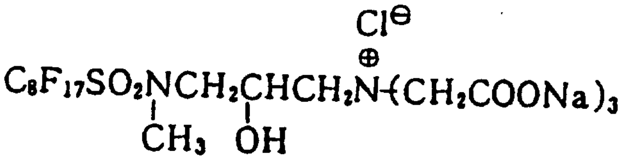
or the formula



R_1 represents the 2-hydroxyethyl group, a group represented by the general formula -$(CH_2)_a$-O-$(CH_2)_b$-CH_3 (where a represents an integer from 2 to 10, and b represents an integer from 1 to 9), or an alkyl group of 1 to 12 carbon atoms, Q_1 represents a straight chain alkylene group of 2 to 6 carbon atoms, the 2-hydroxypropan-1,3-diyl group, or a bivalent group represented by the general formula -$(CH_2)_d$-O-$(CH_2)_e$- (where d and e each represent an integer from 2 to 6), X represents an inorganic or an organic anion, m_1, m_2 and m_3 each represent an independent integer from 1 to 3, and M_1, M_2 and M_3 each represent independently a hydrogen atom, or an inorganic or an organic cation.)

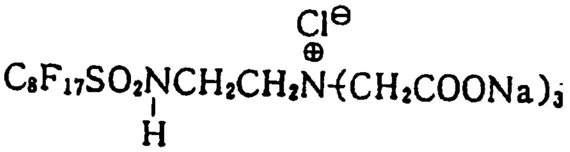
[0045] Specific examples of this (B-5) compound are shown below, although the present invention is not limited by the specific example shown.

B − 5 − a



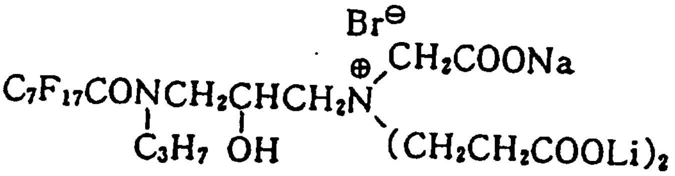
$$C_8F_{17}SO_2\underset{CH_3}{N}CH_2\underset{OH}{C}HCH_2\overset{Cl^{\ominus}}{\overset{\oplus}{N}}(CH_2COONa)_3$$

B − 5 − b



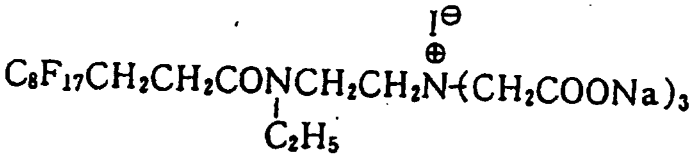
$$C_8F_{17}SO_2\underset{H}{N}CH_2CH_2\overset{Cl^{\ominus}}{\overset{\oplus}{N}}(CH_2COONa)_3$$

B − 5 − c



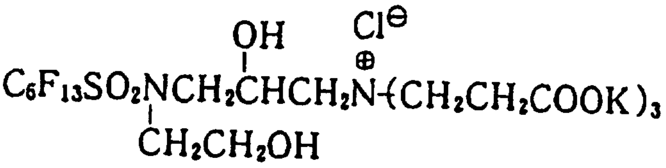
$$C_7F_{17}CO\underset{C_3H_7}{N}CH_2\underset{OH}{C}HCH_2\overset{Br^{\ominus}}{\overset{\oplus}{N}}\begin{matrix}CH_2COONa\\(CH_2CH_2COOLi)_2\end{matrix}$$

B − 5 − d



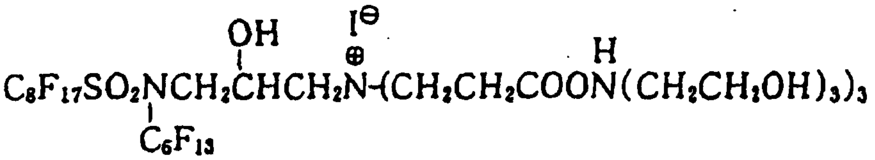
$$C_8F_{17}CH_2CH_2CO\underset{C_2H_5}{N}CH_2CH_2\overset{I^{\ominus}}{\overset{\oplus}{N}}\!\!-\!\!(CH_2COONa)_3$$

B − 5 − e



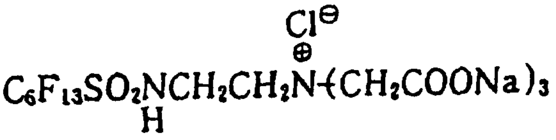
$$C_6F_{13}SO_2\underset{CH_2CH_2OH}{N}CH_2\overset{OH}{C}HCH_2\overset{Cl^{\ominus}}{\overset{\oplus}{N}}\!\!-\!\!(CH_2CH_2COOK)_3$$

B − 5 − f



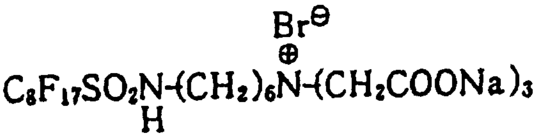
$$C_8F_{17}SO_2\underset{C_6F_{13}}{N}CH_2\overset{OH}{C}HCH_2\overset{I^{\ominus}}{\overset{\oplus}{N}}\!\!-\!\!(CH_2CH_2COO\overset{H}{N}(CH_2CH_2OH)_3)_3$$

B − 5 − g



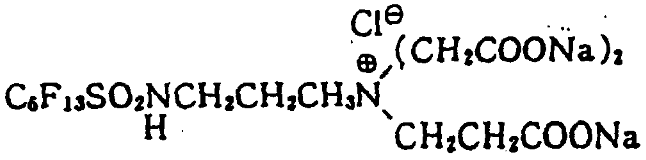
$$C_6F_{13}SO_2\underset{H}{N}CH_2CH_2\overset{Cl^{\ominus}}{\overset{\oplus}{N}}\!\!-\!\!(CH_2COONa)_3$$

B − 5 − h



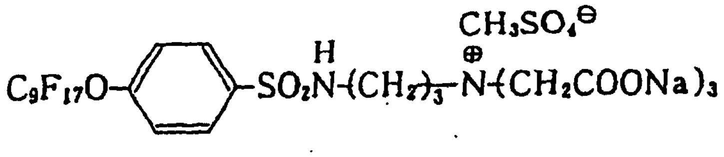
$$C_8F_{17}SO_2\underset{H}{N}\!\!-\!\!(CH_2)_6\overset{Br^{\ominus}}{\overset{\oplus}{N}}\!\!-\!\!(CH_2COONa)_3$$

B − 5 − i

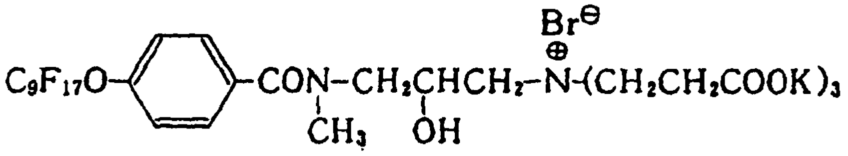


$$C_6F_{13}SO_2\underset{H}{N}CH_2CH_2CH_3\overset{Cl^{\ominus}}{\overset{\oplus}{N}}\begin{matrix}(CH_2COONa)_2\\CH_2CH_2COONa\end{matrix}$$

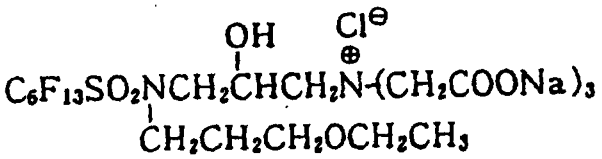
B − 5 − j



B − 5 − k

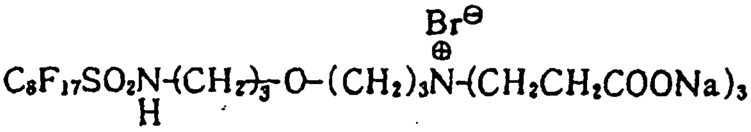


B − 5 − l



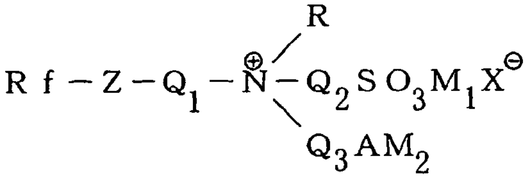
$C_6F_{13}SO_2N(CH_2CH_2CH_2OCH_2CH_3)CH_2CH(OH)CH_2\overset{\oplus}{N}(CH_2COONa)_3\ Cl^{\ominus}$

B − 5 − m



$C_8F_{17}SO_2NH(CH_2)_3O(CH_2)_3\overset{\oplus}{N}(CH_2CH_2COONa)_3\ Br^{\ominus}$

[0046] The fluorine containing sulfobetaine type amphoteric surfactants (B-6) are compounds represented by the general formula (B-6):

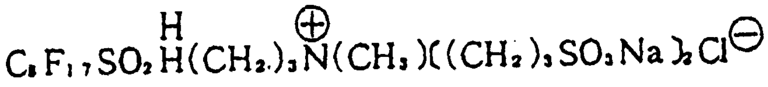


$$Rf-Z-Q_1-\overset{\oplus}{N}(R)(Q_3AM_2)-Q_2SO_3M_1X^{\ominus}$$

(In the formula, Rf represents a group comprising a fluorinated aliphatic group of 3 to 20 carbon atoms, Z represents a bivalent linking group incorporating a sulfonamide group or a carbonamide group, Q_1, Q_2 and Q_3 each represent independently a bivalent aliphatic group of 1 to 12 carbon atoms, an aliphatic hydrocarbon group substituted with a hydroxyl group, an aromatic hydrocarbon group, or a bivalent group formed through a combination of the above groups. R represents a hydrogen atom, a hydrocarbyl group of 1 to 12 carbon atoms, or a $-(CH_2CH_2O)_iH$ or a $-(CH_2CH(CH_3)O)_iH$ group (where i represents an integer of 1 to 20), A represents an anionic atom grouping of $-SO_2^-$, $-COO^-$, $-OSO_2^-$, or $-OP(=O)(OH)O^-$, M_1 and M_2 each represent a hydrogen atom or an inorganic or an organic cation, and X represents an inorganic or an organic anion.)

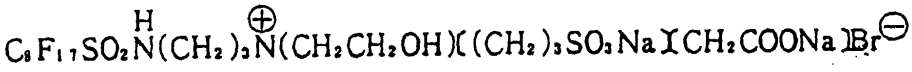
[0047] Specific examples of this (B-6) compound are shown below, although the present invention is not limited by the specific examples shown.

B − 6 − a



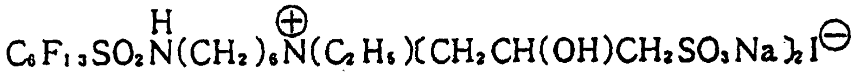
$C_8F_{17}SO_2\overset{H}{H}(CH_2)_3\overset{\oplus}{N}(CH_3)[(CH_2)_3SO_3Na]_2Cl^{\ominus}$

B − 6 − b



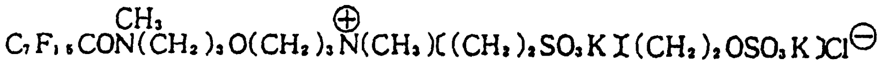
$C_8F_{17}SO_2\overset{H}{N}(CH_2)_3\overset{\oplus}{N}(CH_2CH_2OH)[(CH_2)_3SO_3Na][CH_2COONa]Br^{\ominus}$

B − 6 − c



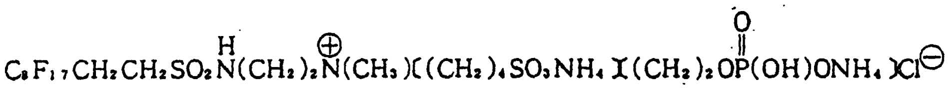
$C_6F_{13}SO_2\overset{H}{N}(CH_2)_6\overset{\oplus}{N}(C_2H_5)[CH_2CH(OH)CH_2SO_3Na]_2I^{\ominus}$

B − 6 − d



$C_7F_{15}CO\overset{CH_3}{N}(CH_2)_3O(CH_2)_3\overset{\oplus}{N}(CH_3)[(CH_2)_3SO_3K][(CH_2)_2OSO_3K]Cl^{\ominus}$

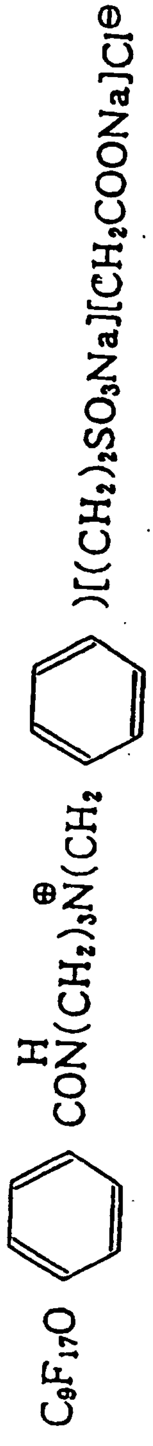
B − 6 − e



$C_8F_{17}CH_2CH_2SO_2\overset{H}{N}(CH_2)_2\overset{\oplus}{N}(CH_3)[(CH_2)_4SO_3NH_4][(CH_2)_2O\overset{\overset{O}{\|}}{P}(OH)ONH_4]Cl^{\ominus}$

B − 6 − f

B－6－g



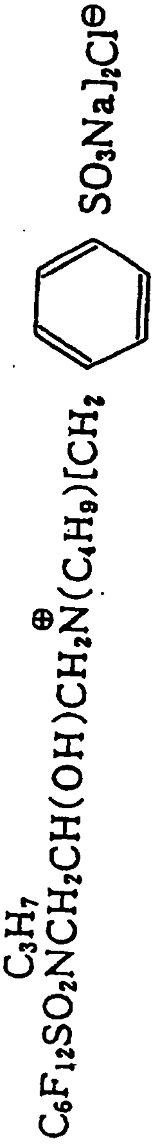
B－6－h

$(C_6F_{13})_2NCF_2CF_2CO\overset{H}{N}(CH_2)_3\overset{\oplus}{N}(CH_3)[(CH_2)_3SO_3Na](CH_2COONa)Cl^{\ominus}$

B－6－i

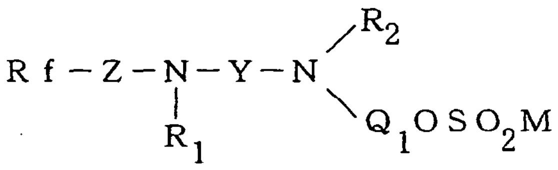
$C_8F_{17}CH_2CH_2CO\overset{C_6H_5}{N}(CH_2)_3\overset{\oplus}{N}(CH_3)[(CH_2)_3SO_3Na][(CH_2)_2OSO_3Na]Cl^{\ominus}$

B－6－j

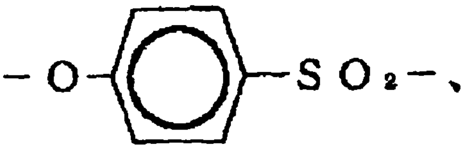


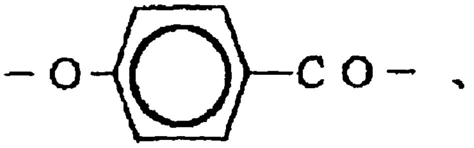
[0048] The fluorine containing aminosulfate type surfactants (B-7) are compounds represented by the general formula

(B-7):



(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, Z represents $-SO_2-$, -CO-, a bivalent group represented by one of the formulae

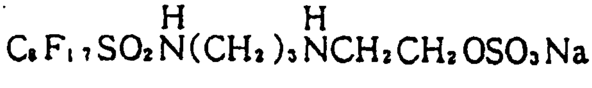




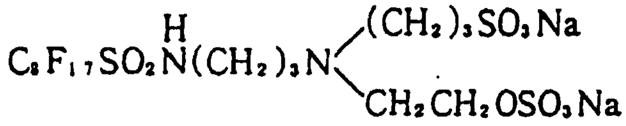
$-(CH_2)_a-SO_2-$

or $-(CH_2)_a-CO-$ (where a represents an integer of 1 to 10), R_1 represents a hydrogen atom, an alkyl group of 1 to 12 carbon atoms, a $-(CH_2)_b-OR_3$ group or a $-(CH_2CH_2O)_d-R_2$ group (where b represents an integer from 1 to 10, d represents an integer of 1 to 20, and R_3 represents a lower alkyl group or alkoxyl group), and Y represents $-(CH_2)_e-$, $-(CH_2)_p-O-(CH_2)_2-O-(CH_2)_q-$ or $-(CH_2)_g-O-(CH_2)_h-$ (where e represents an integer of 2 to 12, p and q each represent independently a value of 2 or 3, and g and h each represent independently an integer of 1 to 6). R_2 represents a hydrogen atom, an alkyl group, alkenyl group, or hydroxyl substituted alkyl group of 1 to 18 carbon atoms, a $-(CH_2CH_2)_m-H$ group (where m represents an integer of 2 to 20), Q_1OSO_3M, Q_1SO_2M or $(CH_2)_iCOOM$ (where i represents an integer from 1 to 4). Q_1 represents a straight chain alkyl group of 2 to 12 carbon atoms, the 2-hydroxypropan-1,3-diyl group or $-(CH_2CH_2O)_k-CH_2CH_2-$ (where k represents an integer from 1 to 50). M represents a hydrogen atom or an inorganic or an organic cation.)

[0049] Specific examples of this (B-7) compound are shown below, although the present invention is not limited by the specific examples shown.

B-7-a 

$C_8F_{17}SO_2\overset{H}{N}(CH_2)_3\overset{H}{N}CH_2CH_2OSO_3Na$

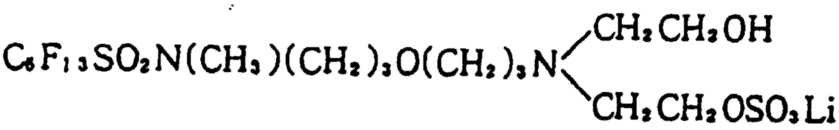
B-7-b 

$C_8F_{17}SO_2\overset{H}{N}(CH_2)_3N\begin{cases}(CH_2)_3SO_3Na\\CH_2CH_2OSO_3Na\end{cases}$

B-7-c $C_7F_{15}CON(CH_3)(CH_2)_3N(CH_3)CH_2CH_2OSO_3NH_4$

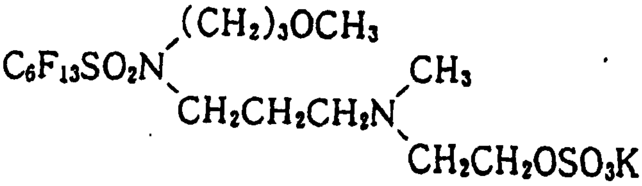
B-7-d $C_7F_{15}CONH(CH_2)_6N(CH_2CH_2OSO_3Na)_2$

B-7-e



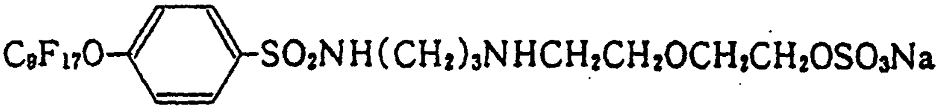
$$C_6F_{13}SO_2N(CH_3)(CH_2)_3O(CH_2)_3N\begin{array}{l}CH_2CH_2OH\\CH_2CH_2OSO_3Li\end{array}$$

B-7-f

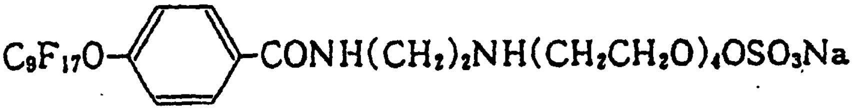


$$C_6F_{13}SO_2N\begin{array}{l}(CH_2)_3OCH_3\\CH_2CH_2CH_2N\begin{array}{l}CH_3\\CH_2CH_2OSO_3K\end{array}\end{array}$$

B-7-g

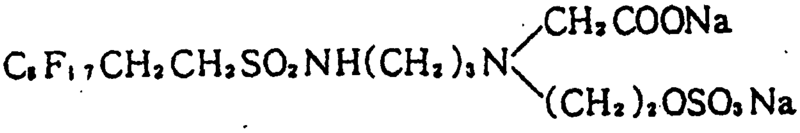


B-7-h

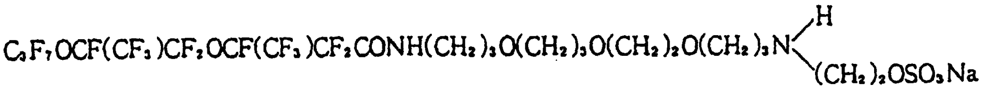


B-7-i $C_8F_{17}CH_2CH_2SO_2NH(CH_2)_3N(CH_3)(CH_2)_4OSO_3Na$

B-7-j

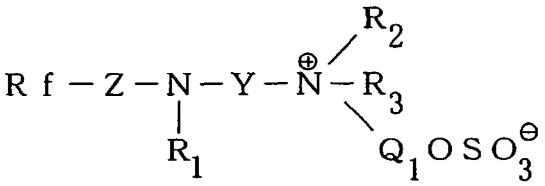


$$C_8F_{17}CH_2CH_2SO_2NH(CH_2)_3N\begin{array}{l}CH_2COONa\\(CH_2)_2OSO_3Na\end{array}$$

B-7-k 

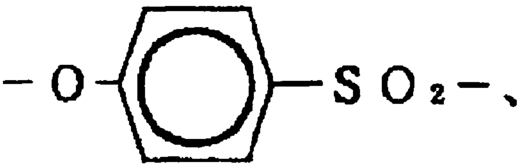
$$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2CONH(CH_2)_3O(CH_2)_3O(CH_2)_2O(CH_2)_3N\begin{matrix}H\\(CH_2)_2OSO_3Na\end{matrix}$$

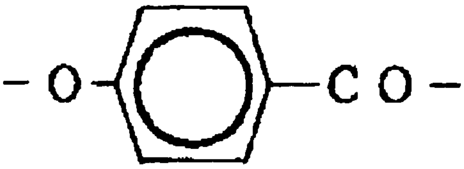
[0050] The fluorine containing sulfatobetaine type surfactants (B-8) are compounds represented by the general formula (B-8):



$$Rf-Z-\underset{R_1}{N}-Y-\overset{\oplus}{N}\begin{matrix}R_2\\R_3\\Q_1OSO_3^{\ominus}\end{matrix}$$

(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms, Z represents $-SO_2-$, $-CO-$,



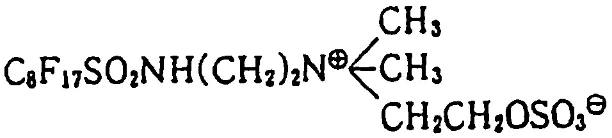


$-(CH_2)_a-SO_2-$

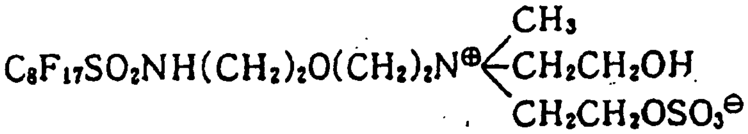
or $-(CH_2)_a-CO-$ (where a represents an integer of 1 to 10), R_1 represents a hydrogen atom, an alkyl group of 1 to 12 carbon atoms, a $-(CH_2)_b-OR_3$ group or a $-(CH_2CH_2O)_d-R_2$ group (where b represents an integer from 1 to 10, d represents an integer of 1 to 20, and R_2 represents a lower alkyl group or alkoxyl group), and Y represents $-(CH_2)_e-$, $-(CH_2)_p-O-(CH_2)_2-O-(CH_2)_q-$ or $-(CH_2)_g-O-(CH_2)_h-$ (where e represents an integer of 2 to 12, p and q each represent independently a value of 2 or 3, and g and h each represent independently an integer of 1 to 6). R_2 and R_3 each represent independently an alkyl group, alkenyl group, hydroxyl substituted alkyl group, or aromatic substituted alkyl group of 1 to 18 carbon atoms, or a $-(CH_2CH_2O)_i-H$ group (where i represents an integer of 2 to 20), or alternatively R_2 and R_3 may be linked together to form a heterocyclic ring with the adjacent nitrogen atom, and Q_1 represents a straight chain alkylene chain of 2 to 12 carbon atoms, the 2-hydroxypropan-1,3-diyl group or $-(CH_2CH_2O)_k-CH_2CH_2-$ (where k represents an integer from 1 to 50).)

[0051] Specific examples of this (B-8) compound are shown below, although the present invention is not limited by the specific examples shown.

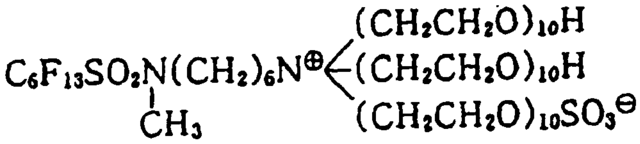
B − 8 − a



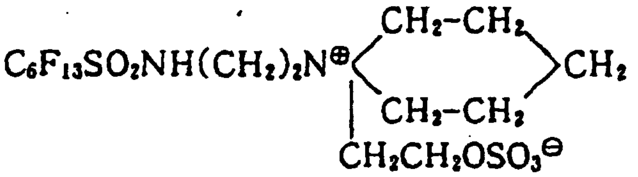
B − 8 − b



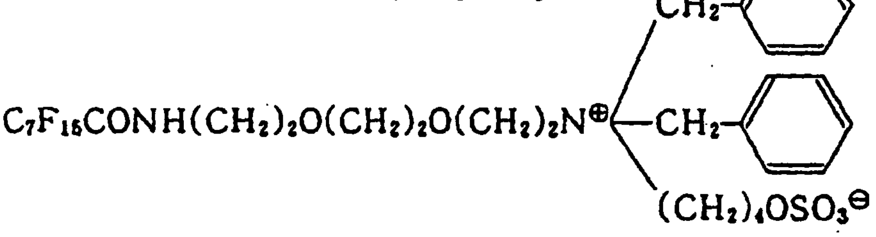
B − 8 − c



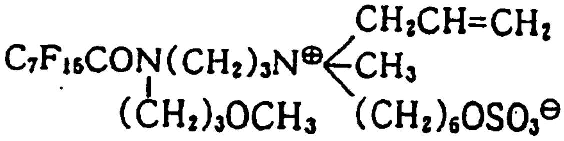
B − 8 − d



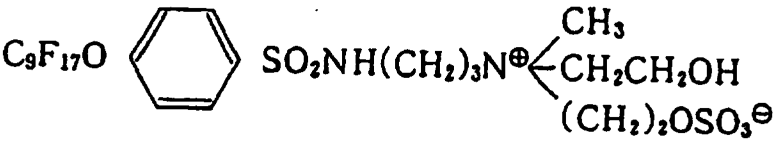
B − 8 − e



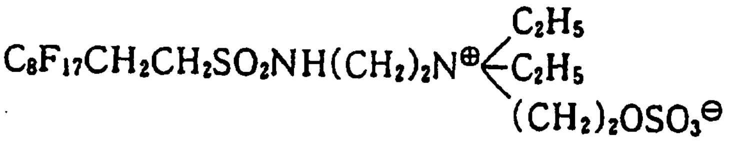
B − 8 − f



B − 8 − g

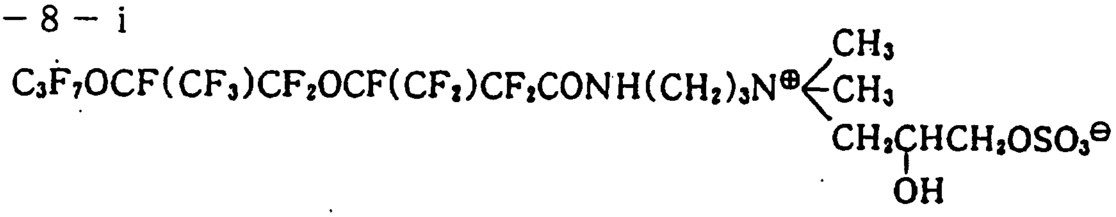


B-8-h



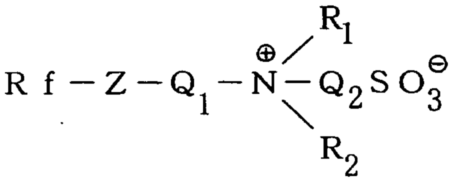
$$C_8F_{17}CH_2CH_2SO_2NH(CH_2)_2N^{\oplus}(C_2H_5)(C_2H_5)(CH_2)_2OSO_3^{\ominus}$$

B-8-i



$$C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2CONH(CH_2)_3N^{\oplus}(CH_3)(CH_3)CH_2CH(OH)CH_2OSO_3^{\ominus}$$

[0052] The fluorine containing sulfobetaine type surfactants (B-9) are compounds represented by the general formula (B-9):



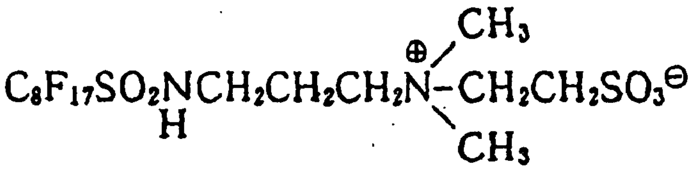
$$Rf-Z-Q_1-N^{\oplus}(R_1)(R_2)-Q_2SO_3^{\ominus}$$

(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms which may incorporate an oxygen atom, or a fluorinated alicyclic group, Z represents a bivalent linking group, Q_1 represents a straight chain alkylene chain of 1 to 6 carbon atoms, or $-(CH_2)_m-O-(CH_2)_n-$ or $-(CH_2)_p-O-(CH_2)_2-O-(CH_2)_q-$ (where m and n each represent an integer of 2 to 6, and p and q each represent independently a value of 2 or 3), Q_2 represents a straight chain alkylene chain of 1 to 6 carbon atoms, the 2-hydroxypropan-1,3-diyl group or $-(CH_2CH_2O)_r-CH_2CH_2-$ (where r represents an integer from 1 to 3), and

R_1 and R_2 each represent independently an alkyl group of 1 to 8 carbon atoms, an alkyl group or alkenyl group which incorporates 1 to 3 ether oxygen atoms, a benzyl group or a $-(CH_2CH_2O)_s-H$ group (where s represents an integer from 1 to 11).)

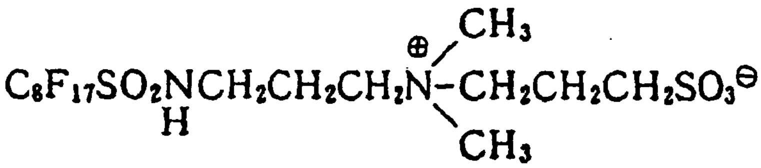
[0053] Specific examples of this (B-9) compound are shown below, although the present invention is not limited by the specific examples shown.

B-9-a



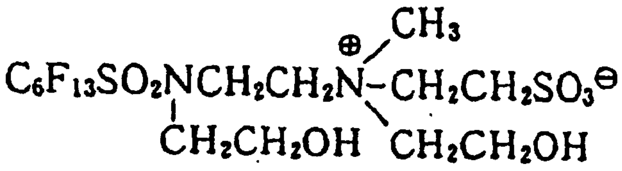
$$C_8F_{17}SO_2NHCH_2CH_2CH_2N^{\oplus}(CH_3)_2-CH_2CH_2SO_3^{\ominus}$$

B-9-b



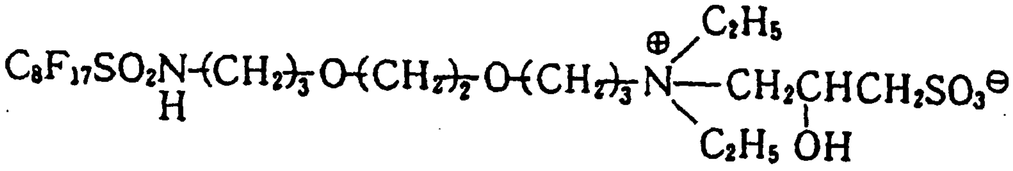
$$C_8F_{17}SO_2NHCH_2CH_2CH_2N^{\oplus}(CH_3)_2-CH_2CH_2CH_2SO_3^{\ominus}$$

B－9－c



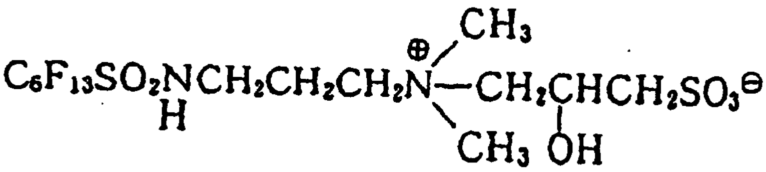
$$C_6F_{13}SO_2\underset{CH_2CH_2OH}{N}CH_2CH_2\overset{\oplus}{N}(CH_3)(CH_2CH_2OH){-}CH_2CH_2SO_3^{\ominus}$$

B－9－d



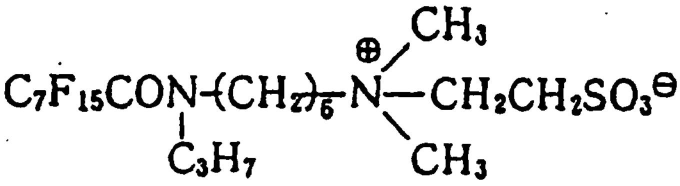
$$C_8F_{17}SO_2\underset{H}{N}{-}(CH_2)_3{-}O{-}(CH_2)_2{-}O{-}(CH_2)_3{-}\overset{\oplus}{N}(C_2H_5)(C_2H_5){-}CH_2\underset{OH}{C}HCH_2SO_3^{\ominus}$$

B－9－e



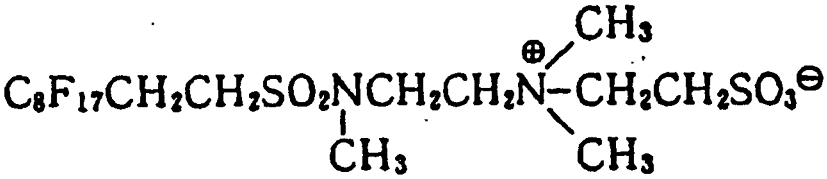
$$C_6F_{13}SO_2\underset{H}{N}CH_2CH_2CH_2\overset{\oplus}{N}(CH_3)(CH_3){-}CH_2\underset{OH}{C}HCH_2SO_3^{\ominus}$$

B－9－f



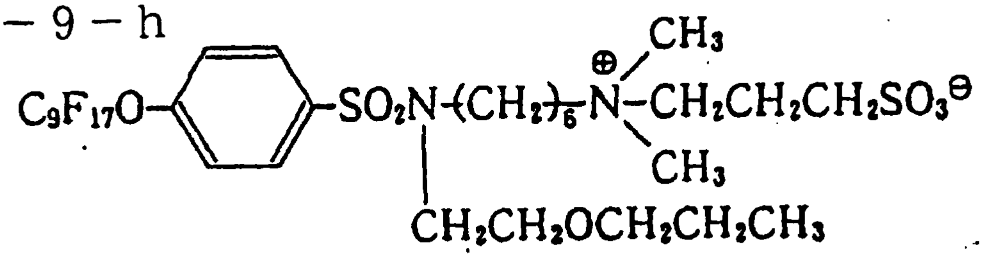
$$C_7F_{15}CO\underset{C_3H_7}{N}{-}(CH_2)_6{-}\overset{\oplus}{N}(CH_3)(CH_3){-}CH_2CH_2SO_3^{\ominus}$$

B－9－g

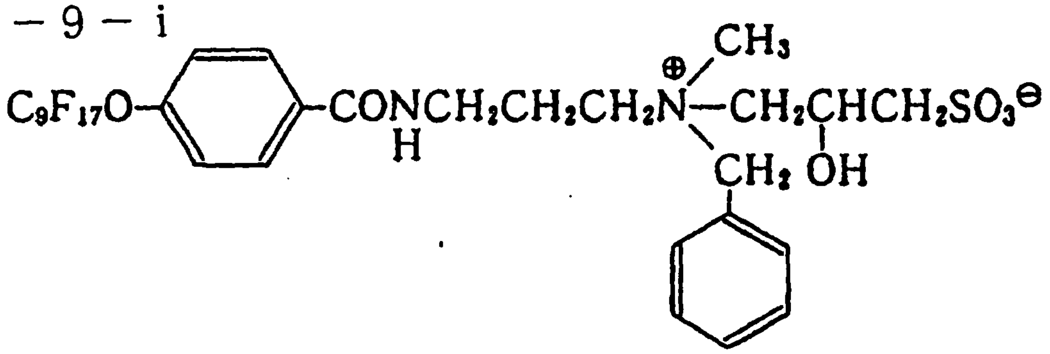


$$C_8F_{17}CH_2CH_2SO_2\underset{CH_3}{N}CH_2CH_2\overset{\oplus}{N}(CH_3)(CH_3){-}CH_2CH_2SO_3^{\ominus}$$

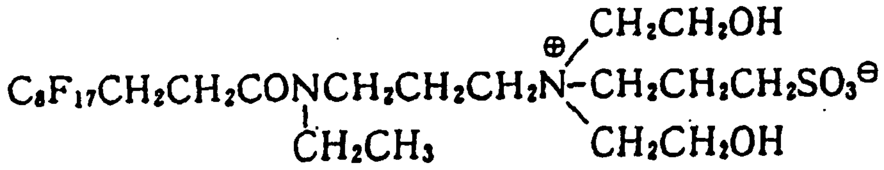
B－9－h



B − 9 − i

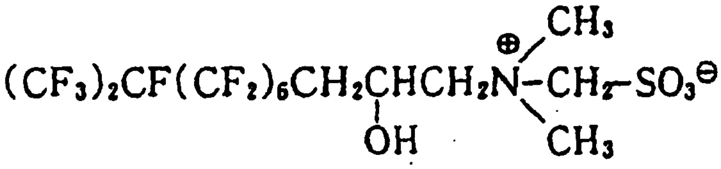


B − 9 − j



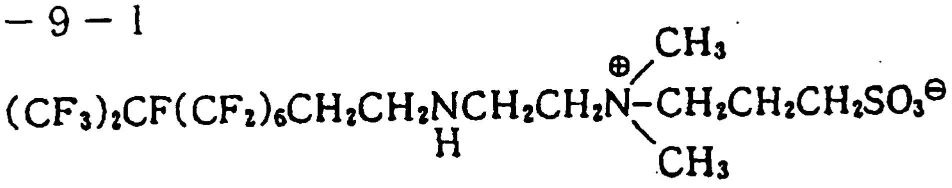
$$C_8F_{17}CH_2CH_2CON(CH_2CH_3)CH_2CH_2CH_2\overset{\oplus}{N}(CH_2CH_2OH)_2{-}CH_2CH_2CH_2SO_3^{\ominus}$$

B − 9 − k



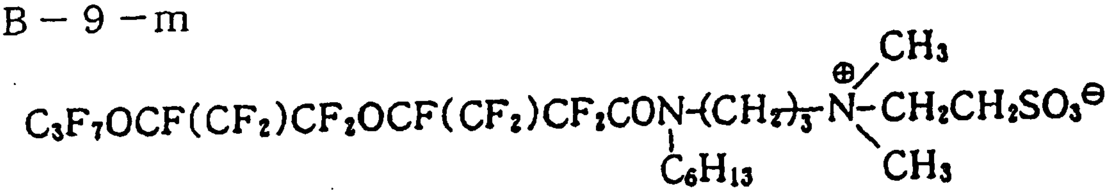
$$(CF_3)_2CF(CF_2)_6CH_2CH(OH)CH_2\overset{\oplus}{N}(CH_3)_2{-}CH_2{-}SO_3^{\ominus}$$

B − 9 − l



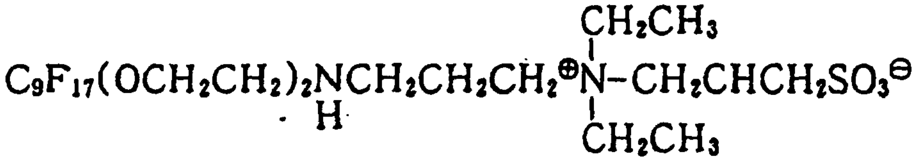
$$(CF_3)_2CF(CF_2)_6CH_2CH_2NHCH_2CH_2\overset{\oplus}{N}(CH_3)_2{-}CH_2CH_2CH_2SO_3^{\ominus}$$

B − 9 − m



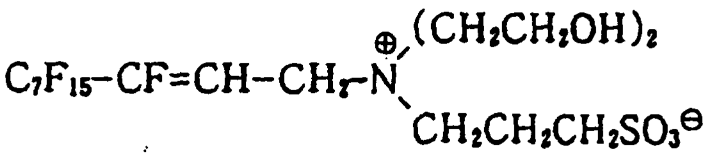
$$C_3F_7OCF(CF_2)CF_2OCF(CF_2)CF_2CON(C_6H_{13}){-}(CH_2)_3{-}\overset{\oplus}{N}(CH_3)_2{-}CH_2CH_2SO_3^{\ominus}$$

B-9-n



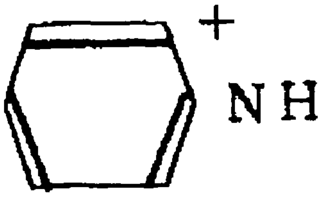
$$C_9F_{17}(OCH_2CH_2)_2\underset{H}{N}CH_2CH_2CH_2{}^{\oplus}\overset{CH_2CH_3}{\underset{CH_2CH_3}{N}}-CH_2CHCH_2SO_3{}^{\ominus}$$

B-9-o



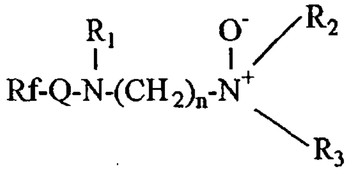
$$C_7F_{15}-CF=CH-CH_2-{}^{\oplus}N\begin{matrix}(CH_2CH_2OH)_2\\ CH_2CH_2CH_2SO_3{}^{\ominus}\end{matrix}$$

[0054] In the compounds from B-1 to B-9 described above, M_1, M_2 and M_3 each represent independently a hydrogen atom or an inorganic or an organic cation. Examples of preferred inorganic or organic cations include Li^+, Na^+, K^+, Ca^+, Mg^+, $[N(H)_s(R)_{4-s}]^+$ (where R is an alkyl group of 1 to 4 carbon atoms or a hydroxyethyl group, and s represents an integer from 0 to 4), or



In contrast, X represents an inorganic or an organic anion. Examples of preferred inorganic or organic anions include OH^-, Cl^-, Br^-, I^-, ClO_4^-, $1/2SO_4^-$, $CH_3SO_4^-$, NO_3^-, CH_3COO^- or the phosphate ion.

[0055] Furthermore, the fluorine containing amine oxide type surfactants (B-10) are compounds represented by the general formula (B-10):



$$Rf\text{-}Q\text{-}\overset{R_1}{N}\text{-}(CH_2)_n\text{-}\overset{O^-}{N^+}\begin{matrix}R_2\\ R_3\end{matrix}$$

------ B-10

(In the formula, Rf represents a fluorinated aliphatic group of 8 to 18 carbon atoms, or a fluorinated alicyclic group of 10 to 20 carbon atoms with either an ether oxygen atom or thioether linkage, Q represents $-SO_2-$ or -CO-, R_1 represents H, an alkyl group of 1 to 6 carbon atoms, a halogenated alkyl group of 1 to 6 carbon atoms, -OH, -SH, an alkoxyl group of 1 to 6 carbon atoms, a thioalkyl group of 1 to 6 carbon atoms, $-NO_2$, -CN, or NRR'- (where R and R' each represent H or an alkyl group of 1 to 6 carbon atoms), R_2 and R_3 each represent H, an alkyl group of 1 to 6 carbon atoms, a halogenated alkyl group of 1 to 6 carbon atoms, -OH, -SH, an alkoxyl group of 1 to 6 carbon atoms, a thioalkyl group of 1 to 6 carbon atoms, $-NO_2$, -CN, NRR'- (where R and R' each represent H or an alkyl group of 1 to 6 carbon atoms), or an alicyclic group which incorporates a hetero atom, an alicyclic group which does not incorporate a hetero atom, or an alicyclic group in which either the entire alicyclic ring, or a portion thereof, is substituted with alkyl groups, and finally n is an integer from 2 to 6).

[0056] Specific examples of this (B-10) compound are the compounds represented by the formulae (B-10-a) to (B-10-o) shown below, although the present invention is not limited to the compounds shown.

B-10-a $C_8F_{17}SO_2NHC_3H_6N(CH_3)_2 \rightarrow O$

B-10-b $C_{10}F_{21}SO_2NHC_3H_6N(CH_3)_2 \rightarrow O$

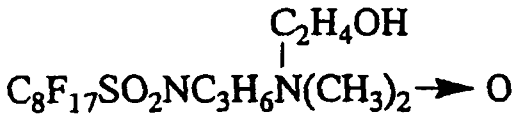
B-10-c $C_9F_{19}CONHC_3H_6N(CH_3)_2 \rightarrow O$

B-10-d $C_{11}F_{23}CONHC_3H_6N(CH_3)_2 \rightarrow O$

B-10-e $C_4F_9O[CF(CF_3)CF_2O]_2CF(CF_3)CONHC_3H_6N(CH_3)_2 \rightarrow O$

B-10-f

B-10-g



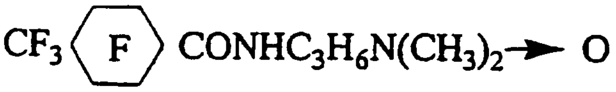
$C_8F_{17}SO_2N(C_2H_4OH)C_3H_6N(CH_3)_2 \rightarrow O$

B-10-h $C_6F_{13}SO_2NHC_3H_6N(CH_3)_2 \rightarrow O$

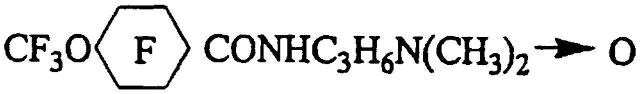
B-10-i $C_6F_{13}C_2H_4SO_2NHC_3H_6N(CH_3)_2 \rightarrow O$

B-10-j $C_7F_{15}CONHC_3H_6N(CH_3)_2 \rightarrow O$

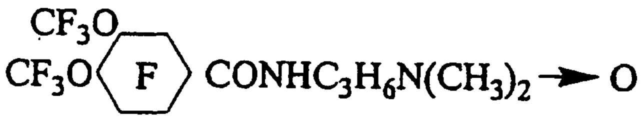
B-10-k



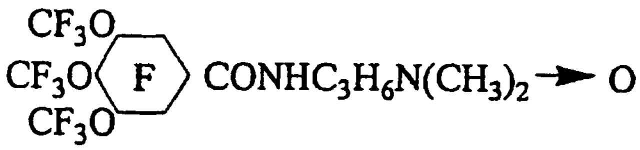
B-10-l



B-10-m



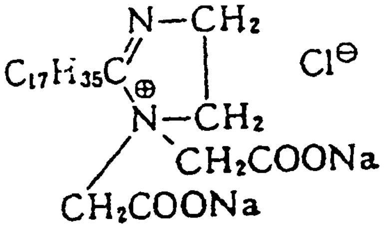
B-10-n



B-10-o $C_5F_{11}C_2H_4C(O)N(H)C_3H_6N(CH_3)_2 \rightarrow O$

[0057] Examples of surfactants (B-11) other than the surfactants (B-1) to (B-10) which are able to be used in the fire extinguishing composition of the present invention include compounds represented by the formulae (B-11-a) to (B-11-g) shown below, although the present invention is not limited to the compounds shown.

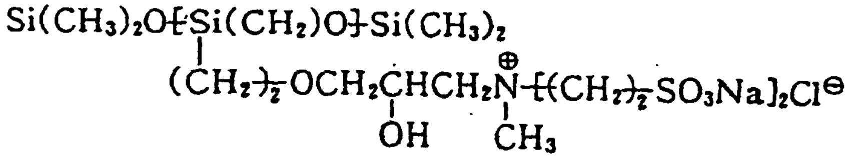
B-11-a



B-11-b $C_{11}H_{23}CONHCH_2CH_2N(CH_2COONa)_2$

B-11-c $C_{17}H_{35}CONH(CH_2)_3\overset{\oplus}{N}((CH_2)_3SO_3Na)_3Cl^{\ominus}$

B-11-d



$$\mathrm{Si(CH_3)_2O\!\left[\underset{\substack{|\\ (CH_2)_2OCH_2\underset{\substack{|\\ OH}}{C}HCH_2\overset{\oplus}{\underset{\substack{|\\ CH_3}}{N}}\!\left[(CH_2)_2SO_3Na\right]_2Cl^{\ominus}}}{Si}(CH_2)O\right]Si(CH_3)_2}$$

B-11-e	$C_8F_{17}SO_2N(C_3H_7)CH_2COOK$
B-11-f	$C_8F_{17}SO_2N(C_3H_7)CH_2CH_2SO_3Na$
B-11-g	$C_7F_{15}CON(C_3H_7)(CH_2)_3SO_3Na$

[0058] The mixing proportions of the cationic polyamine based high molecular weight compound (A) and the surfactant (B) should preferably be within a weight ratio range from 5:1 to 1:3, with ratios within a range from 3:1 to 1:1 being even more desirable.

[0059] By adding a polybasic acid compound (C) to a fire extinguishing composition of the present invention, the polybasic acid compound undergoes an electrostatic interaction with the polyethyleneimine or derivative thereof, thereby improving the flame resistance and fuel resistance of the composition even further.

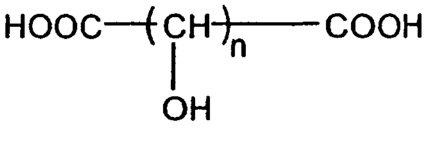
[0060] Provided the polybasic acid compound (C) is a compound which incorporates an acid group within the molecule, there are no restrictions on the type or the number of acid groups, nor on the length of the carbon chain or the molecular weight, and any compound can be used. Furthermore, such a polybasic acid compound (C) is a compound with no surfactant properties, and suitable examples include dibasic, tribasic, tetrabasic, pentabasic or hexabasic acids of 3 to 24 carbon atoms with an aromatic group, an aliphatic group or a heterocyclic ring or the like, or the alkali metal salts or ammonium salts of such acids. The acid group in the polybasic acid compound (C) may be a carboxylic acid group, a sulfonic acid group, or a phosphoric acid group or the like. Furthermore, in those cases where polybasic acid compounds are used, either a single compound, or two or more different compounds may be used in combination. Of these various polybasic acid compounds (C), dibasic acid compounds of 4 to 18 carbon atoms are particularly desirable from the viewpoint of compatibility.

[0061] Specific examples of the polybasic acid compound (C) include compounds represented by the formulae (C-1) to (C-32) shown below, as well as the alkali metal salts (Na salts, K salts, Li salts and the like) or ammonium salts thereof, although the present invention is not limited to these specific compounds.

C-1 $\mathrm{HOOC{-}\!\!\left(CH_2\right)_n\!\!{-}COOH}$

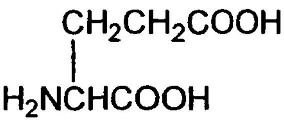
(n is an integer of 2 to 12)

C-2



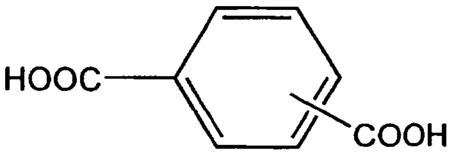
$$\mathrm{HOOC{-}\!\left(\underset{\substack{|\\ OH}}{C}H\right)_n\!{-}COOH}$$

C-3

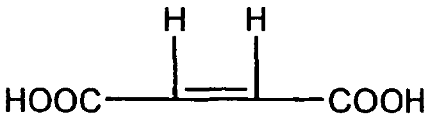


$$\mathrm{\begin{array}{l}\ \ \ \ \ \ CH_2CH_2COOH\\ \ \ \ \ \ \ |\\ H_2NCHCOOH\end{array}}$$

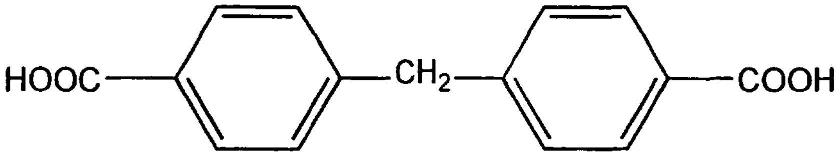
C-4



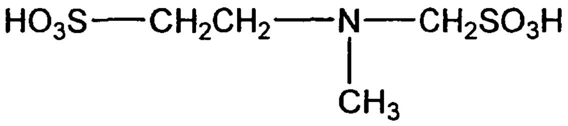
C-5



C-6

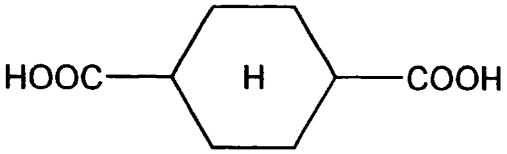


C-7

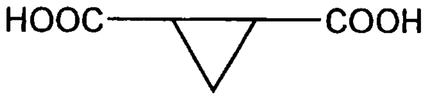


$HO_3S-CH_2CH_2-N(CH_3)-CH_2SO_3H$

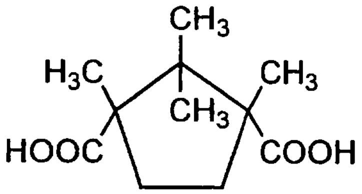
C-8



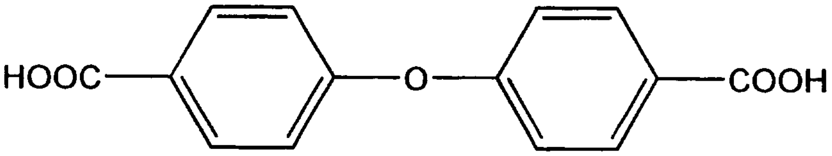
C-9



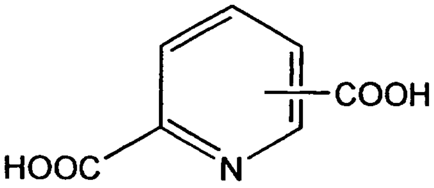
C-10



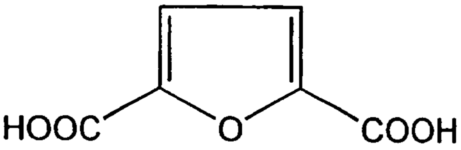
C-11



C-12



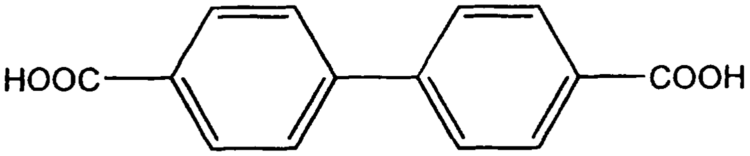
C-13



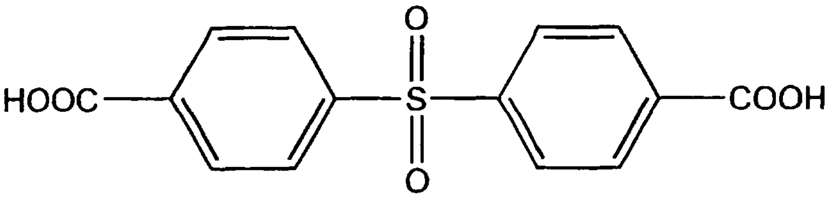
C-14 $HOOC{-}CH_2{-}O{-}CH_2{-}COOH$

C-15 $HOOC{-}CH_2{-}O{-}CH_2CH_2{-}O{-}CH_2{-}COOH$

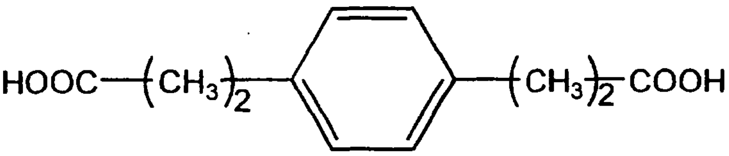
C-16



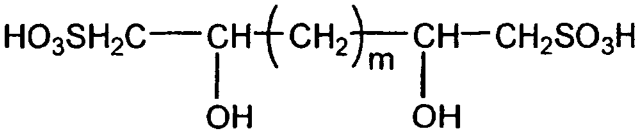
C-17



C-18



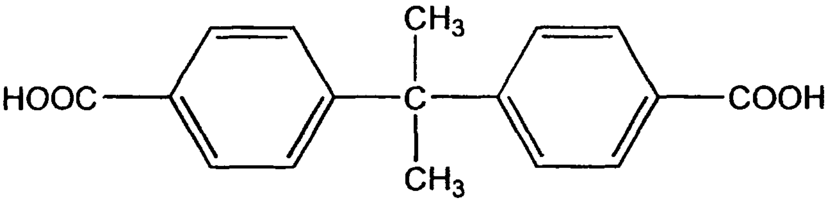
C-19



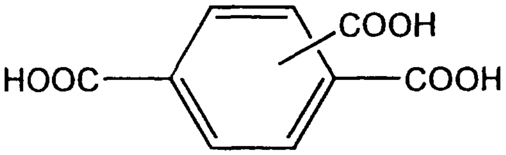
$$HO_3SH_2C-\underset{OH}{\underset{|}{CH}}-(CH_2)_m-\underset{OH}{\underset{|}{CH}}-CH_2SO_3H$$

(m is an integer of 2 of 6)

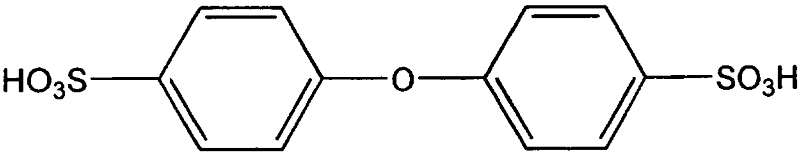
C-20



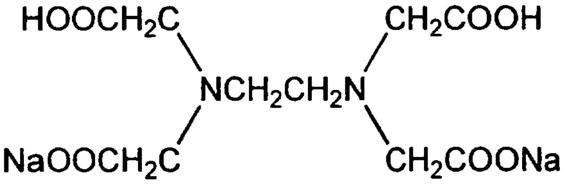
C-21



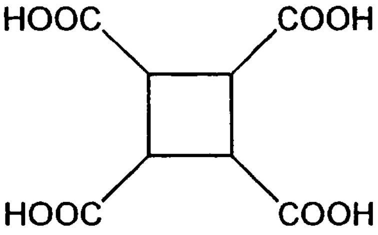
C-23



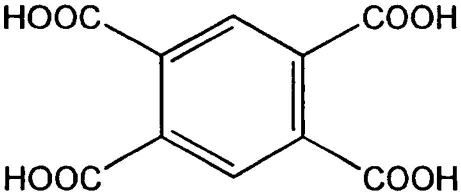
C-24



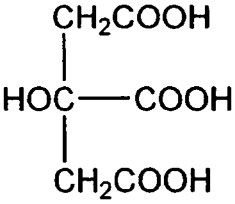
C-25



C-26

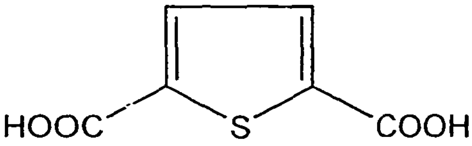


C-27



$$\begin{array}{c} CH_2COOH \\ | \\ HOC - COOH \\ | \\ CH_2COOH \end{array}$$

C-28



C-29 $HO_3S-(CH_2)_l-SO_3H$

(1 is an integer of 2 to 6)

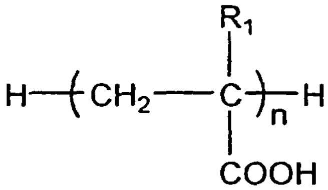
C-30 $HO_3SO-(CH_2)_p-OSO_3H$

(p is an integer of 2 to 6)

C-31 $HO_3PO-(CH_2)_q-OPO_3H$

(q is an integer of 2 to 6)

C-32



$$H\!-\!\left(CH_2-\overset{R_1}{\underset{COOH}{C}}\right)_n\!-\!H$$

(R_1 is a hydrogen atom or a methyl group, and n is an integer of 5 to 11)

[0062] The mixing proportions of the cationic polyamine based high molecular weight compound (A) and the polybasic acid compound (C) should preferably be within a weight ratio range from 5:1 to 1:3, with ratios within a range from 4:1 to 1:1 being even more desirable.

[0063] In the fire extinguishing composition of the present invention where a surfactant with an anionic hydrophilic group (B) and a polybasic acid compound (C) are included in the fire extinguishing composition of the present invention, the mixing proportions of the cationic polyamine based high molecular weight compound (A) with the surfactant with an anionic hydrophilic group (B) and the polybasic acid compound (C) will vary depending on the combination of the constituents, although typically weight ratios (B):[(A)+(C)] within a range from 2:1 to 1:50 are preferable, with ratios within a range from 1:1 to 1:10 being even more desirable. By maintaining the mixing ratio of the other constituents relative to the surfactant with an anionic hydrophilic group (B) within the above range, a water insoluble complex does not form with the surfactant with an anionic hydrophilic group (B), and so the foaming properties can be maintained. Even if the mixing ratio is greater than the above range, no marked deterioration is observed in foaming ability, flame resistance, heat resistance or fuel resistance, but by maintaining the mixing ratio within the above range, large increases in the viscosity of the fire extinguishing composition concentrate can be avoided, and corresponding reductions in the commercial value of the composition can be prevented.

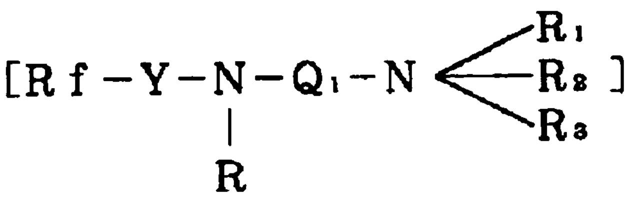
[0064] The fire extinguishing composition of the present invention displays superior solubility stability in both concentrated and diluted forms, and as such offers excellent extended storage. Furthermore, because of the superior solubility and low viscosity of the composition, a strong concentrate with a high dilution ratio can be easily manufactured. The kinematic viscosity of a concentrate with a 3% dilution ratio can be suppressed to a value of no more than 100 mm^2/s at 20°C, which results in excellent handling properties. Furthermore, because the amount of the cationic polyamine based high molecular weight compound (A) added can be kept to a reasonably small amount, little deleterious effect is observed on the performance of the composition, and the freezing point of the fire extinguishing composition concentrate can be kept below -5°C.

[0065] According to the present invention, in order to improve the fire extinguishing performance against non-polar solvents such as petroleum, a suitable amount of a surfactant (D) with a cationic hydrophilic group may also be included in the composition with the aim of effectively lowering the surface tension and the interfacial tension with petroleum of the aqueous solution of the fire extinguishing composition.

[0066] There are no restrictions on the surfactant with a cationic hydrophilic group (D) provided the surfactant incorporates a cationic hydrophilic group. Examples of the cationic hydrophilic group of the surfactant with a cationic hydrophilic group (D) include pyridinium salts, quaternary ammonium salts, imidazaolinium salts, and benzalkonium salts. Of these cationic hydrophilic groups, pyridinium salts and quaternary ammonium salts are preferred from the viewpoint of compatibility, and quaternary ammonium salts are particularly desirable. Furthermore, examples of suitable counter ions for the cationic group include organic and inorganic anions.

[0067] Examples of the hydrophobic group of the surfactant (D) include aliphatic hydrocarbon groups of 6 or more carbon atoms, dihydrocarbyl siloxane chains, or fluorinated aliphatic groups of 3 to 20 carbon atoms and preferably 6 to 16 carbon atoms. Of these surfactants (D), surfactants with fluorinated aliphatic groups are particularly desirable as they offer improved fire extinguishing performance.

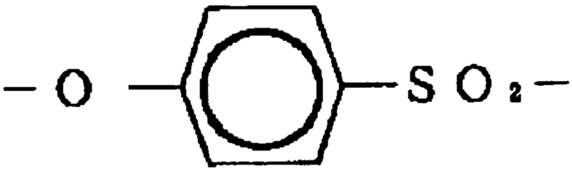
[0068] Examples of the surfactant with a cationic hydrophilic group (D) include compounds represented by the general formula (D-1):



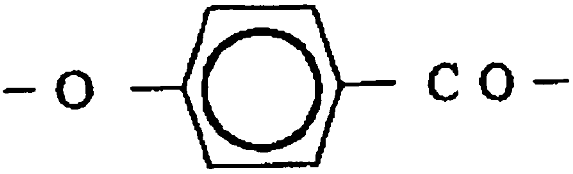
$$\left[Rf-Y-\underset{\underset{\displaystyle R}{|}}{N}-Q_1-N\begin{array}{l} R_1\\ R_2\\ R_3\end{array}\right]^{+}X^{-}$$

··· (D−1)

(In the formula, Rf represents a fluorinated aliphatic group of 3 to 20 carbon atoms which may also incorporate oxygen atoms, and Y represents a bivalent group such as $-(CH_2CH_2)_i-$, $-CH_2CH_2SCH_2COO-$, $-(CH_2CH_2)_i-SO_2-$, $-(CH_2CH_2)_i-CO-$,



or



(where i represents an integer from 1 to 6). R represents a hydrogen atom or an aliphatic hydrocarbon group of 1 to 6 carbon atoms, and Q_1 represents an aliphatic hydrocarbon group, an aliphatic hydrocarbon group substituted with a hydroxyl group, an aromatic hydrocarbon group or a substituted aromatic hydrocarbon group, although a straight chain alkylene group of 1 to 6 carbon atoms is preferred. R_1 to R_3 can represent the same group or different groups, and each represent a hydrogen atom or an aliphatic hydrocarbon group of 1 to 6 carbon atoms, and X^- represents an organic or an inorganic anion.)

[0069] In addition, a variety of additives may also be added to a fire extinguishing composition of the present invention. Such additives include additional foam stabilizers, freezing point depressants, rust prevention agents, and pH regulators and the like.

[0070] Additional foam stabilizers are mainly additives used for adjusting the expansion ratio or drainage, and suitable examples include non-ionic surfactants such as glycerin aliphatic esters, propylene glycol fatty acid esters, sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters, polyoxyethylene alkyl ethers, polyoxyethylene polyoxypropylene ethers, polyethylene glycol fatty acid esters, alkyl alkanol amides and alkyl polyglucosides; amphoteric surfactants such as betaine alkyl dimethylaminoacetate, alkyl dimethylamine oxides, alkyl carboxymethylhydroxyethyl imidazolium betaine, alkylamide propyl betaine, and alkylhydroxy sulfobetaine; as well as polyethylene glycol, polyvinyl alcohol, polyvinyl pyrrolidone, carboxymethyl cellulose, gum arabic, sodium alginate, polypropylene glycol and polyvinyl resin.

[0071] Examples of suitable freezing point depressants include ethylene glycol, propylene glycol, the cellosolve compounds (ethyl cellosolve and butyl cellosolve), caribtol compounds (ethyl carbitol, butyl carbitol, hexyl carbitol and octyl carbitol), lower alcohols (isopropyl alcohol, butanol, octanol), and urea.

[0072] Rust prevention agents and pH regulators can utilize any of the various commonly known compounds, and there are no particular restrictions.

[0073] As follows is a description of a method of using a fire extinguishing composition of the present invention.

[0074] The fire extinguishing composition of the present invention can be used as a fire extinguishing agent by using known methods for blowing in, or mixing, air, carbon dioxide, nitrogen, a low boiling point fluorocarbon such as difluorodicholoromethane, or another suitable non-flammable gas with the composition.

[0075] In other words, because the viscosity of the fire extinguishing composition concentrate of the present invention is comparatively low, a strong concentrate can be stored in a storage tank, and then at the time of use, normal methods can be used for introducing the composition into a water flow and adjusting the dilution ratio at some point before the mixture reaches a device such as a fire extinguishing apparatus or foam nozzle. Foam is then generated by blowing in, or mixing a non-flammable gas such as air, and the foam is discharged over the flame or sent under the surface of the flame. Alternatively, the composition can be prediluted to a usable concentration, and then used to fill devices such as fire extinguishers, parking lot fire extinguishing equipment, fixed fire extinguishing equipment for hazardous materials, or packaged fire extinguishing equipment.

[0076] Furthermore, examples of suitable methods for discharging the fire extinguishing composition of the present invention include the use of any of those discharge nozzles commonly used in the industry for delivering fire extinguishing compositions, and desired performance levels are able to be achieved.

[0077] Examples of suitable nozzles include the foam chamber and ISO standard compliant nozzle most widely used for petroleum tanks and the like, UL standard compliant nozzles, MIL standard compliant nozzles, hand nozzles attached to chemical fire engines and the like, air foam hand nozzles, SSI nozzles, the Japan Marine Standards Association specified HK nozzle, as well as foam heads used in driving lot fire extinguishing equipment, and spray heads and the like.

[0078] As described above, fire extinguishing compositions of the present invention can be used in a wide variety of discharge methods. Furthermore, a fire extinguishing composition of the present invention can also be applied to a wider range of fires than conventional fire extinguishing compositions. Specific examples of the use of the compositions of this invention include deployment on chemical fire engines and concentrate carrier vehicles employed by public fire fighting organizations, as well as deployment at petroleum sites or industrial sites with crude oil tanks or other hazardous material facilities, airport facilities, harbor facilities or shipping vessels involved in the loading of hazardous materials, gas stands, underground parking lots, buildings, tunnels and bridges. Furthermore, in addition to hazardous liquid material fires, the compositions can also be used on general fires such as timber fires in housing, or rubber and plastic fires such as tire fires.

[0079] In addition, because fire extinguishing compositions of the present invention display superior qualities of fuel resistance, flame resistance, heat resistance and foam forming properties, the strong concentrate or diluted aqueous solution can also be used for extinguishing cooking oil or salad oil fires by pouring directly onto the combustion surface to smother or cool the fire. Furthermore, a fire extinguishing composition of the present invention also displays superior stability of the diluted solution, and so the diluted solution can be used for filling spray cans and then used as simple household fire extinguishers.

[0080] Moreover, the foam generated from a fire extinguishing composition of the present invention is able to exist in a stable manner on aqueous solutions based on water, sol-gel type materials, sludge and pollutants, as well as various organic solvents and organic materials. Consequently, the volatilization of volatile materials from this wide range of materials can be suppressed, enabling the compositions of the present invention to also be used for preventing the ignition of flammable materials, and preventing the generation of odors.

[0081] Furthermore, the fire extinguishing compositions of the present invention may also be used in combination with powdered fire extinguishing compositions, protein based foam fire extinguishing compositions and synthetic interface foam fire extinguishing compositions comprising materials such as sodium bicarbonate, potassium bicarbonate, magnesium bicarbonate, ammonium sulfate, ammonium phosphate, and calcium carbonate.

EXAMPLES

[0082] As follows is a more detailed description of the present invention with reference to examples. In the following examples and comparative examples, all % values refer to weight percentage values.

Synthetic Example 1

[0083] In a stainless steel flask equipped with a thermometer, a nitrogen gas inlet tube, a stirrer, and a reflux condenser fitted with a dehydration tube, was placed 60 g of acetic acid, and 473 g of polyethyleneimine with a weight ratio between the primary amine, secondary amine, and tertiary amine groups of 39:45:16, and a dehydration reaction was then permitted to proceed under an atmosphere of nitrogen for 10 hours at a temperature of 180 to 240°C. Following completion of the reaction, ion exchange water was added to the reaction products to yield solid matter which was 50% by weight N-acylated polyethyleneimine (A-II-1). Analysis of the N-acylated polyethyleneimine (A-II-1) revealed that 10% of the total cationic groups had been acylated.

Synthetic Example 2

[0084] In a stainless steel flask equipped with a thermometer, a nitrogen gas inlet tube, a stirrer, and a reflux condenser fitted with a dehydration tube, was placed 60 g of acetic acid, and 473 g of polyethyleneimine with a weight ratio between the primary amine, secondary amine, and tertiary amine groups of 55:33:12, and a dehydration reaction was then permitted to proceed under an atmosphere of nitrogen for 10 hours at a temperature of 180 to 240°C. Following completion of the reaction, ion exchange water was added to the reaction products to yield solid matter which was 50% by weight N-acylated polyethyleneimine (A-II-2). Analysis of the N-acylated polyethyleneimine (A-II-2) revealed that 10% of the total cationic groups had been acylated.

Analysis Example

[0085] FIG. 1 is an NMR spectrum of a sample of a polyethyleneimine (A-I) representing the cationic polyamine based high molecular weight compound (A), which was measured using an EX-27 FT-NMR device manufactured by NEC Corporation, Ltd. The measurement conditions are listed below.

Solvent: D_2O
Measurement temperature: 28°C
Measurement mode: COM
Nucleus observed: ^{13}C
Illuminating nucleus: 1H (67.70 MHz)
Pulse width: 4.1 μs

[0086] The ratios between the primary amine, secondary amine and tertiary amine groups were calculated from the integral curve for the peaks A to G in FIG. 1, using the following formulae.

$$\text{Amount of primary amine (a)} = F+G$$

$$\text{Amount of secondary amine (b)} = (F+D/2+E)/2$$

$$\text{Amount of tertiary amine (c)} = (A+B+(C-F)/2)/3$$

$$\text{Primary amine proportion (weight \%)} = a/(a+b+c) \times 100$$

$$\text{Secondary amine proportion (weight \%)} = b/(a+b+c) \times 100$$

$$\text{Tertiary amine proportion (weight \%)} = c/(a+b+c) \times 100$$

[0087] Table 1 shows the relative proportions of primary amine, secondary amine and tertiary amine groups measured by the above method for polyethyleneimine (A-I) samples representing the cationic polyamine based high molecular weight compound (A), including "EPOMIN P-1050" manufactured by Nippon Shokubai Co. Ltd. (hereafter abbreviated as (A-I-1)), "LUPASOL P" manufactured by BASF Corporation Ltd. of Germany (and hereafter abbreviated as (A-I-2)), N-acylated polyethyleneimine (A-II-1) and (A-II-2) produced by the synthetic example 1 and the synthetic example 2 respectively, as well as derivatives thereof.

Table 1

Cationic polyamine based high molecular weight compound (A)	Primary amines	Secondary amines	Tertiary amines
A-I-1	38 % by weight	42 % by weight	20 % by weight
A-I-2	44 % by weight	33 % by weight	23 % by weight

(continued)

Cationic polyamine based high molecular weight compound (A)	Primary amines	Secondary amines	Tertiary amines
A-II-1	35 % by weight	45 % by weight	20 % by weight
A-II-2	50 % by weight	30 % by weight	20 % by weight

Examples 1 to 40

Composition

[0088]

Cationic polyamine based high molecular weight compound (A)	6%
Surfactant with an anionic hydrophilic group (B)	3%
Polybasic acid compound (C)	4%
Butyl carbitol	15%
Ethylene glycol	15%
Water	57%

[0089] A cationic polyamine based high molecular weight compound (A), a surfactant with an anionic hydrophilic group (B), and a polybasic acid compound (C) as shown in table 2 and table 3 below, were mixed together in the proportions listed above, and a small amount of 5(N) hydrochloric acid was added to adjust the pH to 7.5. The external appearance, freezing point, kinematic viscosity as measured at -10°C, and the amount of sedimentation in a 3% solution diluted with water from the water supply, for the produced fire extinguishing compositions (3% concentrates), are shown in Table 2 and Table 3 in accordance with the technical specifications listed in the Ministry of Home Affairs Ordinance No. 26.

Table 2

Example No.	(A)	(B)	(C)	External appearance	Freezing point	Kinematic viscosity	Sedimentation amount
Example 1	A-I-1	B-1-a	C-1 (n=4)	totally transparent	-19°C	126 cst	trace
Example 2	A-I-1	B-1-m	C-1 (n=4)	totally transparent	-18°C	133 cst	trace
Example 3	A-I-1	B-1-t	C-1 (n=6)	totally transparent	-17°C	132 cst	trace
Example 4	A-II-1	B-1-e	C-2	totally transparent	-17°C	100 cst	trace
Example 5	A-II-1	B-1-h	C-4	totally transparent	-17°C	144 cst	trace
Example 6	A-II-1	B-1-n	C-3	totally transparent	-18°C	122 cst	trace
Example 7	A-II-1	B-1-m	C-13	totally transparent	-16°C	119 cst	trace
Example 8	A-I-1	B-1-u	C-16	totally transparent	-19°C	136 cst	trace
Example 9	A-I-1	B-2-a	C-23	totally transparent	-18°C	140 cst	trace
Example 10	A-I-1	B-2-c	C-1 (n=4)	totally	-18°C	97 cst	trace

(continued)

Example No.	(A)	(B)	(C)	External appearance	Freezing point	Kinematic viscosity	Sedimentation amount
				transparent			
Example 11	A-I-1	B-2-j	C-24	totally transparent	-17°C	111 cst	trace
Example 12	A-I-1	B-2-o	C-31 (q=2)	totally transparent	-20°C	125 cst	trace
Example 13	A-II-1	B-2-g	C-28	totally transparent	-16°C	133 cst	trace
Example 14	A-II-1	B-2-c	C-1 (n=6)	totally transparent	-18°C	124 cst	trace
Example 15	A-II-1	B-2-c	C-16	totally transparent	-17°C	129 cst	trace
Example 16	A-II-1	B-2-k	C-10	totally transparent	-17°C	130 cst	trace
Example 17	A-I-1	B-3-i	C-17	totally transparent	-16°C	117 cst	trace
Example 18	A-II-1	B-3-d	C-7	totally transparent	-16°C	140 cst	trace
Example 19	A-I-1	B-4-b	C-1 (n=4)	totally transparent	-19°C	118 cst	trace
Example 20	A-I-1	B-4-e	C-14	totally transparent	-18°C	123 cst	trace

Table 3

Example No.	(A)	(B)	(C)	External appearance	Freezing point	Kinematic viscosity	Sedimentation amount
Example 21	A-I-1	B-4-g	C-14	totally transparent	-16°C	117 cst	trace
Example 22	A-I-1	B-5-c	C-1 (n=2)	totally transparent	-17°C	134 cst	trace
Example 23	A-I-1	B-5-i	C-10	totally transparent	-17°C	128 cst	trace
Example 24	A-I-1	B-6-d	D-1 (n=4)	totally transparent	-18°C	139 cst	trace
Example 25	A-I-1	B-6-c	C-11	totally transparent	-18°C	131 cst	trace
Example 26	A-I-1	B-6-b	C-28	totally transparent	-19°C	113 cst	trace
Example 27	A-II-1	B-6-a	C-16	totally transparent	-16°C	122 cst	trace
Example 28	A-II-1	B-6-f	C-22	totally transparent	-20°C	137 cst	trace
Example 29	A-II-1	B-6-e	C-3	totally	-18°C	140 cst	trace

(continued)

Example No.	(A)	(B)	(C)	External appearance	Freezing point	Kinematic viscosity	Sedimentation amount
				transparent			
Example 30	A-II-1	B-6-a	C-26	totally transparent	-17°C	117 cst	trace
Example 31	A-II-1	B-7-g	C-16	totally transparent	-18°C	130 cst	trace
Example 32	A-I-1	B-7-k	C-18	totally transparent	-16°C	109 cst	trace
Example 33	A-I-1	B-8-d	C-23	totally transparent	-17°C	122 cst	trace
Example 34	A-I-1	B-8-e	C-24	totally transparent	-18°C	150 cst	trace
Example 35	A-I-1	B-9-a	C-28	totally transparent	-18°C	149 cst	trace
Example 36	A-II-1	B-9-e	C-31	totally transparent	-17°C	128 cst	trace
Example 37	A-I-1	B-9-l	C-1 (n=8)	totally transparent	-17°C	134 cst	trace
Example 38	A-I-1	B-9-a	C-1 (n=4)	totally transparent	-16°C	133 cst	trace
Example 39	A-I-1	B-10-a	C-1 (n=4)	totally transparent	-18°C	162 cst	trace
Example 40	A-I-1	B-10-b	C-10	totally transparent	-19°C	169 cst	trace

[0090] In addition, fire extinguishing experiments were conducted on a non-polar solvent (a solvent for which the solubility in 100 g of water at 20°C is less than 1 g) based on the methods described in the Ministry of Home Affairs Ordinance No. 26, and the results of these experiments are shown in table 4, table 5, table 6 and table 7. Specifically, 200 L of n-heptane was used as fuel in a fire model with a combustion surface area of 4 m^2 (B-20 scale), and the precombustion period was set at 1 minute. The dilute solutions for use in the fire extinguishing experiments were generated by diluting the concentrated solutions shown in each of the examples with water by a factor of 33.3 times. Each dilute solution was then used for filling a pressurized tank with 100 liters of solution, and subsequent foam generation was carried out with a standard foam generation nozzle used for testing aqueous film forming foam fire extinguishing compositions (as per national certification), using a nitrogen pressure of 7 kg/cm^2, a discharge speed of 10 liters/minute, and a total discharge time of 5 minutes. The temperature of the dilute solution was adjusted to a value of $20°C \pm 2°C$ in each case. Experiments were conducted on the time taken for a 90% coverage of the combustion surface area (90% control time) as an indication of the relative superiority of the foam expansion speed, and the time taken for complete fire extinguishing which represents the most salient measure of fire extinguishing speed. In addition, a vapor seal experiment which acts as an indication of reignition prevention, and a burn back experiment which acts as an indication of flame resistance were also performed.

Table 4

	Diluting water used	Dilution ratio	Combustion solvent	90% control time	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment
Example 1	fresh water	3%	n-heptane	30 seconds	71	no ignition	5 cm^2
	sea water	3%	n-heptane	31 seconds	86	no ignition	20 cm^2
Example 2	fresh water	3%	n-heptane	30 seconds	78	no ignition	10 cm^2
	sea water	3%	n-heptane	36 seconds	84	no ignition	10 cm^2
Example 3	fresh water	3%	n-heptane	33 seconds	68	no ignition	6 cm^2
	sea water	3%	n-heptane	34 seconds	80	no ignition	15 cm^2
Example 4	fresh water	3%	n-heptane	31 seconds	73	no ignition	20 cm^2
	sea water	3%	n-heptane	36 seconds	79	no ignition	30 cm^2
Example 5	fresh water	3%	n-heptane	36 seconds	80	no ignition	0 cm^2
	sea water	3%	n-heptane	33 seconds	85	no ignition	0 cm^2
Example 6	fresh water	3%	n-heptane	33 seconds	73	no ignition	8 cm^2
	sea water	3%	n-heptane	37 seconds	78	no ignition	11 cm^2
Example 7	fresh water	3%	n-heptane	30 seconds	69	no ignition	0 cm^2
	sea water	3%	n-heptane	32 seconds	76	no ignition	20 cm^2
Example 8	fresh water	3%	n-heptane	31 seconds	72	no ignition	0 cm^2
	sea water	3%	n-heptane	31 seconds	78	no ignition	0 cm^2
Example 9	fresh water	3%	n-heptane	29 seconds	67	no ignition	2 cm^2
	sea water	3%	n-heptane	28 seconds	72	no ignition	3 cm^2
Example 10	fresh water	3%	n-heptane	36 seconds	80	no ignition	30 cm^2
	sea water	3%	n-heptane	34 seconds	82	no ignition	35 cm^2
Example 11	fresh water	3%	n-heptane	35 seconds	79	no ignition	0 cm^2
	sea water	3%	n-heptane	36 seconds	87	no ignition	0 cm^2
Example 12	fresh water	3%	n-heptane	30 seconds	84	no ignition	10 cm^2
	sea water	3%	n-heptane	33 seconds	88	no ignition	20 cm^2

Table 5

	Diluting water used	Dilution ratio	Combustion solvent	90% control time	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment
Example 13	fresh water	3%	n-heptane	29 seconds	73	no ignition	0 cm^2
	sea water	3%	n-heptane	28 seconds	79	no ignition	0 cm^2
Example 14	fresh water	3%	n-heptane	37 seconds	86	no ignition	10 cm^2
	sea water	3%	n-heptane	35 seconds	93	no ignition	0 cm^2
Example 15	fresh water	3%	n-heptane	35 seconds	77	no ignition	20 cm^2
	sea water	3%	n-heptane	34 seconds	81	no ignition	30 cm^2
Example 16	fresh water	3%	n-heptane	34 seconds	82	no ignition	0 cm^2
	sea water	3%	n-heptane	35 seconds	78	no ignition	0 cm^2
Example 17	fresh water	3%	n-heptane	38 seconds	90	no ignition	50 cm^2
	sea water	3%	n-heptane	39 seconds	96	no ignition	10 cm^2
Example 18	fresh water	3%	n-heptane	37 seconds	87	no ignition	0 cm^2
	sea water	3%	n-heptane	38 seconds	91	no ignition	0 cm^2
Example 19	fresh water	3%	n-heptane	29 seconds	71	no ignition	18 cm^2
	sea water	3%	n-heptane	29 seconds	74	no ignition	31 cm^2
Example 20	fresh water	3%	n-heptane	31 seconds	75	no ignition	22 cm^2
	sea water	3%	n-heptane	33 seconds	77	no ignition	0 cm^2
Example 21	fresh water	3%	n-heptane	29 seconds	70	no ignition	0 cm^2
	sea water	3%	n-heptane	28 seconds	75	no ignition	0 cm^2
Example 22	fresh water	3%	n-heptane	35 seconds	88	no ignition	45 cm^2
	sea water	3%	n-heptane	36 seconds	86	no ignition	30 cm^2
Example 23	fresh water	3%	n-heptane	33 seconds	90	no ignition	0 cm^2
	sea water	3%	n-heptane	34 seconds	93	no ignition	10 cm^2
Example 24	fresh water	3%	n-heptane	29 seconds	75	no ignition	0 cm^2
	sea water	3%	n-heptane	28 seconds	74	no ignition	0 cm^2

Table 6

	Diluting water used	Dilution ratio	Combustion solvent	90% control time	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment
Example 25	fresh water	3%	n-heptane	32 seconds	76	no ignition	20 cm^2
	sea water	3%	n-heptane	31 seconds	76	no ignition	30 cm^2
Example 26	fresh water	3%	n-heptane	35 seconds	82	no ignition	26 cm^2
	sea water	3%	n-heptane	36 seconds	90	no ignition	12 cm^2
Example 27	fresh water	3%	n-heptane	31 seconds	71	no ignition	0 cm^2
	sea water	3%	n-heptane	29 seconds	76	no ignition	0 cm^2
Example 28	fresh water	3%	n-heptane	29 seconds	74	no ignition	30 cm^2
	sea water	3%	n-heptane	28 seconds	76	no ignition	35 cm^2
Example 29	fresh water	3%	n-heptane	31 seconds	82	no ignition	10 cm^2
	sea water	3%	n-heptane	33 seconds	85	no ignition	0 cm^2
Example 30	fresh water	3%	n-heptane	31 seconds	81	no ignition	38 cm^2
	sea water	3%	n-heptane	30 seconds	87	no ignition	25 cm^2
Example 31	fresh water	3%	n-heptane	36 seconds	95	no ignition	50 cm^2
	sea water	3%	n-heptane	38 seconds	98	no ignition	60 cm^2
Example 32	fresh water	3%	n-heptane	37 seconds	97	no ignition	5 cm^2
	sea water	3%	n-heptane	35 seconds	93	no ignition	0 cm^2
Example 33	fresh water	3%	n-heptane	36 seconds	99	no ignition	0 cm^2
	sea water	3%	n-heptane	36 seconds	91	no ignition	0 cm^2
Example 34	fresh water	3%	n-heptane	31 seconds	93	no ignition	14 cm^2
	sea water	3%	n-heptane	31 seconds	92	no ignition	15 cm^2
Example 35	fresh water	3%	n-heptane	30 seconds	80	no ignition	10 cm^2
	sea water	3%	n-heptane	33 seconds	83	no ignition	30 cm^2
Example 36	fresh water	3%	n-heptane	31 seconds	80	no ignition	20 cm^2
	sea water	3%	n-heptane	33 seconds	79	no ignition	26 cm^2

Table 7

	Diluting water used	Dilution ratio	Combustion solvent	90% control time	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment
Example 37	fresh water	3%	n-heptane	29 seconds	83	no ignition	50 cm^2
	sea water	3%	n-heptane	28 seconds	85	no ignition	35 cm^2
Example 38	fresh water	3%	n-heptane	33 seconds	78	no ignition	48 cm^2
	sea water	3%	n-heptane	35 seconds	76	no ignition	25 cm^2
Example 39	fresh water	3%	n-heptane	40 seconds	102	no ignition	50 cm^2
	sea water	3%	n-heptane	39 seconds	99	no ignition	0 cm^2
Example 40	fresh water	3%	n-heptane	38 seconds	100	no ignition	60 cm^2
	sea water	3%	n-heptane	38 seconds	103	no ignition	45 cm^2

[0091] Furthermore, fire extinguishing experiments were also conducted on a polar solvent (a solvent for which the solubility in 100 g of water at 20°C is at least 1 g) based on the methods described in the Fire Fighting Hazards No. 71, and the results of these experiments are shown in table 8, table 9, table 10 and table 11. Specifically, 400 L of each solvent was used as fuel in a fire model with a combustion surface area of 4 m^2 (B-20 scale: coefficient 1), and the precombustion period was set at 1 minute. The dilute solutions for use in the fire extinguishing experiments were generated by diluting the concentrated solutions shown in each of the examples with water by a factor of 33.3 times. Each dilute solution was then used for filling a pressurized tank with 100 liters of solution, and subsequent foam generation was carried out with a standard foam generation nozzle used for testing aqueous film forming foam fire extinguishing compositions (as per national certification), using a nitrogen pressure of 7 kg/cm^2, a discharge speed of 10 liters/minute, and a total discharge time of 5 minutes. The temperature of the dilute solution was adjusted to a value of 20°C±2°C in each case. Experiments were conducted on the time taken for a 90% coverage of the combustion surface area (90% control time) as an indication of the relative superiority of the foam expansion speed (and also as a measure of the fuel resistance of the foam relative to the polar solvent), and the time taken for complete fire extinguishing which represents the most salient measure of fire extinguishing speed. In addition, a vapor seal experiment which acts as an indication of reignition prevention, and a burn back experiment which acts as an indication of flame resistance were also performed in the same manner as for the non-polar solvents described above.

Table 8

Example No.	Diluting water used	Dilution ratio	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)
Example 1	fresh water	3%	2-propanol	6.2	42	111	no ignition	65
	sea water	3%	2-propanol	6.4	44	112	no ignition	70
Example 2	fresh water	3%	2-propanol	6.3	45	115	no ignition	68
	sea water	3%	2-propanol	6.3	46	113	no ignition	75
Example 3	fresh water	3%	methanol	6.3	34	70	no ignition	10
	sea water	3%	methanol	6.3	38	65	no ignition	15
Example 4	fresh water	3%	acetone	6.2	30	81	no ignition	45
	sea water	3%	acetone	6.2	30	85	no ignition	36
Example 5	fresh water	3%	acetone	6.0	33	79	no ignition	33
	sea water	3%	acetone	6.0	33	77	no ignition	31
Example 6	fresh water	3%	propylene oxide	6.1	29	55	no ignition	20
	sea water	3%	propylene oxide	6.1	27	54	no ignition	26
Example 7	fresh water	3%	2-propanol	6.3	41	111	no ignition	75
	sea water	3%	2-propanol	6.4	45	108	no ignition	68
Example 8	fresh water	3%	acetone	6.1	30	75	no ignition	20
	sea water	3%	acetone	6.3	29	81	no ignition	18
Example 9	fresh water	3%	methanol	6.2	29	68	no ignition	14
	sea water	3%	methanol	6.3	28	62	no ignition	10
Example 10	fresh water	3%	methanol	6.1	30	74	no ignition	20
	sea water	3%	methanol	6.1	31	72	no ignition	33

Table 9

Example No.	Diluting water used	Dilution ratio	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)
Example 11	fresh water	3%	acetone	6.3	35	82	no ignition	36
	sea water	3%	acetone	6.2	38	77	no ignition	17
Example 12	fresh water	3%	methanol	5.9	26	61	no ignition	5
	sea water	3%	methanol	6.0	29	63	no ignition	14
Example 13	fresh water	3%	propylene oxide	6.4	26	57	no ignition	20
	sea water	3%	propylene oxide	6.3	24	56	no ignition	26
Example 14	fresh water	3%	2-propanol	6.2	39	119	no ignition	64
	sea water	3%	2-propanol	6.2	33	104	no ignition	62
Example 15	fresh water	3%	acetone	6.0	39	87	no ignition	40
	sea water	3%	acetone	6.0	41	81	no ignition	39
Example 16	fresh water	3%	acetone	6.3	44	90	no ignition	24
	sea water	3%	acetone	6.4	43	95	no ignition	27
Example 17	fresh water	3%	acetone	6.1	37	88	no ignition	75
	sea water	3%	acetone	6.3	34	79	no ignition	66
Example 18	fresh water	3%	2-propanol	5.8	45	131	no ignition	76
	sea water	3%	2-propanol	5.7	47	122	no ignition	80
Example 19	fresh water	3%	acetone	6.1	38	83	no ignition	33
	sea water	3%	acetone	6.1	37	80	no ignition	44
Example 20	fresh water	3%	propylene oxide	6.1	24	61	no ignition	10
	sea water	3%	propylene oxide	6.2	26	59	no ignition	11

Table 10

Example No.	Diluting water used	Dilution ratio	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Burn back Vapor seal experiment (cm^2)	
Example 21	fresh water	3%	acetone	5.9	31	94	no ignition	32
	sea water	3%	acetone	6.0	35	98	no ignition	36
Example 22	fresh water	3%	propylene oxide	6.2	24	55	no ignition	20
	sea water	3%	propylene oxide	6.2	23	54	no ignition	22
Example 23	fresh water	3%	acetone	6.1	29	82	no ignition	18
	sea water	3%	acetone	6.1	28	80	no ignition	19
Example 24	fresh water	3%	2-propanol	6.1	47	122	no ignition	55
	sea water	3%	2-propanol	6.0	44	126	no ignition	74
Example 25	fresh water	3%	methanol	6.3	25	59	no ignition	10
	sea water	3%	methanol	6.2	24	57	no ignition	13
Example 26	fresh water	3%	acetone	6.0	30	86	no ignition	33
	sea water	3%	acetone	6.0	29	83	no ignition	31
Example 27	fresh water	3%	acetone	6.1	32	85	no ignition	29
	sea water	3%	acetone	6.1	33	86	no ignition	22
Example 28	fresh water	3%	methanol	6.2	22	58	no ignition	22
	sea water	3%	methanol	6.2	23	56	no ignition	18
Example 29	fresh water	3%	2-propanol	6.5	43	119	no ignition	80
	sea water	3%	2-propanol	6.3	46	112	no ignition	68
Example 30	fresh water	3%	acetone	6.0	26	91	no ignition	40
	sea water	3%	acetone	6.0	24	98	no ignition	35

Table 11

Example No.	Diluting water used	Dilution ratio	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)
Example 31	fresh water	3%	methanol	5.7	24	89	no ignition	36
	sea water	3%	methanol	6.1	28	91	no ignition	17
Example 32	fresh water	3%	acetone	6.2	27	89	no ignition	34
	sea water	3%	acetone	6.2	29	84	no ignition	44
Example 33	fresh water	3%	methanol	6.0	27	91	no ignition	33
	sea water	3%	methanol	6.0	31	90	no ignition	32
Example 34	fresh water	3%	methanol	5.9	23	64	no ignition	13
	sea water	3%	methanol	6.2	24	67	no ignition	15
Example 35	fresh water	3%	2-propanol	6.1	45	139	no ignition	77
	sea water	3%	2-propanol	6.1	47	136	no ignition	69
Example 36	fresh water	3%	2-propanol	6.2	44	113	no ignition	77
	sea water	3%	2-propanol	6.2	45	117	no ignition	61
Example 37	fresh water	3%	2-propanol	6.2	49	131	no ignition	76
	sea water	3%	2-propanol	6.1	48	134	no ignition	71
Example 38	fresh water	3%	methanol	6.5	21	61	no ignition	22
	sea water	3%	methanol	6.4	24	69	no ignition	23
Example 39	fresh water	3%	methanol	6.3	26	76	no ignition	9
	sea water	3%	methanol	6.1	27	79	no ignition	6
Example 40	fresh water	3%	methanol	6.0	33	85	no ignition	20
	sea water	3%	methanol	6.0	31	84	no ignition	35

Experimental methods and Evaluation standards

Foam magnification:

[0092] Foam generated from an experimental standard foam generation nozzle used for testing aqueous film forming foam fire extinguishing compositions (as per national certification) was used to fill a foam collection tank (volume V: 1400 ml, weight W1 g) as prescribed in the Ministry of Home Affairs Ordinance No. 26, and the total weight (W2 g) of the foam filled collection tank was measured. The foam magnification was then calculated using the formula below.

$$\text{Expansion ratio} = \frac{V}{W2 - W1}$$

90% Control time:

[0093] This value represents the time period from commencement of the foam discharge, until 90% of the combustion surface area of the fire model (combustion surface area 4 m^2: B-20 scale) was covered with foam.

Extinguishing time:

[0094] This value represents the time period from commencement of the foam discharge until the flames on the fire model had been completely extinguished.

Vapor seal experiment:

[0095] On three occasions, namely 1 minute, 7 minutes and 11 minutes after the completion of the foam discharge, a torch was ignited and the flame brought close enough to touch the foam surface. The flame was then moved across the entire foam surface to observe whether or not the fuel would reignite.

Burn back experiment:

[0096] 15 minutes after the completion of the foam discharge, a 225 cm^2 hole was opened up in the center of the fire model, and the fuel thereunder was forcibly reignited. Five minutes after this ignition, the degree to which the combustion surface had expanded was evaluated.

Comparative Examples 1 to 21

[0097] For comparative purposes, fire extinguishing compositions (3% concentrates) were prepared using the same compositions and mixing methods as the examples described above, but with the exception that a polyethyleneimine or an N-propyl polyethyleneimine in which the amount of primary amine groups exceeds 40% and the amount of secondary amine groups is less than 35%, was used as the cationic polyamine based high molecular weight compound (A) of the present invention.

[0098] The compounds used for the cationic polyamine based high molecular weight compound (A), the surfactant with an anionic hydrophilic group (B) and the polybasic acid compound (C) are shown in table 12, together with the external appearance, freezing point, kinematic viscosity, and the amount of sedimentation in a 3% solution diluted with water from the water supply, for the produced fire extinguishing compositions (3% concentrates) carried out in accordance with the technical specifications listed in the Ministry of Home Affairs Ordinance No. 26.

[0099] In addition, fire extinguishing experiments were conducted for thixotropic water soluble high molecular weight material containing fire extinguishing compositions (incorporating a fluorine based surfactant, a commercially available product), and the results of the experiments for non-polar solvents are shown in table 13, table 14 and table 15, whereas the results of the experiments for polar solvents are shown in table 16, table 17 and table 18. In these tables the number in the right hand most column refers to the example corresponding with that particular comparative example.

Table 12

Comparative Example No.	(A)	(B)	(C)	External appearance	Freezing point	Kinematic viscosity	Sedimentation amount
1	A-I-2	B-1-a	C-1 (n=4)	totally transparent	-19°C	126 cst	0.5 v%
2	A-I-2	B-1-t	C-1 (n=6)	totally transparent	-17°C	132 cst	0.5 v%
3	A-II-2	B-1-h	C-4	totally transparent	-17°C	144 cst	0.3 v%
4	A-II-2	B-1-m	C-13	totally transparent	-16°C	119 cst	0.4 v%
5	A-I-2	B-2-a	C-23	totally transparent	-18°C	140 cst	0.5 v%
6	A-I-2	B-2-j	C-24	totally transparent	-17°C	111 cst	0.6 v%
7	A-II-2	B-2-g	C-28	totally transparent	-16°C	133 cst	0.3 v%
8	A-II-2	B-2-c	C-16	totally transparent	-17°C	129 cst	0.2 v%
9	A-I-2	B-3-i	C-17	totally transparent	-16°C	117 cst	0.5 v%
10	A-I-2	B-4-b	C-1 (n=4)	totally transparent	-19°C	118 cst	0.5 v%
11	A-I-2	B-4-g	C-14	totally transparent	-16°C	117 cst	0.5 v%
12	A-I-2	B-5-i	C-10	totally transparent	-17°C	128 cst	0.4 v%
13	A-I-2	B-6-c	C-11	totally transparent	-18°C	131 cst	0.5.%
14	A-II-2	B-6-a	C-16	totally transparent	-16°C	122 cst	0.5 v%
15	A-II-2	B-6-e	C-3	totally transparent	-18°C	140 cst	0.4 v%
16	A-II-2	B-7-g	C-16	totally transparent	-18°C	130 cst	0.3 v%
17	A-I-2	B-8-d	C-23	totally transparent	-17°C	122 cst	0.5 v%
18	A-I-2	B-9-a	C-28	totally transparent	-18°C	149 cst	0.5 v%
19	A-I-2	B-9-l	C-1 (n=8)	totally transparent	-17°C	134 cst	0.4 v%
20	A-I-2	B-10-b	C-1 (n=4)	totally transparent	-18°C	162 cst	0.5 v%
21	A-I-2	B-10-b	C-10	totally transparent	-19°C	169 cst	trace

Table 13

Comparative Example	Diluting water used	Dilution ratio	Combustion solvent	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
1	fresh water	3%	n-heptane	46	111	no ignition	100	1
	sea water	3%	n-heptane	50	127	no ignition	97	
2	fresh water	3%	n-heptane	44	119	no ignition	50	3
	sea water	3%	n-heptane	45	135	no ignition	120	
3	fresh water	3%	n-heptane	50	131	no ignition	100	5
	sea water	3%	n-heptane	48	133	no ignition	122	
4	fresh water	3%	n-heptane	41	108	no ignition	90	7
	sea water	3%	n-heptane	43	125	no ignition	80	
5	fresh water	3%	n-heptane	39	150	no ignition	90	9
	sea water	3%	n-heptane	44	177	no ignition	154	
6	fresh water	3%	n-heptane	50	164	no ignition	99	11
	sea water	3%	n-heptane	47	172	no ignition	112	
7	fresh water	3%	n-heptane	45	156	no ignition	130	13
	sea water	3%	n-heptane	43	168	no ignition	140	

Table 14

Comparative Example	Diluting water used	Dilution ratio	Combustion solvent	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
8	fresh water	3%	n-heptane	42	129	no ignition	100	15
	sea water	3%	n-heptane	44	146	no ignition	122	
9	fresh water	3%	n-heptane	53	153	no ignition	166	17
	sea water	3%	n-heptane	55	176	no ignition	177	
10	fresh water	3%	n-heptane	38	131	no ignition	188	19
	sea water	3%	n-heptane	40	148	no ignition	130	
11	fresh water	3%	n-heptane	42	120	no ignition	98	21
	sea water	3%	n-heptane	41	125	no ignition	70	
12	fresh water	3%	n-heptane	42	142	no ignition	120	23
	sea water	3%	n-heptane	45	144	no ignition	129	
13	fresh water	3%	n-heptane	37	114	no ignition	189	25
	sea water	3%	n-heptane	38	115	no ignition	150	
14	fresh water	3%	n-heptane	46	164	no ignition	123	27
	sea water	3%	n-heptane	48	152	no ignition	144	

Table 15

Comparative Example	Diluting water used	Dilution ratio	Combustion solvent	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
15	fresh water	3%	n-heptane	43	153	no ignition	118	29
	sea water	3%	n-heptane	42	160	no ignition	150	
16	fresh water	3%	n-heptane	49	180	no ignition	200	31
	sea water	3%	n-heptane	46	197	no ignition	120	
17	fresh water	3%	n-heptane	43	142	no ignition	120	33
	sea water	3%	n-heptane	48	157	no ignition	102	
18	fresh water	3%	n-heptane	45	141	no ignition	111	35
	sea water	3%	n-heptane	47	149	no ignition	122	
19	fresh water	3%	n-heptane	39	163	no ignition	167	37
	sea water	3%	n-heptane	40	174	no ignition	155	
20	fresh water	3%	n-heptane	59	181	no ignition	180	39
	sea water	3%	n-heptane	53	191	no ignition	168	
21	fresh water	3%	n-heptane	71	253	no ignition	235	
	sea water	3%	n-heptane	77	283	no ignition	250	

Table 16

Comparative Example	Diluting water used	Dilution ratio %	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
1	fresh water	3%	2-propanol	6.3	56	171	no ignition	211	1
	sea water	3%	2-propanol	6.1	59	187	no ignition	153	
2	fresh water	3%	methanol	6.2	45	114	no ignition	95	3
	sea water	3%	methanol	6.3	44	118	no ignition	75	
3	fresh water	3%	acetone	5.9	50	137	no ignition	100	5
	sea water	3%	acetone	6.1	51	142	no ignition	90	
4	fresh water	3%	2-propanol	6.2	66	205	no ignition	185	7
	sea water	3%	2-propanol	6.2	70	194	no ignition	154	
5	fresh water	3%	methanol	6.2	47	135	no ignition	99	9
	sea water	3%	methanol	6.3	46	123	no ignition	77	
6	fresh water	3%	acetone	6.3	52	143	no ignition	112	11
	sea water	3%	acetone	6.3	51	133	no ignition	123	
7	fresh water	3%	propylene oxide	6.3	41	126	no ignition	95	13
	sea water	3%	propylene oxide	6.3	42	127	no ignition	90	

Table 17

Comparative Example	Diluting water used	Dilution ratio %	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
8	fresh water	3%	acetone	6.1	50	142	no ignition	123	15
	sea water	3%	acetone	6.2	49	163	no ignition	115	
9	fresh water	3%	acetone	6.0	49	178	no ignition	203	17
	sea water	3%	acetone	6.1	50	193	no ignition	177	
10	fresh water	3%	acetone	6.0	51	135	no ignition	180	19
	sea water	3%	acetone	6.1	52	131	no ignition	175	
11	fresh water	3%	acetone	6.1	46	142	no ignition	235	21
	sea water	3%	acetone	6.0	48	139	no ignition	201	
12	fresh water	3%	acetone	6.0	44	141	no ignition	154	23
	sea water	3%	acetone	6.0	43	164	no ignition	132	
13	fresh water	3%	methanol	6.2	40	106	no ignition	94	25
	sea water	3%	methanol	6.1	41	115	no ignition	88	
14	fresh water	3%	acetone	6.0	45	139	no ignition	120	27
	sea water	3%	acetone	6.0	43	135	no ignition	116	

Table 18

Comparative Example	Diluting water used	Dilution ratio %	Combustion solvent	Foam magnification (times)	90% control time (seconds)	Extinguishing time (seconds)	Vapor seal experiment	Burn back experiment (cm^2)	Corresponding Example
15	fresh water	3%	2-propanol	6.3	53	181	no ignition	200	29
	sea water	3%	2-propanol	6.3	57	170	no ignition	185	
16	fresh water	3%	methanol	5.9	40	200	no ignition	160	31
	sea water	3%	methanol	6.0	39	216	no ignition	144	
17	fresh water	3%	methanol	5.9	41	149	no ignition	120	33
	sea water	3%	methanol	6.0	43	146	no ignition	109	
18	fresh water	3%	2-propanol	6.1	61	202	no ignition	277	35
	sea water	3%	2-propanol	6.0	58	200	no ignition	255	
19	fresh water	3%	2-propanol	6.3	58	180	no ignition	188	37
	sea water	3%	2-propanol	6.3	55	131	no ignition	164	
20	fresh water	3%	acetone	6.2	37	174	no ignition	70	39
	sea water	3%	acetone	6.2	37	169	no ignition	65	
21	fresh water	3%	2-propanol	6.2	80	*	not performed	-	
	sea water	3%	2-propanol	6.0	78	*	not performed	-	

* means the fire was not extinguished.

Claims

1. A fire extinguishing composition comprising a cationic polyamine based high molecular weight compound (A) which incorporates primary, secondary, and tertiary cationic groups within each molecule, a surfactant with an anionic hydrophilic group (B) and a polybasic acid compound (C) **characterized in that** said primary cationic groups account for no more than 40% by weight of all cationic groups.

2. A fire extinguishing composition according to claim 1, wherein secondary cationic groups in said cationic polyamine based high molecular weight compound (A) account for at least 35% by weight of all cationic groups.

3. A fire extinguishing composition according to claim 1, wherein said cationic polyamine based high molecular weight compound (A) is polyethyleneimine or a derivative thereof.

4. A fire extinguishing composition according to claim 1, wherein said polybasic acid compound (C) is a dibasic acid compound of 4 to 18 carbon atoms.

5. A fire extinguishing composition according to claim 1, wherein said surfactant with an anionic hydrophilic group (B) is a fluorine based surfactant with a fluorinated aliphatic group of 3 to 20 carbon atoms as a hydrophobic group.

6. A method for extinguishing fire, comprising the steps of providing a fire extinguishing composition according to any one of claims 1 to 5; and applying the composition to a fire.

Patentansprüche

1. Feuerlöschende Zusammensetzung, umfassend eine hochmolekulargewichtige Verbindung (A) auf der Basis von kationischem Polyamin, welche primäre, sekundäre und tertiäre kationische Gruppen in jedem Molekül enthält, ein Tensid mit einer anionischen hydrophilen Gruppe (B) und eine mehrbasige Säure-Verbindung (C), **dadurch gekennzeichnet, dass** die primären kationischen Gruppen nicht mehr als 40 Gew.-% aller kationischen Gruppen ausmachen.

2. Feuerlöschende Zusammensetzung gemäß Anspruch 1, wobei sekundäre kationische Gruppen in der hochmolekulargewichtigen Verbindung (A) auf der Basis von kationischem Polyamin wenigstens 35 Gew.-% aller kationischen Gruppen ausmachen.

3. Feuerlöschende Zusammensetzung gemäß Anspruch 1, wobei die hochmolekulargewichtige Verbindung (A) auf der Basis von kationischem Polyamin Polyethylenimin oder ein Derivat davon ist.

4. Feuerlöschende Zusammensetzung gemäß Anspruch 1, wobei die mehrbasige Säure-Verbindung (C) eine dibasige Säure-Verbindung mit 4 bis 18 Kohlenstoffatomen ist.

5. Feuerlöschende Zusammensetzung gemäß Anspruch 1, wobei das Tensid mit einer anionischen hydrophilen Gruppe (B) ein Tensid auf Fluorbasis mit einer fluorierten aliphatischen Gruppe mit 3 bis 20 Kohlenstoffatomen als eine hydrophobe Gruppe ist.

6. Verfahren zum Löschen von Feuer, umfassend die Schritte Bereitstellen einer Feuer löschenden Zusammensetzung gemäß einem der Ansprüche 1 bis 5 und Aufbringen der Zusammensetzung auf ein Feuer.

Revendications

1. Composition extinctrice d’incendie comprenant un composé de poids moléculaire élevé à base de polyamine cationique (A) qui comporte des groupes cationiques primaires, secondaires et tertiaires à l’intérieur de chaque molécule, un surfactant ayant un groupe anionique hydrophile (B) et un composé d’un acide polybasique (C), **caractérisé en ce que** les groupes cationiques primaires ne dépassent pas 40 % en poids de tous les groupes cationiques.

2. Composition extinctrice d’incendie selon la revendication 1, dans laquelle des groupes cationiques secondaires dans le composé de poids moléculaire élevé à base de polyamine cationique (A) constitue au moins 35 % en poids

des tous les groupes cationiques.

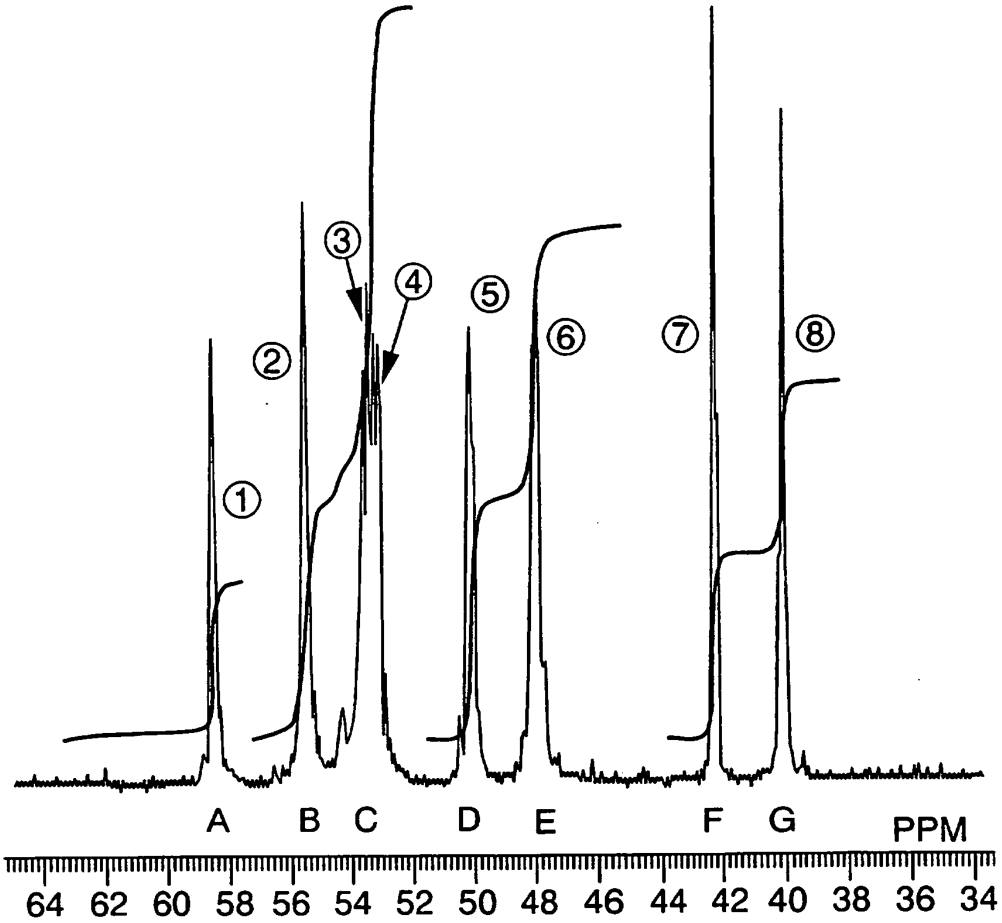
3. Composition extinctrice d'incendie selon la revendication 1, dans laquelle le composé de poids moléculaire élevé à base de polyamine cationique (A) est le polyéthylène imine ou un dérivé de celui-ci.

4. Composition extinctrice d'incendie selon la revendication 1, dans laquelle le composé d'un acide polybasique (C) est un composé d'un acide dibasique ayant de 4 à 18 atomes de carbone.

5. Composition extinctrice d'incendie selon la revendication 1, dans laquelle le surfactant ayant un groupe anionique hydrophile (B) est un surfactant à base de fluor ayant un groupe aliphatique fluoré de 3 à 20 atomes de carbone en tant qu'un groupe hydrophobe.

6. Procédé pour éteindre un incendie comprenant les étapes consistant à fournir une composition extinctrice d'incendie selon l'une quelconque des revendications 1 à 5 et appliquer la composition à l'incendie.

Fig. 1


①
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PPM
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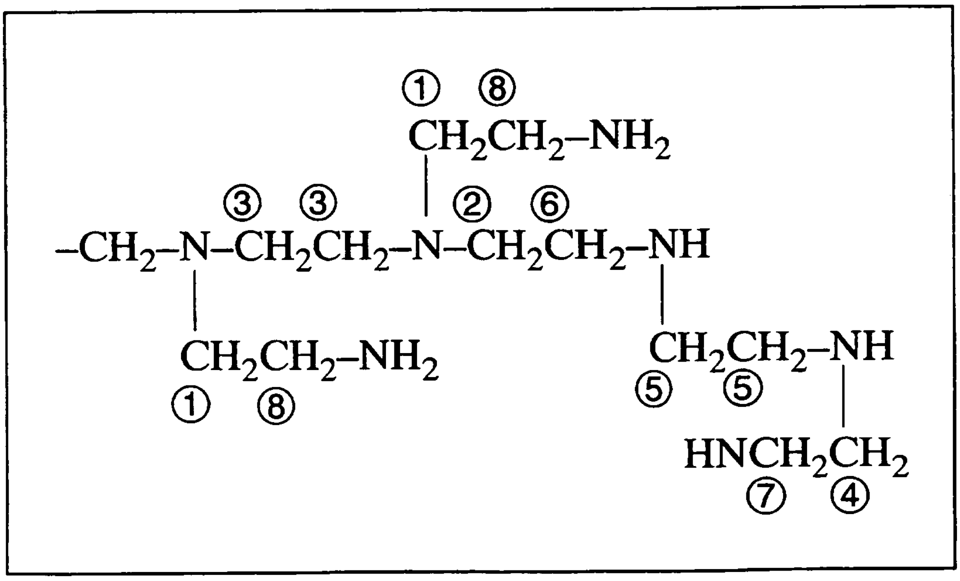
Fig. 2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③ ③ ② ⑥
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CH2CH2–NH2
① ⑧
CH2CH2–NH
⑤ ⑤
HNCH2CH2
⑦ ④

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 59230566 A **[0006]**
- US 4536298 A **[0008]**
- WO 9605889 A **[0009]**