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METHOD OF EXTINGUISHING LIQUID HYDROCARBON FIRES

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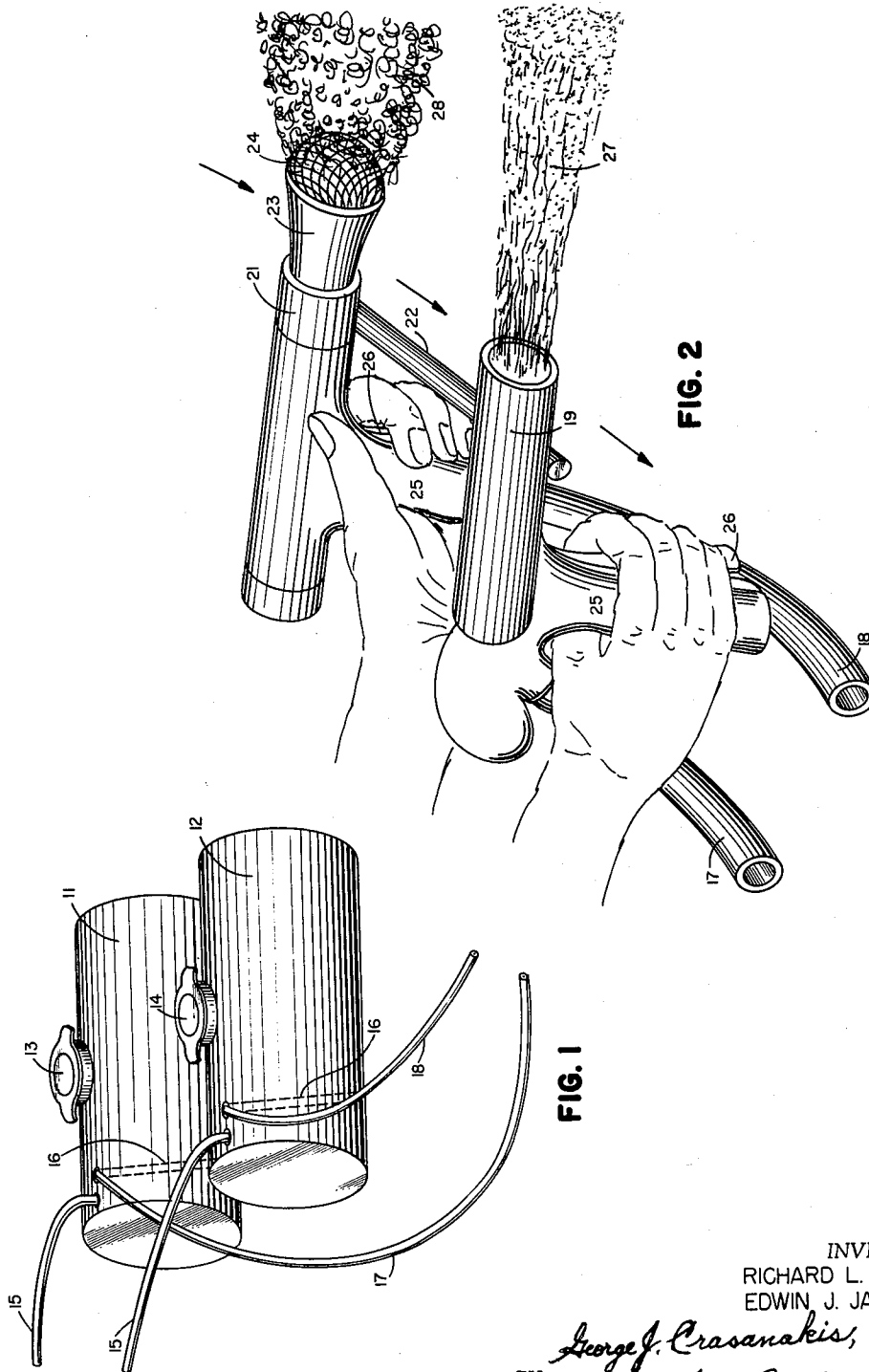


FIG. 1

FIG. 2

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**METHOD OF EXTINGUISHING LIQUID
 HYDROCARBON FIRES**

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 9 Claims. (Cl. 252-3)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to novel compositions for covering a low flash point flammable liquid to prevent ignition or reignition of the same when exposed to a nearby flame or source of ignition. More particularly, it relates to a method for using prior art fire extinguishing agents in conjunction with novel foam compositions for blanketing newly extinguished fuel surfaces which are susceptible to fire flashback.

Heretofore, finely-divided dry chemicals, such as sodium and potassium bicarbonate have been used as fire extinguishing agents due to their fast and efficient flame-suppressing ability. The superiority of potassium bicarbonate as a fire extinguishing agent over the previously employed sodium bicarbonate has been demonstrated and reported in a Naval Research Laboratory Report 5183 on August 21, 1958, by R. R. Neill. The dispersion of a finely divided mass of powder directly within the combustion zone of a flaming fuel provides rapid extinguishment of the flames, but the occurrence of flashbacks over the extinguished area is certain unless the fire has been completely extinguished and no possible source of reignition remains.

Methods have also been devised for the application of fire-fighting foams by spraying or by injecting a coherent foam blanket on the surface of a burning fuel. Stable foams which were spread in sufficient thickness over the entire burning area have been capable of resisting the heat and flame attack to suppress and smother a conflagration. Prior art foams which have been used for fire-fighting purposes were formed of proteinaceous substances, such as, keratins, albumins, globulins, hemoglobins, seed meal, etc., which were modified by hydrolysis and stabilized with salts of polyvalent metals, e.g., ferrous sulfate.

Protein foams, however, are disadvantageous for fighting hydrocarbon fires because of the heavy blanket of foam which must be spread over the entire burning surface, while any disruption of the foam barrier results in a flare-up of burning fuel. Protein foams have also been found to be adversely affected by finely-divided dry chemicals which have been treated with a silicone film; the silicone acts as a defoamer and causes the protein foam to collapse at a high rate.

Dry chemical agents are treated with a silicone surface to provide free-flowing, moisture-resistant powders, to act in the nature of a fluid, said powders being readily discharged by pressure from a hose line or nozzle.

The present invention provides novel foam compositions which have proven to be effective in extinguishing fires when utilized singly or in combination with other fire extinguishing agents. The present foam compositions display a remarkable effect in their ability to protect newly extinguished flammable fuel surfaces from possible recurrence of fire. In this respect, the novel foams have been found to be especially useful in combating fires in gasoline, naphtha, ether, benzene and other combustibles of a highly flammable vapor; they are also useful in combating fires in other hydrocarbons, which are capable under the heat conditions of a fire to give

off considerable vapor, for example, kerosene, jet fuels, diesel oils, etc.

The present foams serve the fire extinguishing process in two ways: they block the feedback of radiant energy to a fuel surface and they also prevent further release of flammable vapor after the flames have been suppressed.

The foams disclosed herein are suitably employed with dry chemical agents, in particular potassium bicarbonate powder, the foams displaying complete stability in the presence of silicone-coated powder. Moreover, foams by their very nature, enhance the extinguishing properties of KHCO_3 powder by eliminating the possibility of flashbacks. With rampart fuel fires such as those occurring at aircraft sites where a powder cloud of KHCO_3 is applied, the present foam is then sprayed on the surface of the fuel to secure the extinguishment of the fire. The foam spray will prevent flashbacks on the extinguished fuel surface while the remainder of the flames are extinguished. Thus, the chief limitation of KHCO_3 powder, because of its inability to cope with flashbacks, has now been successfully overcome as a result of the present powder-foam method of combating fires.

A further desirable effect noted in the use of the present foam compositions is based on their remarkable ability to extend their usefulness even after the air-liquid bubbles are disintegrating. The foams release a thin surface film which persists on the fuel surface and which has been found to be impervious to flammable fuel vapors. The thin film is capable of spreading over the fuel-foam interface and also over fuel areas which are not fully covered with foam. The film is quickly reformed whenever it becomes ruptured. Thus, the thin film is equally effective as the foam itself in preventing the release of fuel vapor. Previous foams cannot be utilized in this manner, for the foamy coating is somewhat transient and can be ruptured, and previous foams are therefore susceptible to reignition of fuel.

Thus, it is an object of the present invention to provide a more efficient foam composition for suppressing and extinguishing fires.

Another object of the invention is to provide a fire extinguishing technique which employs a foam to prevent flammable vapor release from a fuel surface after the flames have been suppressed.

A further object of the invention is to provide novel foam compositions that can be used effectively with any dry powder agents to effect rapid and complete extinguishment of hydrocarbon fires.

A further object of the invention resides in the formation of a water-containing film which prevents the release of flammable vapor from a hydrocarbon surface.

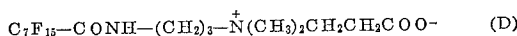
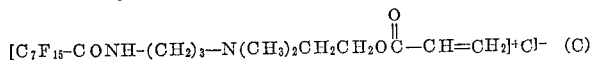
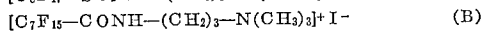
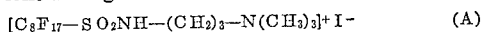
Other objects and advantages of the invention will become more fully apparent from the following detailed description and as illustrated in the accompanying sheet of drawings in which:

FIG. 1 schematically illustrates a system by which a dry powder and a foam composition are delivered to twin discharge nozzles for combating hydrocarbon fires in accordance with the teachings of the present invention; and

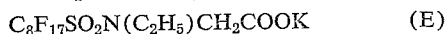
FIG. 2 is a view of the twin discharge nozzles under operating conditions.

In accordance with the present invention, novel foam compositions are formed from solutions containing therein as foaming agents one or more fluorocarbon compounds; said compositions are capable of forming a frothy mass when blown or mixed with air, Freon-12, nitrogen, or other suitable gaseous media. The fluorocarbon foam-formers of the present invention are de-

derivatives of the perfluorocarboxylic and perfluorosulfonic acids, represented by the general formula, R_fCO_2H and R_fSO_2H , respectively. In the carboxylic acid molecule, the R_f is a perfluoroalkyl chain of seven carbon atoms, C_7F_{15} —, and in the sulfonic acid molecule, the R_f is a perfluoroalkyl chain of eight carbon atoms, C_8F_{17} —. The perfluoroalkyl R_f may be a straight chain or a branched chain. Preferred fluorocarbons which are useful for the purposes of the present invention comprise the following quaternary nitrogen compounds which have in their molecular structure an intermediate amidopolymethylene linkage:



An additional fluorocarbon which is also suitable for the preparation of the present foam is the sulfonamido aliphatic acid salt represented by the formula:



The above fluorocarbon compounds provide long-chain, surface active cations and anions which have a terminal perfluoroalkyl chain that is both hydrophobic and oleophobic and therefore repellent to water and to hydrocarbons. The molecules are capable of concentrating on the surface of water or hydrocarbon fuel and form an oriented surface film with the perfluorocarbon end pointed upward.

The molecular structures (A), (B), (C) and (D) consist of an anion electrostatically united to a long chain cation, owing to the positive charge of the quaternary nitrogen atom. The molecule (D) is cationic, but it is also anionic due to the presence of the carboxylic group which is able to release hydrogen atoms in aqueous solutions. The ionized (D) molecule is amphoteric and ampholytic and thus presents both cationic and anionic properties, since both positive and negative ionization sites exist in the ion. The molecule (E) is a carboxylic acid salt, and the carboxylate group in this compound is anionic.

Other perfluoro compounds showing similar characteristics may be used as the foam formers in accordance with the invention.

When the present fluorocarbons are used in relatively small concentration in water, they are capable of forming frothy emulsions that are especially useful as fire extinguishing foams. The present fluorocarbons possess the necessary thermal and chemical stability which is essential for foam compositions. The fluorine-carbon bond provides improved stability to the molecule. The fluorine in the terminal portions renders the molecules more stable in the presence of heat. Moreover, the above molecular structures possess extraordinary activity in reducing the surface tension of solutions even when they are present in very small concentrations.

The fluorocarbon compounds are especially useful in foams which are designated as vapor-controlling or securing agents concomitant with the use of flame-suppressing dry powders. The present foams do not disintegrate nor react with a dry powder such as the Purple-K Powder (P-K-P). Purple-K Powder is a term used to designate potassium bicarbonate fire extinguishing agent which is free-flowing and easily sprayed as a powder cloud in flammable liquid and other fires.

Features of this invention relate to the water-containing film at the foam-fuel interface, and to the ability of the film to persist during and after the foam has disintegrated due to external effects. The fluorocarbon film, which retains a certain amount of water on its surface, is capable of preventing vapor release from the fuel surface. Additionally, the surface film exhibits a great

mobility and self-sealing ability and is thus capable of resealing the surface after it has been pierced. Previous fire-fighting foams provide an initial foam blanket, but once the foam layer is broken the surface is open to reflash.

The foams pertaining to this invention are prepared by forming a water solution containing the perfluoro compound in a sufficient amount when suitably acted upon to form a foamy mass. Foams of good water retention and adequate resistance to breakdown contain the perfluoro compounds in concentrations of about 0.10 to about 10% or more by weight, depending on the particular compound used for this purpose. At higher concentrations, the solutions have a tendency to gel and become stratified. Preferably, the foam compositions contain one or more of said fluorocarbon compounds in concentrations in the range of from about 0.25 to about 4% by weight of solution.

Solutions containing a perfluoro compound, for example the compound designated (A) in concentrations of 0.25% or more, will form a frothy mass by aerating with a gas, such as Freon-12 or with air to form relatively stable foams. The solutions may be readily expanded to volumes as high as 40-50, based on the ratio of air to liquid.

Freon-12 is a trade name for the low-boiling difluoro dichloro methane commonly known as a refrigerant gas.

The water content in foams determines their ability to withstand thermal shock and also their ability to spread and level off readily, consequently, volume expansion plays a very important role in providing good fire extinguishing properties. Therefore, it is preferred to employ the present foams at volume expansions of approximately 8 or 10, that provide thereby a water content of about 0.025 gal./ft.² of surface area. The lower volume expansion displays good action in flowing around and up against surfaces.

The compounds designated (A) and (D) have been found to be more effective in their ability to form resistant foams capable of protecting low flash point fuels from ignition or reignition for periods of from 5 to 10 minutes or more. Compounds (A) and (D) may be used in about 0.5% concentration to form foams of maximum stability.

Alternately, compounds (A) and (D) may be combined in a single solution in any relative amount up to 4%, but, preferably, they form foams of maximum usefulness by using equal amounts of compounds (A) and (D) in a total concentration of about 0.50%, consisting of 0.25% of (A) and 0.25% of (D) by weight of solution, based on a final foam volume expansion of 8 to 10.

Improved stability in the present foams, especially with the lower expansion foams, is obtained by means of an additive that improves the resistance of the foam to heat and its capacity to maintain its surface and liquid content. A foam improver in the form of a water-soluble polymeric material combined in solution before foaming will increase the stability of the foam. Foam improvers which may be advantageously combined in solution involve the high molecular weight polymers of ethylene oxide, polyvinyl resins, polyglycols, carboxy vinyl polymer, etc. A polymer containing between 2000-4000 units of ethylene oxide has been found to be a useful additive, imparting greater resistance to foam disintegration. A polyethylene polymer commercially available is the Polyox WSR-35 manufactured by the Union Carbide Chemical Co. Foam additives of this type are included in the foam composition in an amount in the range of from about 0.5 to 5% by weight of the final solution.

A preferred foaming composition in accordance with the invention has the following composition by weight:

Component:	Percentage
(A) -----	0.25
(D) -----	0.25
Polyox WSR-35 -----	0.50
Water -----	99.0

The above solution is blown or mixed with Freon-12 or any other gas (including air) to form a gas-liquid emulsion.

The following test procedures are illustrative of the fire extinguishing characteristics of the present foam compositions. The presence of the film barrier which forms on the fuel surface and its effective interference with the ignition and propagation of flame is hereby vividly demonstrated.

Test 1

The compound (A) is formed into a 1% aqueous solution and expanded with air to a volume of about 10. The foam is then applied as a thin layer of about ¼ inch to the surface of motor grade gasoline. The foam prevented ignition by an open flame and when ignition was finally effected only a small amount of vapor was present to permit a brief flash across the surface. Agitation with a probe disclosed that it was difficult to break open the barrier to get a sustained flame. When exposed surfaces of fuel was finally obtained, the exposed fuel would not take fire until repeated agitation in one area and then it was quickly extinguished. This test indicated the presence of a useful film that forms a surface barrier capable of suppressing fuel vaporization.

Test 2

The formation of a surface film was further demonstrated by means of a small amount of fluorescent material in the foam solution employed in Test 1. A small amount of foam containing the fluorescent material, sodium fluorescein, was placed on the surface of gasoline, and the area of foam and surrounding surface were observed under ultraviolet light. The green glow of the foam was soon observed spreading in all directions on the surface of the gasoline. As the foam began to disintegrate with time, the green glow on the surface grew larger. After the foam had completely disintegrated, the green coloration had spread out over an area many times larger than the area previously occupied by the foam.

Test 3

In a field scale test involving a 14-foot diameter gasoline fire, the presence of the film barrier along with its mobility and self-sealing ability was further demonstrated. A container lid 19 inches in diameter was placed in the gasoline fire prior to the application of foam. A foam containing about 0.5% of compound (D) was blown with air and applied to give a density of about 0.06 gallon of solution per square foot of fuel surface over the entire burning surface until the fire was extinguished. After a lapse of about one minute, a torch was brought over the opening left by the lid. The surface could not be ignited even with agitation. Gaps also occurred in the foam blanket, and the foam was subject to considerable movement by the wind. However, the open surfaces could not be ignited even with agitation proving that the surface film had formed and held together by resealing itself throughout the period in which the gasoline surface was being agitated.

The present fire extinguishing method is best disclosed by a certain illustrative embodiment which will now be described in detail.

Illustrated in FIG. 1 is a pressurized system for discharging a dry chemical and a perfluorocarbon foam of the type described herein from a dry chemical container 11 and a solution container 12; said containers may form a part of a mobile unit that can be readily dispatched to the scene of hydrocarbon fire. The dry chemical in container 11 may be potassium or sodium bicarbonate, ammonium dihydrogen phosphate or CO₂ gas under pressure. In container 12, the foam solution may consist of a mixture of the perfluoro compounds (A) and (D) in a concentration of about 0.25% of each compound and including therein a foam stabilizer, such as polyethylene polymer, and a pour point depressant, such as ethylene glycol. The dry chemical and solution are charged through

openings 13 and 14 in the respective containers. The containers are then suitably provided with means for pressuring said containers through pressure lines 15; the discharge pressure forces the contents through outlet lines 16 near the bottom of said containers.

The powder and foam are conveyed through discharge lines 17 and 18, respectively, and discharged as a spray through separate nozzles, as shown in FIG. 2. The solution is made into a foaming mass by mechanically mixing with air or other gas. More conveniently, the foam may be readily formed by adding a suitable amount of Freon liquid to discharge line 18. Upon leaving the nozzle 21, the Freon flashes into the vapor phase forming a foaming mixture 28.

Turning now to FIG. 2, the powder nozzle 19 and the foam nozzle 21 are mounted in a fixed position relative to each other on a rod holder 22. The foam nozzle 21 is equipped with a discharge tip 23, which may be the fog-foam tip SG-2559, manufactured by the Rockwood Sprinkler Corporation, said tip being rated at 50 gallons per minute at 100 p.s.i. The tip has a convex screen 24 mounted in the front to cause the foam to fan out in a wide arc upon discharge.

The dual nozzle arrangement is designed with pistol grips 25 that have trigger type shut-off valves 26 to permit an easy on-off operation with one hand on each pistol grip. The operator begins with the dry chemical discharge 27 initially and moves in a given direction. He then directs the foam discharge 28 over the area covered by the powder until the entire area is blanketed successively with dry chemical and with foam. The foam covers the area after the dry chemical has extinguished the flames.

150 square feet of gasoline fire may be extinguished with about 20 lbs. of KHCO₃ powder and 5 gallons of perfluorocarbon foam. The foam is preferably applied with a water density of 0.03 gal./ft.².

The present foams constitute essentially air-water emulsions that display a substantial capability to distribute a thin layer of water in an active film. The term "light water" has been coined to describe the present foamy mass with its active film. The oriented, surface-active film is capable of distributing a useful water content which does not drain rapidly from a hydrocarbon surface. This water-containing film with a specific gravity of nearly 1.0 is capable of floating on a hydrocarbon surface with a specific gravity of only 0.7 and to persist thereon for an extended period. A further distinction of "light water" is its ability to foam from very dilute solutions containing a small concentration of the perfluorocarbon foaming materials. The complete disintegration of these foams results essentially in water deposition containing a soluble compound.

Past experience has shown that the water content of foams is of great importance in determining their ability to withstand thermal shock. The breakdown of foam involves evaporation from the surface; it also involves drainage of liquid from the bubble wall and interstices. The retardation of foam decay is thus affected by the volume of water in the foam. A unique property of the fluorocarbon foams is that their heat resistance is not entirely related to their water content. The present foams lose their water liquid phase at a higher rate than protein foams, but they exhibit good heat resistance and vapor suppression qualities.

The present fluorocarbon composition may be formulated more conveniently as concentrates which may then be diluted with water to form the active foaming solution to generate the foam. The concentrate may also contain stabilizers and pour point depressants and other additives.

In a projected fire-fighting situation a hydrolyzed protein foam and the perfluoro, "light water" foam may be used simultaneously or successively in a single locale. The two foams may also be combined and applied as a mixed blanket of foam without adverse effects. When

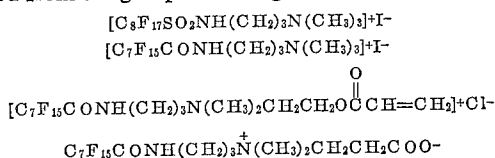
the mixed foam is employed on a fuel surface, the vapor-suppressing film of "light water" is clearly evident and equally effective in preventing reignition.

The invention therefore provides novel perfluorocarbon foams which have been found to be very advantageous in combating fuel fires, especially hydrocarbon fuel of high flammable vapor. In addition, the present invention provides an improved method for combating hydrocarbon fires by discharging a flame-suppressing dry powder and then blanketing the extinguished flames with a perfluorocarbon foam to prevent further flashbacks.

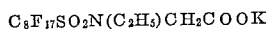
Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A method of extinguishing a liquid hydrocarbon fire which comprises covering the burning area of the liquid hydrocarbon with an aqueous foam having a non-combustible gas phase and an aqueous liquid phase which contains in solution from about 0.1 to 10% by weight thereon of a surface active fluorocarbon compound selected from the group consisting of



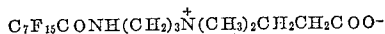
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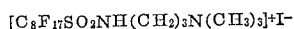
2. A method as defined in claim 1, wherein the concentration of surface active fluorocarbon compound in the aqueous liquid phase of the foam is from about 0.25 to 4% by weight thereon.

3. A method as defined in claim 2, wherein the aqueous foam has a gas to liquid volume ratio of from about 8 to 10.

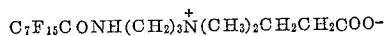
4. A method as defined in claim 3, wherein the surface active fluorocarbon compound in the aqueous liquid phase of the foam is



5. A method of extinguishing a liquid hydrocarbon fire which comprises covering the burning area of the liquid hydrocarbon with an aqueous foam having a non-combustible gas phase and an aqueous liquid phase which contains in solution about 0.25% by weight thereon of each of the surface active fluorocarbon compounds



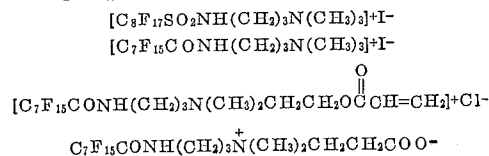
and



and the gas to liquid volume ratio thereof is about 8 to 10.

6. A method as defined in claim 5, wherein the gas phase of the aqueous foam is difluorodichloromethane.

7. A method of extinguishing a liquid hydrocarbon fire which comprises covering the burning area of the liquid hydrocarbon with a dry powder capable of extinguishing flames at the surface of the liquid hydrocarbon and in amount to extinguish said flames and immediately thereafter covering the dry powder covered area of the surface of the liquid hydrocarbon with an aqueous foam having a non-combustible gas phase and an aqueous liquid phase which contains in solution from about 0.25 to 4% by weight thereon of a surface active fluorocarbon selected from the group consisting of

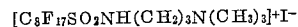


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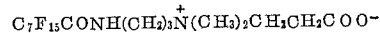


8. A method as defined in claim 7, wherein the aqueous foam contains in solution a foam stabilizer which is a water-soluble high molecular weight polymer and in a small amount sufficient to improve the thermal stability of the foam.

9. A method as defined in claim 7, wherein the dry powder is potassium bicarbonate powder and the aqueous liquid phase of the foam contains in solution about 0.25% by weight thereon of each of the surface active fluorocarbon compounds



and



and the gas to liquid volume ratio of the foam is about 8 to 10.

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