United States Patent

Rainaldi et al.

[15] **3,684,018**

[45] **Aug. 15, 1972**

[54] **FOAM-FORMING FLAME-EXTINGUISHING COMPOSITIONS CONTAINING ALKYLPOLYALKOXYSULFATES, POLYOXYETHYLENE RESIN AND SYMMETRICAL DIBROMOTETRAFLUOROETHANE**

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[21] Appl. No.: **109,620**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 827,959, May 26, 1969, Pat. No. 3,609,074, and a continuation-in-part of Ser. No. 83,603, Oct. 23, 1970.

[30] **Foreign Application Priority Data**

Jan. 27, 1970 Italy.....19827 A/70
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[52] **U.S. Cl.**.....**169/1 A,** 252/3, 252/8, 252/8.05, 252/307

[51] **Int. Cl.**.....**A62d 1/00**

[58] **Field of Search**.....252/3, 8.05, 307, 8; 169/1 A

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[57] **ABSTRACT**

A foam-forming flame-extinguishing composition containing an aqueous solution of a water soluble alkyl-polyalkoxy-sulfates, preferably in combination with a polyoxyethylene resin and advantageously, with symmetrical-dibromotetrafluoroethane.

6 Claims, No Drawings

FOAM-FORMING FLAME-EXTINGUISHING COMPOSITIONS CONTAINING ALKYLPOLYALKOXYSULFATES, POLYOXYETHYLENE RESIN AND SYMMETRICAL DIBROMOTETRAFLUOROETHANE

CROSS REFERENCE TO CO-PENDING APPLICATIONS

The present application is a continuation-in-part of our co-pending application Ser. No. 827,959 filed 26 May 1969 (now U.S. Pat. No. 3,609,074, issued 28 Sept. 1971) and a continuation-in-part of our application Ser. No. 83,603, filed 23 Oct. 1970 as a continuation-in-part of application Ser. No. 827,959.

FIELD OF THE INVENTION

Our present invention relates to foam-forming flame-extinguishing compositions and, more particularly, to flame-extinguishing compositions particularly adapted to quench, extinguish or confine fires fueled by hydrocarbons.

BACKGROUND OF THE INVENTION for

It has been proposed heretofore to extinguish fires by various techniques based generally upon exclusion of oxygen from the combustion site, abstraction of heat from the combustion site or physical elimination of the flame from a fuel substance. Considerable effort has been expended upon developing foam-forming flame-extinguishing compositions of this purpose since the foam functions as a mechanical barrier to the transport of oxygen to the combustion site, covers the fuel to prevent or limit ignition, and provides substances of high heat capacity for removal of heat from the source of combustion. For the most part, such foam-forming compositions have been found to require an aqueous medium, a foam-stabilizing or foam-producing surfactant and a propellant.

However, such foam-forming flame-extinguishing compositions have been inadequate for extinguishing fires fueled by hydrocarbons as may develop at industrial installations, refineries, tank farms and with the like, and burning hydrocarbons on water.

THE DISCLOSURE OF THE CO-PENDING APPLICATIONS

In the aforementioned co-pending applications, we have described flame-extinguishing compositions constituting improvements over the prior art systems and having greater foam stability, and ability to extinguish fires on hydrocarbons more rapidly, the capability of preventing flashback (i.e. re-ignition of a combustible substance covered by the foam) etc.

In application Ser. No. 827,959, for example, we have described a flame-extinguishing foam-forming liquid composition which contains one or more fluorobromoalkanes in addition to the substances commonly provided in flame-extinguishing foams. Such substances included water, emulsifying and foam-stabilizing surface active agents, propellants and foaming agents, antifreezing agents capable of lowering the freezing point of the composition, buffering agents, corrosion inhibitors and thickening and carrying agents. The fluorobromoalkanes which were employed,

in an amount of 5 to 25 percent by weight of the composition, were the bromine-containing halogen-saturated alkanes of low carbon number, e.g. having one to six carbon atoms in the main chain.

As pointed out in this application, best results are obtained with compounds containing at least four fluorine atoms and at least two bromine atoms per molecule and preference was given to symmetrical-dibromotetrafluoroethane, 1,2-dibromo-1,1, 2,2-tetrafluoroethane. In that application, we have also pointed out that the surface-active agents have been found to be most suitable as the organic sulfonates and sulfates, alkylarylpolyethyleneglycol ethers, esters of alcohol such as sorbitol with higher fatty acids such as lauric, stearic, palmitic acids, sodium or ammonium salts or sulfocarboxylic acids such as dialkylsulfosuccinic acid with up to eight carbon atoms in each alkyl group.

In our later application Ser. No. 83,603, we further pointed out that the composition can be improved by associating with the bromofluoroalkane a foaming agent of the ammonium alkylpolyalkoxysulfate type to produce a binary combination with the bromofluoroalkane. The binary combination, used as an aqueous solution or dispersion, provided markedly improved results. It appeared that the result is a consequence of some association of the ammonium alkypolyalkoxysulfate and the bromofluoroalkane which yields a more stable form (against heat and mechanical disruption) than is obtainable when the bromofluoroalkane is used with other foaming agents and also of greater stability than foams using the ammonium polyalkoxysulfate in association with, say, chlorofluoroalkanes in equivalent quantities. Equally surprising was the fact that the improvement was particularly marked when the fluorobromoalkane was the 1,2-dibromotetrafluoroethane mentioned earlier. Best results were found to be obtained when the foaming agent was ammoniumlaurylpolyethoxysulfate, the polyethoxy group having two to 30 ethoxy units.

OBJECTS OF THE INVENTION

It is the principal object of the present invention to provide an improved foam-forming flame-extinguishing composition capable of rapidly extinguishing flames, especially of hydrocarbon fires, with a minimum of flashback and a maximum of foam stability.

It is another object of the invention to extend the principles originally set forth in the above-mentioned co-pending applications to foam-forming flame-extinguishing compositions of an improved nature.

SPECIFIC DESCRIPTION

We have now discovered, most surprisingly, that alkylpolyalkoxysulfate in the form of water-soluble salts, constitute excellent flame-extinguishing substances in their own right, especially when dispersed as a foam upon a hydrocarbon fire. Advantageously, the alkylpolyalkoxysulfate is used as an ammonium salt, possesses ethoxy groups in a chain of two to 30 ethoxy groups and has an alkyl group with eight to 22 carbon atoms, preferably 12–14. Best results are obtained with ammoniumlaurylpolyethoxysulfate.

We have further found that ammoniumlaurylpolyethoxysulfate acts synergistically or symbiotically

with water-soluble high molecular weight polyoxyethlene resins in creating flame-extinguishing foams under the action of a blowing agent or propellant. Surprisingly, the fire-fighting properties of a water-soluble surface active substance capable of generating foam under the action of a blowing agent, especially the ammoniumalkylpolyalkoxysulfate, are greatly improved by the addition to the solution of the water-soluble high-molecular weight polyoxyethylene resin.

We have found, moreover, that the flame-extinguishing activity of a composition containing both the amoniumalkylpolyalkoxysulfate and the high molecular weight polyoxyethylene resin is improved still further by the addition of a symmetrical-dibromotetrafluoroethane as a third active component.

It is self-understood that compositions of the present invention may also contain propellants, dispersing agents and other conventional adjuvants, such as corrosion inhibitors and anti-freezing agents, in the amounts and of the type described in the aforementioned co-pending application.

A preferred subgroup of water-soluble alkylpolyalkoxysulfate is the ammonium salts of alxylpolyethoxy sulfuric acids in which the alkyl radical contains 12 to 14 atoms in the main chain and the number of ethoxy groups is two to 30 as noted earlier. Because the ammoniumalkylpolyalkoxysulfates generally have peculiar foaming characteristics, it has been found to be advantageous to use the ammonium salt of lauryltriethoxysulfate, commonly in the form of a water solution containing 10 percent by weight of the active substance.

The polyoxyethylene resin is a polymer having 7,000 to 200,000 oxyethylene units per molecule, an average molecular weight of 250,000 to 8,000,000, and a viscosity of 5,000 to 8,000 cps in an 0.5 to 5 percent aqueous solution.

The liquid composition of the present invention may comprise the three active components individually or in combination, together making up 2 to 70 percent by weight of the composition, the balance being water and adjuvants as noted earlier. When ammoniumlauryltriethoxysulfate and the polyoxyethylene are used together, they are present in a ratio by weight of 2 to 0.5 while dibromotetrafluoroethane may be employed in an amount of 3.5 to 35 times the total weight of the ammonium salt and the polyoxyethylene resin.

Preferably, the flame-extinguishing material has the following composition:

1–10 percent by weight of a 10 percent aqueous solution of lauryltriethoxysulfate;

1–10 percent by weight of a 0.5 to 5 percent aqueous solution of polyoxyethylene resin of a viscosity between 5,000 and 8,000 cps and an average molecular chain containing 7,000 to 200,000 oxyethylene units;

0–70 percent by weight 1,2-dibromotetrafluoroethane; and

10–98 percent water.

Substantially any technique may be used for dispensing the composition of the present invention. The composition may be projected onto the fire site with conventional foam-throwing apparatus to which the components of the composition are fed separately and are combined at the nozzle under the action of the propellant or blowing agent. It has been found that, for practical use in mobile fire-extinguishing installations, a mixture containing an aqueous solution of ammoniumlaurylpolyethyoxysulfate and the polyoxyethylene resin should be provided in one tank while the dibrotetrafluoroethane is supplied in another tank, the contents of the tanks being fed to the foam-projecting nozzle together with a blowing agent such as carbon dioxide or one of the other propellants set forth in the above-identified co-pending application.

SPECIFIC EXAMPLES

EXAMPLE I

A rectangular metal container 8 × 5 meters, 25 cm deep, was filled with water to a height of 10 cm; over this water layer 260 liters of gasoline and 140 liters of kerosene were poured.

The fuel was ignited and permitted to burn; after 60 seconds of precombustion, a single operator began to extinguish the fire with an aqueous foam-forming composition. The fire was completely extinguished within 60 seconds.

The extinguishing composition was a 20 percent solution of foaming agents based on ammoniumlauryl-polytriethoxysulfate, commercially known as "-METEOR-HIEX-MR-200," a trademark of Svenskaa Skumslacknings A.B.

13.8 kg of this solution was used during the extinguishing of the fire, projected from a tank of a mobile fire-extinguishing installation through a normal fireman's nozzle together with 186.2 liters of water, at a pressure of 4 atm, under blowing with air.

The expansion ratio (liters of foam generated by 1 liter of the final aqueous solution, which is now 0.6 percent by weight in ammoniumlauryltriethoxysulfate) was 1:10.

EXAMPLE II

Under the same operative conditions of Example I, after 40 seconds of precombustion, the fire was completely extinguished within 50 seconds, with a fire-extinguishing composition prepared by admixing, under blowing with air (expansion ratio 1:10) 2 volumes of an aqueous solution consisting of:

1 volume of a 20 percent aqueous solution of foaming agents based on ammoniumlaurylpolyethoxysulfate

1 volume of a 5 percent aqueous solution of a polyoxyethylene resin having the molecular weight of 250,000 to 8,000,000 and the viscosity range from 5,000 to 8,000 cPs (this solution is commercially known as "POLYOX–WRS–750", a trademark of the Union Carbide Company)

20 volumes of water.

The consumption of the aqueous solution was 4.1 liters (plus 410 liters of water).

EXAMPLE III

Example I was repeated, but with a mixture of 400 liters of gasoline and 100 liters of kerosene as the fuel. The fuel was ignited and let burn for 60 seconds; after this precombustion period, the fire was put out within 23 seconds, using the following liquid composition:

a)	1,2-dibromo-1,1,2,2-tetrafluoroethane (propelled from a separate tank of the mobile fire-fighting installation	kg16
b)	an aqueous solution	kg0.86

consisting of
1 volume of a 20% aqueous solution of foaming agents based on ammonium laurylpolyethoxysulphate
1 volume of a 5% aqueous solution of polyoxyethylene resin
(propelled from a separate tank of the mobile fire-fighting installation)

c) water kg8.6

The flame-extinguishing composition was blown under pressure with air, maintaining an expansion ratio of 1:10.

EXAMPLE IV

Example 3 was repeated.

After 60 seconds of precombustion, the following liquid composition:

a)	1,2-dibromo-1,1,2,2-tetrafluoroethane	kg8
b)	aqueous solution of the two components cited in Example III, 1:1 by volume	kg2.2
c)	water	kg22

extinguished the fire within 22 seconds (expansion ratio, as previously defined, 1:10).

EXAMPLE V

Example III was repeated.

After 60 seconds of precombustion, the fire was put out within 32 seconds using the following mixture:

a)	1,2-dibromo-1,1,2,2-tetrafluoroethane	kg24.4
b)	20% aqueous solution of foaming agents based on ammonium laurylpolyethoxysulphate	kg7.11
c)	water	kg110.

We claim:

1. A flame-extinguishing foam-forming composition comprising as active fire-extinguishing components, 1,2-dibromotetrafluoroethane, ammoniumlauryltriethoxysulfate and a polyoxyethylene resin, in aqueous solution, of an average molecular weight of 250,000 to 8,000,000.

2. The composition defined in claim 1 wherein the ratio by weight between said ammonium lauryltriethoxy-sulfate and said polyoxyethylene resin ranges between 2 and 0.5.

3. The composition defined in claim 2 wherein said polyoxyethylene resin has a viscosity in 0.5 to 5 percent aqueous solution of 5,000 to 8,000 cPs.

4. The composition defined in claim 3 wherein said polyoxyethylene resin, said ammoniumlauryltriethoxysulfate and said 1,2-dibromotetrafluoroethane are present in an amount of 2 to 70 percent by weight of the composition.

5. The composition defined in claim 4 consisting essentially of 1 to 10 percent by weight of a 10 percent aqueous solution of ammoniumlauryltriethoxysulfate, 1 to 10 percent by weight of a 0.5 to 5 percent aqueous solution of said polyoxyethlene resin, 2 to 70 percent by weight 1,2-dibromotetrafluoroethane, and 10 to 98 percent by weight water.

6. A method of extinguishing a hydrocarbon fire, comprising the step of projecting the foaming composition defined in claim 5 thereupon.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. **3,684,018** Dated **7 September 1972**

Inventor(s) **Nicolino RAINALDI et al**

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading, prior to line [22] insert

-- [73] Assignee: MONTECATINI EDISON S.p.A., Milano, ITALY --

Signed and sealed this 3rd day of April 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents