(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
05 May 2022 (05.05.2022)

WIPO | PCT

(10) International Publication Number
WO 2022/094399 A1

(51) International Patent Classification:
A62D 1/02 (2006.01) *C08G 77/452* (2006.01)
C08G 77/392 (2006.01)

(21) International Application Number:
PCT/US2021/057562

(22) International Filing Date:
01 November 2021 (01.11.2021)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/108,216 30 October 2020 (30.10.2020) US

(71) Applicant: **PERIMETER SOLUTIONS LP** [US/US]; 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US).

(72) Inventors: **HAVELKA-RIVARD, Pamela**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **CASTRO, Javier**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **SIEM, Mark**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **HUBERT, Mitch**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **PEREZ, Covadonga**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **PAULICK, Robert**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US). **KIM, Melissa**; c/o Perimeter Solutions LP, 8000 Maryland Avenue, Suite 350, St. Louis, Missouri 63105 (US).

(74) Agent: **WEGMAN, Andrew C.** et al.; Stinson LLP, 7700 Forsyth Boulevard, Suite 1100, Saint Louis, Missouri 63105 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*

WO 2022/094399 A1

(54) **Title:** FLUORINE-FREE FIREFIGHTING FOAMS CONTAINING ONE OR MORE BIOPOLYMERS

(57) **Abstract:** The present invention is directed to fluorine-free firefighting foams containing one or more biopolymers. The biopolymers of the compositions of the present invention include for example, diutan, guar, xanthan, scleroglucan, and combinations thereof.

FLUORINE-FREE FIREFIGHTING FOAMS CONTAINING ONE OR MORE BIOPOLYMERS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The present application claims priority to U.S. Provisional Patent Application No. 63/108,216, filed October 30, 2020, which is hereby incorporated by reference in its entirety for all relevant purposes.

FIELD OF THE INVENTION

[0002] The present invention is directed to fluorine-free firefighting foams containing one or more biopolymers. The biopolymers of the compositions of the present invention include for example, diutan, guar, xanthan, scleroglucan, and combinations thereof.

BACKGROUND OF THE INVENTION

[0003] Aqueous firefighting foams are used against Class B fires (i.e., fires fueled by flammable liquids). Such firefighting foams include both aqueous film-forming foams (AFFF) and alcohol-resistant aqueous film-forming foams (AR-ARFF). In recent years, due to toxicity concerns fluorine-free aqueous firefighting foams have been developed. Suitable fluorine-free foams have been developed, but opportunities exist for improvements in certain properties of the foams to provide enhanced performance. These properties include, for example, reduced foam coalescence, which provides longer drain times. The foams of the present invention are also suitable for preparing a shear thinning concentrate (e.g., having a target viscosity of from 3000 to 5000 centipoise (cps)). The fluorine-free foams of the present invention are also currently believed to provide improved polar fuel resistance, which allows for lower application rates, and are also currently believed to be highly foam forming and therefore suitable for use with non-aspirated sprinkler heads.

BRIEF SUMMARY OF THE INVENTION

[0004] Briefly, therefore, the present invention is directed to fire-fighting foam compositions for fighting Class B fires.

[0005] In various embodiments, the composition comprises diutan gum, an anionic surfactant, a zwitterionic surfactant, and an organic solvent, wherein the composition is free of fluorinated surfactants, nonionic surfactants, and fluorine-containing polymers.

[0006] In other embodiments, the composition comprises a first biopolymer, or polysaccharide selected from the group consisting of diutan gum, scleroglucan, and combinations thereof; a second biopolymer, polysaccharide selected from the group consisting of guar gum, cellulose, micro-fibrillated cellulose (MFC), and combinations thereof; and a third biopolymer, or polysaccharide selected from the group consisting of xanthan gum, rhamsam gum, gellan, and combinations thereof, wherein the composition is free of fluorinated surfactants and fluorine-containing polymers.

[0007] In further embodiments, the composition comprises a first biopolymer, or polysaccharide selected from the group consisting of diutan gum, scleroglucan, and combinations thereof; a second biopolymer, or polysaccharide selected from the group consisting of guar gum, cellulose, micro-fibrillated cellulose (MFC), and combinations thereof; and a third biopolymer, or polysaccharide selected from the group consisting of xanthan gum, rhamsam gum, gellan and combinations thereof, wherein the combined proportion of the first biopolymer (polysaccharide), second biopolymer (polysaccharide), and third biopolymer (polysaccharide) is less than about 5.0 wt.% of the composition.

[0008] In still further embodiments, the composition comprises diutan gum in a proportion of from about 0.1 to about 1.2wt.% of the composition; guar gum in a proportion of from about 0.1 to about 0.4 wt.% of the composition; xanthan gum in a proportion of from about 0.1 to about 3.5 wt.% of the composition; an anionic surfactant, wherein the anionic surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates, sulfosuccinates, and combinations thereof and is

present in a proportion of from about 0.5 to about 30 wt.% of the composition; and an organic solvent, wherein the organic solvent is selected from the group consisting of glycols, alcohols, glycol ethers, and combinations thereof and is present in a proportion of from about 0.5 to about 25 wt.% of the composition, wherein the composition is free of fluorinated surfactants.

[0009] In still other embodiments, the composition comprises one or more biopolymers selected from the group consisting of diutan gum, guar gum, xanthan gum, scleroglucan, cellulose, protein, and combinations thereof; an anionic surfactant, wherein the anionic surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates, sulfosuccinates and combinations thereof; and an organic solvent, wherein the organic solvent is selected from the group consisting of glycols, alcohols, glycol ethers and combinations thereof; wherein: the weight ratio of 20 to 28 is from about 7:1 to about 11:1; and/or the weight ratio of 4 to 32 is from about 1:1 to about 12:1.

[0010] In various of the above embodiments and other embodiments described herein, the composition further comprises water.

[0011] The present invention is further directed to methods for suppressing and/or extinguishing a Class-B fire.

[0012] Other objects and features will be in part apparent and in part pointed out hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention is directed to aqueous, fluorine-free firefighting foams containing one or more biopolymers. In accordance with the present invention it has been discovered that foams exhibiting improved performance based on selection of a particular biopolymer or a particular combination of biopolymer can be prepared. Further, it has been discovered that a lower proportion of biopolymer(s) may be utilized in the present compositions.

[0014] The firefighting compositions of the present invention include water, one or more gums, an organic solvent and one or more surfactants. Various other

additives may be included in the compositions as well. The compositions of the present invention are free from fluorine, in particular fluorine-containing surfactants and fluorinate-containing polymers.

Biopolymer(s)

[0015] The compositions of the present invention include one or more biopolymers, which serve one or more functions. One function of the biopolymer is to form vapor barriers on the surface of the fuels. They also modify viscosity of the compositions and are also shear thinning.

[0016] In accordance with the present invention it has been discovered that the selection of the biopolymer can allow for use of a relatively low proportion thereof. Typically, the total proportion of biopolymer(s) included in the composition is less than about 5 wt%, less than about 4wt%, less than about 3.5 wt%, less than about 3 wt%, or less than about 2.5 wt%. Often, the total proportion of biopolymer in the composition is from about 0.1 to about 5 wt%, from about 1 wt% to about 4 wt%, or from about 2 wt% to about 2.5 wt%.

[0017] Where containing multiple biopolymers the compositions of the present invention can be described as including a first biopolymer and a second biopolymer, or a first biopolymer, a second biopolymer, and a third biopolymer. In various embodiments each of the biopolymers is a polysaccharide, thus the composition includes a first polysaccharide, a second polysaccharide, and a third polysaccharide. Typically, each biopolymer is present in a proportion of less than about 1.5 wt% or less than about 1 wt%.

[0018] In certain embodiments, a first polysaccharide (e.g., diutan gum) is present in a proportion of from about 0.1 wt% to about 1.5 wt% (e.g., from about 0.1 wt% to about 1.2 wt%), a second polysaccharide (e.g., guar gum) is present in a proportion of from about 0.1 wt% to about 0.5 wt%. (e.g., from about 0.1 wt% to about 0.4 wt%), and a third polysaccharide (e.g., xanthan gum) is present in a proportion of from about 0.1 wt% to about 3.5 wt% (e.g., from about 0.5 wt% to about 1.5 wt%) of the composition.

[0019] Suitable biopolymers (i.e., stabilizers and/or viscosity modifiers) include alginate, acacia, agar, carrageenan, gellan gum, guar gum, inulin, konjac, locust bean gum, pectin, tara gum, alginate, carboxymethylcellulose (CMC), xanthan, carrageenan, diutan gum, gellan gum, locust bean gum, scleroglucan, chitin, modified guar gum, casein, and combinations thereof.

[0020] In certain embodiments, the composition includes one or more biopolymers selected from the group consisting of diutan, guar gum, xanthan, scleroglucan, welan gum, konjac gum, and combinations thereof. In various embodiments, the composition comprises guar gum, or a derivative thereof (e.g., hydroxypropylguar and carboxymethyl hydroxypropyl guar gum) as one of the biopolymers. In these and other embodiments, the composition may contain a cellulose biopolymer (e.g., microfibrillated cellulose, hydroxyethyl cellulose, and hydroxypropylmethyl cellulose).

[0021] Other suitable stabilizers, viscosity modifiers, and film formers include silk fibroin, gelatin, starch, cellulose, collagen, citrus fiber, whey protein, micro-fibrillated cellulose, clays, silica, and combinations thereof.

[0022] In various embodiments, the viscosity modifier or film former is selected from the group consisting of diutan gum, guar gum, xanthan gum, scleroglucan, cellulose, whey protein, and combinations thereof.

[0023] In certain embodiments, it is currently believed the particular combination of biopolymers and performance of its substituents provides performance improvements. For example, diutan gum is believed to provided improved nonpolar fuel performance, while xanthan gum forms a vapor barrier on polar fuels and the inclusion of guar gum allows for use of a lower proportion of xanthan gum. Additionally, it is currently believed that guar gum and xanthan gum interact in a synergistic fashion to improve fire extinguishment and increase burnback resistance.

Organic Solvent

[0024] Suitable organic solvents include alkyl glycols, polyols, and glycol ethers. Exemplary alkyl glycol diols include propylene glycol, butyl glycol, neopentyl

glycol, ethylene glycol, 2-methyl-2,4-pentanediol, and combinations thereof. In accordance with certain embodiments, the organic solvent is an alkyl glycol diol selected from propylene glycol, butyl glycol, ethylene glycol, and combinations thereof. In certain embodiments, the organic solvent is butyl glycol. In still further embodiments, the organic solvent is an alky glycol triol including, for example, glycerine.

[0025] Further in accordance with the present invention, the organic solvent may be a glycol ether. Suitable glycol ethers include propylene, n-butyl glycol ether, dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, dipropylene glycol phenyl ether, dipropylene glycol dimethyl ether, propylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether, dipropylene glycol methyl ether acetate, tripropylene glycol methyl ether, ethylene glycol hexyl ether; diethylene glycol hexyl ether; ethylene glycol propyl ether; diethylene glycol phenyl ether, ethylene glycol phenyl ether, poly(oxy-1,2- ethanediyl), alphaphenyl- omegahydroxy, diethylene glycol ethyl ether, diethylene glycol n-butyl ether, ethylene glycol n-butyl ether, butyl carbitol, and combinations thereof. In certain embodiments, the glycol ether is selected from the group consisting of propylene glycol, n-butyl glycol ether, butyl glycol, butyl carbitol,and combinations thereof.

[0026] In various embodiments, the organic solvent is selected from the group consisting of glycols, alcohols, glycol ethers, and combinations thereof. In certain embodiments, the compositions include two organic solvents. Suitable alcohols may include butanol and/or octanol, which may function as freeze point depressants.

[0027] Typically, the compositions contain organic solvent(s) in a proportion of at least about 10 wt%, at least about 15 wt%, or at least about 20 wt%. Often, the organic solvent(s) is present in a proportion of from about 0.5 wt% to about 30 wt%, from about 0.5 wt% to about 25 wt%, from about 10 wt% to about 25 wt% or from about 10 wt% to about 20 wt%.

Surfactants

[0028] The compositions of the present invention include one or more surfactants, typically an anionic surfactant selected from alkyl sulfates, alkyl ether sulfates (e.g., those having a degree of ethoxylation of from 1 to 3 moles), sulfosuccinates, and combinations thereof.

[0029] Suitable alkyl sulfates include sodium or amine C_8-C_{16} octyl sulfate, decyl sulfate, lauryl sulfate, sodium lauryl sulfoacetate, alpha olefin sulfonate (14-16). In various embodiments, the composition includes an alkyl sulfate selected from the group consisting of decyl sulfate, lauryl sulfate, octyl sulfate, and combinations thereof.

[0030] Suitable alkylether sulfates include sodium laureth sulfate and sodium C_8-C_{14} ammonium laureth sulfate.

[0031] Suitable sulfosuccinates include C_8-C_{16} disodium laureth sulfosuccinate, sodium dioctyl sulfosuccinate, sodium bistridecyl sulfosuccinate, disodium ethoxylated alcohol half ester of sulfosuccinic acid, sodium diisopropyl naphthalene sulfonate. In various embodiments, the composition includes a sulfosuccinate selected from sodium dioctyl sulfosuccinate and C_8-C_{16} disodium laueth sulfosuccinate.

[0032] In various embodiments, the composition includes more than one anionic surfactant, for example, one or more surfactants selected from alkyl sulfates, alkyl ether sulfates, sulfosuccinates, and combinations thereof. In certain embodiments, the composition includes decyl sulfate, and octyl sulfate, and lauryl sulfate.

[0033] Further in accordance with the present invention, the composition can include a zwitterionic surfactant selected from sultaines and betaines. Suitable sultaines include cocamidopropyl hydroxysultaine and lauramidopropyl hydroxysultaine. In certain embodiments, the composition includes cocamidopropyl hydroxysultaine. Suitable betaines include cocamidopropyl betaine, lauramidopropyl betaine, disodium lauriminodipropionate, octyliminodipropionate, and combinations thereof. In various embodiments, the composition includes more

than one zwitterionic surfactant (e.g., cocoamidopropyl hydroxysultaine and cocamidopropyl betaine). In still other embodiments, the composition comprises a C12 betaine surfactant and one of the suitable sultaine surfactants listed above.

[0034] Further in accordance with the present invention in various embodiments, the composition includes a surfactant (e.g., an anionic surfactant) while not including a nonionic surfactant. Since nonionic surfactants tend to aggregate in high saline or high electrolyte solutions, removing the nonionic surfactants is currently believed to improve the overall stability of the foam concentrates under certain conditions.

[0035] Typically, the total proportion of surfactant is at least about 5 wt%, at least about 10 wt%, or at least about 15 wt% of the composition. Often, the total proportion of surfactant is from about 0.1 wt% to about 20 wt%, from about 1 wt% to about 20 wt%, from about 5 wt% to about 20 wt% or from about 10 wt% to about 20 wt%.

Additional Components

[0036] In addition to the above components, the compositions may also include inorganic bridging ligands as a viscosity modifier. Suitable such components include magnesium sulfate, magnesium chloride, sodium chloride, potassium chloride, iron sulfate, iron chloride, and combinations thereof.

[0037] The compositions of the present invention may also include a foam stabilizer selected from C_{12}-C_{18} amines, sorbitan esters, C_4-C_{20} alcohols, polysorbates, fatty acids, and combinations thereof.

[0038] Further in accordance with the present invention, the composition may include a polyol such as a sugar alcohol selected from the group consisting of fructose, galactose, dextrose, sucrose, maltose, lactose, xylose, glucose, and combinations thereof as a foam stabilizer. In various embodiments, the polyol is selected from the group consisting of sucrose, xylose, dextrose, and combinations thereof.

[0039] Compositions of the present invention may further include a preservative (e.g., tolytriazole).

[0040] Overall, in accordance with the present invention the weight ratio of total proportion of biopolymer(s) to surfactant is from about 1:5 to about 1:10 (e.g., from about 1:7 to about to about 1:10).

[0041] The weight ratio of the total proportion of biopolymer(s) to organic solvent is typically from about 1:0.5 to about 1:1.

[0042] The weight ratio of the total proportion of biopolymer(s) to any alcohol component (e.g., as a foam stabilizer) is typically from about 1:4 to about 1:10 (e.g., from about 1:5 to about 1:10).

[0043] There are a variety of suitable water sources, including fresh water, salt water, municipal water, and brackish water. Typically, water constitutes from about 30 wt% to about 65 wt%, from about 35 wt% to about 60 wt%, or from about 40 wt% to about 55 wt% of the composition.

[0044] The compositions of the present invention are typically in the form of a concentrate and provided in equipment suitable for generation of foam. Suitable foam generating equipment includes aspirated foam generating devices, non-aspirated foam generating devices foam chambers, and sprinkler systems.

[0045] Foams of the present invention can be applied directly or indirectly to or onto a Class-B fire or directly or indirectly to or onto the fuel ahead of a potentially advancing Class-B fire front.

[0046] Having described the invention in detail, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims.

Example 1

[0047] Compositions containing one or more of xanthan, guar and/or diutan gum as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared):

Component	wt.%
Water	38-61%
Diutan	0.3-1.2%
Guar	0-0.3%

Xanthan	0.7-1.2%
Anionic C6-C18	0-7%
Anionic C9-C15 Alkyl Ether Sulfate	0-15%
Anionic C8-C12 Succinate Salt	0-2.3%
C8-C18 Zwitterionics	3-11%
C8-C18 Hydroxysultaine	0-11%
Propylene Glycol	0-22%
Diethylene Glycol Butyl Ether	0-12%
C5-C12Polyol	0-18%
C10-C16 Fatty Alcohol	0.8-1.5%
Preservative 0-0.2%	0-0.2%
Total	100.00%

Example 2

[0048] Compositions containing one or more of xanthan, guar and/or diutan gum as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared). These compositions did not contain water.

Component	wt.%
Diutan	0.7-2.1%
Guar	0-0.6%
Xanthan	0.7-2.1%
Anionic C6-C18	0-31%
Anionic C9-C15 Alkyl Ether Sulfate	0-39%
C8-C18 Hydroxysultaine	0-20%
C8-C18 Zwitterionics	0-20%
Diethylene Glycol Butyl Ether	0-10%
C10-16 Fatty Alcohol	7-9%
Total	100.00%

Example 3

[0049] Compositions containing welan gum and/or diutan gum as biopolymers including the following additional components (e.g., one or more of the

listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared).

Chemical Name	wt. %
glycol ether solvent	8-10%
Welan Gum	0-1.6%
Diutan Gum	0-0.9%
C5-C12Polyol	0-18%
C10-C18 sulfate	5-7%
Ethoxylated sulfate C8-C16	3-5%
C8-C22 Zwitterionics	0-8%
C8-C22 sultaine	0-8%
Silicon surfactant	0-3.0%
Liner or branched alcohol C8-C16	0-1.3%
Preservative	0-0.2%
Water	60-75%
Total	100.00%

Example 4

[0050] Compositions containing xanthan, diutan gum and/or konjac as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared).

Chemical Name	wt. %
glycol ether solvent	4-30%
Xanthan	0.6-2.0%
Diutan	0-0.2%
Konjac	0.1-0.5%
C10-C18 sulfate	1-15%
C8-C22 Zwitterionics	0-2%
Propylene Glycol	0-8%
Liner or branched alcohol C8-C16	0.65-1.3%
Preservative	0-0.2%

Water	25.5-68%
Total	100.00%

Example 5

[0051] Compositions containing xanthan, diutan gum, guar gum, and/or microfibrillated cellulose as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared).

Chemical Name	wt. %
glycol ether solvent	8-10%
Xanthan	0.6-2.0%
Diutan	0-0.2%
Guar	0.5-1%
Cellulose	33.5-55%
C10-C18 sulfate	0.6-2%
C8-C22 Zwitterionics	22-40%
Propylene Glycol	8-15%
Liner or branched alcohol C8-C16	0.65-1.35%
Preservative	0-0.2%
Water	25.5-68%
Total	100.00%

Example 6

[0052] Compositions containing diutan gum, hydroxyethyl cellulose and/or hydroxypropylmethyl cellulose as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared).

Chemical Name	wt. %
glycol solvents	12-22%
Glycerine	0-15
Diutan	0-0.7%
Cellulose	0.22-1.3%
Linear alcohol C12	1.35%
C8-C12 alkylsulfate	1.4-2.1%

C12 Zwitterionics	18 %
Preservative	0-0.2%
Water	50-70
Total	100.00%

Example 7

[0053] Compositions containing diutan gum, hydroxyethyl cellulose and/or hydroxypropylmethyl cellulose as biopolymers including the following additional components (e.g., one or more of the listed surfactant(s) at the listed concentration(s) in accordance with the following were prepared).

Chemical Name	wt. %
glycol solvents	14-16%
Diutan	0.5-0.62%
Cellulose	0.08-0.2%
Linear alcohol C12	1.35%
C8-C12 alkylsulfate	2.1%
C12 Zwitterionics	18 %
Preservative	0-0.2%
Water	50-70
Total	100.00%

Example 8

[0054] The following Example provides First Test Data for compositions of the present invention.

Formulation	Fuel	Water Type	Flow Rate	Expansion	25% Drain Time	90% Control	99% Control	Extinguishment	BurnBack
			GPM		(min:sec)	(min:sec)	(min:sec)	(min:sec)	(min:sec)
65R	Heptane	Fresh	3.0	7.1	21:45	1:01	1:43	2:18	--- Fail
65R	IPA	Fresh	7.4	6.9	20:50	1:40	2:50	3:15	SE @ 3 sec
2020-01-119	Heptane	Fresh	3.0	6.3	105:60	1:15	1:40	2:19	SE @15 sec
2020-01-119	Methanol	Fresh	3.0	7.2	68:24	1:03	2:10	3:40	SE @ 3 sec
2020-01-119	IPA	Fresh	5.0	7.0	123:60	2:28	3:31	4:06	SE @ 8 sec
2020-01-119/132	IPA	Fresh	7.2	6.5	96:32	1:23	2:20	2:33	SE @ 3 sec
2020-01-119/132	IPA	Fresh	5.0	7.0	123:60	2:28	3:31	4:06	SE @ 8 sec
2020-01-119A	IPA	Fresh	5.0	7.4	67:15	2:28	3:31	4:06	Pass 10% @ 5 min
2020-01-132	Heptane	Fresh	3.0	6.6	74:10	1:04	1:25	1:50	SE @ 21 sec
2020-01-140	Heptane	Fresh	3.0	6.9	29:51	1:07	1:40	1:50	Fail @ 2:30
2020-01-141	Heptane	Fresh	3.0	7.3	45:00	1:03	1:50	2:03	Fail @ 4:30
2020-01-142	Heptane	Fresh	3.0	7.2	61:43	1:02	1:35	1:45	SE @ 23 sec
2020-01-142	IPA	Fresh	5.0	7.1	60:48	2:10	3:45	4:05	Pass 5% @ 5 min

2020-01-213 Series

Formulation	Fuel	Water Type	Flow Rate	Expansion	25% Drain Time	90% Control	99% Control	Extinguishment	BurnBack
			GPM		(min:sec)	(min:sec)	(min:sec)	(min:sec)	(min:sec)
2020-01-213	Heptane	Fresh	3.0	6.0	8:35				
2020-01-213	IPA	Fresh	5.0	7.1	24:30	3:05	4:31	5:41	---
2020-01-216A	Heptane	Fresh	3.0	7.3	25:30	1:08	1:25	1:58	---
2020-01-216A	IPA	Fresh	5.0	7.5	35:30	---	---	---	---
2020-01-249	Heptane	Fresh	3.0	7.3	25:30	1:02	1:30	1:50	SE @ 26 sec
2020-01-251	Heptane	Fresh	3.0	6.5	53:30	1:10	1:16	1:55	SE @ 41 sec
2020-01-255	Heptane	Fresh	3.0	6.5	53:30	0:54	1:18	1:36	SE@ 23 sec
2020-01-255	IPA	Fresh	6.2	7.2	64:10	2:15	3:21	4:06	Pass 10% @ 5 min
2020-01-277	Heptane	Fresh	3.0	7.0	57:17	1:03	1:32	2:00	Pass 15% @ 5 min
2020-01-277	IPA	Fresh	6.0	6.1	43:48	1:58	2:29	3:41	Pass 2% @ 5 min
2020-01-290/A108	Heptane	Fresh	3.0	7.0	66:30	1:00	1:30	1:59	SE @ 21 sec
2020-01-290/A108	IPA	Fresh	6.0						

80-10 Series

Formulation	Fuel	Water Type	Flow Rate	Expansion	25% Drain Time	90% Control	99% Control	Extinguishment	BurnBack
80-10	Heptane	Fresh	3.0	6.9	123:08	1:10	1:30	1:45	SE @ 11 sec
80-10	Heptane	Salt	3.0	6.2	96:06	1:02	1:30	1:43	SE @ 10 sec
80-10F	IPA	Fresh	5.5	8.5	110:10	3:10	5:00	5:45	--
80-10F	IPA	Salt	5.5	5.5	65:50	3:00	4:40	5:45	--
80-10F	IPA	Fresh	6.0	8.5	90:10	3:10	3:35	3:50	Pass 6% @ 5 min
80-10F	IPA	Salt	6.0	5.5	65:50	2:30	3:40	4:18	Pass 17% @5 min

Sprinkler Testing

Formulation	Fuel	Grid	Flow Rate	K factor	Application Rate	90% Control	99% Control	Extinguishment	Burnback
			GPM			(min:sec)	(min:sec)	(min:sec)	(min:sec)
2020-01-213	Heptane	UL	96.0	11.2	0.16		5:00	Failed	
2020-01-213	Heptane	UL	180.0	11.2	0.3	1:45	1:55	2:00	Fail Deluge
2020-01-213	IPA	UL	260.0	11.2	0.4	3:15	3:25	3:30	SE @ 5 sec
2020-01-213	Heptane	FM	160.0	11.2	0.4	1:20	1:30	1:45	Fail Deluge
2020-01-213	IPA	FM	160.0	11.2	0.4	1:30		Failed	
2020-01-213	IPA	FM	240.0	11.2	0.6	1:30	1:55	2:10	SE @ 5 sec
2020-01-255	Heptane	FM	120.0	11.2	0.3	4:55		Failed	
2020-01-255	IPA	FM	200.0	11.2	0.5	2:30	2:55	2:58	SE @ 2 sec
80-10F	Heptane	FM	120.0	8.0	0.3	1:30	1:55	2:02	Fail Deluge*
39-25	IPA	FM	160.0	11.2	0.4	1:09	1:51	1:59	SE @ 2 sec
39-25	Heptane	FM	120.0	11.2	0.3	1:18	2:34	2:44	7:00

Agent	Extinguishment Time
UL Listed 3x3	Did not extinguish
- 142	3:06
-132	Did not extinguish
- 190	Did not extinguish
65R	Did not extinguish
A108	Did not extinguish

The plunging test is a 9.5 sqft fire that's conducted using premium gasoline with an application rate of about 0.5 gallons per minute (gpm) for 3 minutes

[0055] When introducing elements of the present invention or the preferred embodiments(s) thereof, the articles "a", "an", "the" and "said" are intended to mean that there are one or more of the elements. The terms "comprising", "including" and "having" are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0056] In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

[0057] As various changes could be made in the above compositions without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

CLAIMS:

1. A fire-fighting foam composition for fighting a Class B fire, the composition comprising:

diutan gum;

an anionic surfactant;

a zwitterionic surfactant, and

an organic solvent, wherein the composition is free of fluorinated surfactants, nonionic surfactants, and fluorine-containing polymers.

2. A fire-fighting foam composition for fighting a Class B fire, the composition comprising:

a first biopolymer selected from the group consisting of diutan gum, scleroglucan, and combinations thereof;

a second biopolymer selected from the group consisting of guar gum, cellulose, micro-fibrillated cellulose (MFC), and combinations thereof;

a third biopolymer selected from the group consisting of xanthan gum, rhamsam gum, gellan, and combinations thereof, wherein the composition is free of fluorinated surfactants and fluorine-containing polymers.

3. A fire-fighting foam composition for fighting a Class B fire, the composition comprising:

a first biopolymer selected from the group consisting of diutan gum, scleroglucan, and combinations thereof;

a second biopolymer selected from the group consisting of guar gum, cellulose, micro-fibrillated cellulose (MFC), and combinations thereof; and

a third biopolymer selected from the group consisting of xanthan gum, rhamsam gum, gellan and combinations thereof, wherein the combined proportion of the first polysaccharide, second polysaccharide, and third polysaccharide is less than about 5.0 wt.% of the composition.

4. A fire-fighting foam composition for fighting a Class B fire, the composition comprising:

diutan gum in a proportion of from about 0.1 to about 1.2wt.% of the composition;

guar gum in a proportion of from about 0.1 to about 0.4 wt.% of the composition;

xanthan gum in a proportion of from about 0.1 to about 3.5 wt.% of the composition;

an anionic surfactant, wherein the anionic surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates, sulfosuccinates, and combinations thereof and is present in a proportion of from about 0.5 to about 30 wt.% of the composition; and

an organic solvent, wherein the organic solvent is selected from the group consisting of glycols, alcohols, glycol ethers, and combinations thereof and is present in a proportion of from about 0.5 to about 25 wt.% of the composition, wherein the composition is free of fluorinated surfactants.

5. A fire-fighting foam composition for fighting a Class B fire, the composition comprising:

one or more biopolymers selected from the group consisting of diutan gum, guar gum, xanthan gum, scleroglucan, cellulose, protein, and combinations thereof;

an anionic surfactant, wherein the anionic surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates, sulfosuccinates and combinations thereof; and

an organic solvent, wherein the organic solvent is selected from the group consisting of glycols, alcohols, glycol ethers and combinations thereof; wherein:

the weight ratio of 20 to 28 is from about 7:1 to about 11:1; and/or

the weight ratio of 4 to 32 is from about 1:1 to about 12:1.

6. The composition of any of claims 1 to 5, the composition further comprising water.

7. The composition of claim 6, wherein water constitutes from about 30 wt% to about 65 wt%, from about 35 wt% to about 60 wt%, or from about 40 wt% to about 55 wt% of the composition.

8. The composition of any of the preceding claims, wherein the total proportion of polysaccharides is less than about 5 wt%, less than about 4wt%, less than about 3.5 wt%, less than about 3 wt%, less than about 2.5 wt%, from about 0.1 to about 5 wt%, from about 1 wt% to about 4 wt%, or from about 2 wt% to about 2.5 wt%.

9. The composition of any of the preceding claims, the composition further comprising a stabilizer, viscosity modifier, and/or film former.

10. The composition of claim 9, the composition comprising silk fibroin, gelatin, starch, cellulose, collagen, citrus fiber, whey protein, micro-fibrillated cellulose, clays, silica, or a combination thereof.

11. The composition of claim 9, the composition further comprising a viscosity modifier or film former selected from the group consisting of diutan gum, guar gum, xanthan gum, scleroglucan, cellulose, whey protein, and combinations thereof.

12. The composition of any of the preceding claims, the composition further comprising an organic solvent.

13. The composition of claim 12, wherein the organic solvent is selected from alkyl glycols, polyols, and glycol ethers.

14. The composition of claim 13, wherein the organic solvent is an alkyl glycol diol selected from propylene glycol, butylglycol, neopentyl glycol, ethylene glycol, 2-methyl-2,4-pentanediol, and combinations thereof.

15. The composition of claim 13, wherein the organic solvent is an alkyl glycol diol selected from propylene glycol, butylglycol, ethylene glycol, and combinations thereof.

16. The composition of claim 13, wherein the organic solvent is an alky glycol triol (e.g., glycerine).

17. The composition of claim 13, wherein the organic solvent is a glycol ether selected from propylene, n-butyl glycol ether, dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, dipropylene glycol phenyl ether, dipropylene glycol dimethyl ether, propylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether, dipropylene glycol methyl ether acetate, tripropylene glycol methyl ether, ethylene glycol hexyl ether; diethylene glycol hexyl ether; ethylene glycol propyl ether; diethylene glycol phenyl ether, ethylene glycol phenyl ether, poly(oxy-1,2- ethanediyl), alphaphenyl- omegahydroxy, diethylene glycol ethyl ether, diethylene glycol n-butyl ether, ethylene glycol n-butyl ether, butyl carbitol, and combinations thereof.

18. The composition of claim 13, wherein the organic solvent is a glycol ether selected from the group consisting of propylene, n-butyl glycol ether, butyl carbitol, and combinations thereof.

19. The composition of claim 12, wherein the composition comprises an organic solvent selected from the group consisting of glycols, alcohols, glycol ethers, and combinations thereof.

20. The composition of claim 12, wherein the composition comprises two organic solvents.

21. The composition of claim 12, wherein the composition comprises butyl carbitol and propylene glycol.

22. The composition of claim 19, wherein the composition comprises butanol and/or octanol.

23. The composition of claim 12, wherein the composition comprises three organic solvents.

24. The composition of claim 23, wherein the composition comprises butyl carbitol, hexylene glycol, and glycerine

25. The composition of any of claims 12 to 24, wherein the organic solvent is present in a proportion of at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, from about 0.5 wt% to about 30 wt%, from about 0.5 wt% to about 25 wt%, from about 10 wt% to about 25 wt%, or from about 10 wt% to about 20 wt%.

26. The composition of any of the preceding claims, the composition comprising one or more surfactants.

27. The composition of claim 26, the composition comprising an anionic surfactant selected from alkyl sulfates, alkyl ether sulfates, sulfosuccinates, and combinations thereof.

28. The composition of claim 27, the composition comprising an alkyl sulfate surfactant selected from sodium or amine C_8-C_{16} octyl sulfate, decyl sulfate, lauryl sulfate, sodium lauryl sulfoacetate, alpha olefin sulfonate (14-16), and combinations thereof.

29. The composition of claim 28, the composition comprising an alkyl sulfate surfactant selected from the group consisting of decyl sulfate, lauryl sulfate, octyl sulfate, and combinations thereof.

30. The composition of claim 26, the composition comprising an alkylether sulfate selected from the group consisting of sodium laureth sulfate, sodium C_8-C_{14} ammonium laureth sulfate, and combinations thereof.

31. The composition of claim 26, the composition comprising a sulfosuccinate selected from sodium dioctyl sulfosuccinate, sodium bistridecyl sulfosuccinate, disodium ethoxylated alcohol half ester of sulfosuccinic acid, sodium diisopropyl naphthalene sulfonate, C_8-C_{16} disodium laureth sulfosuccinate, and combinations thereod.

32. The composition of claim 31, the composition comprising a sulfosuccinate selected from sodium dioctyl sulfosuccinate, C_8-C_{16} disodium laureth sulfosuccinate, and combinations thereof.

33. The composition of any of the preceding claims, the composition comprising more than one anionic surfactant selected from alkyl sulfates, alkyl ether sulfates, sulfosuccinates, and combinations thereof.

34. The composition of claim 33, the composition comprising decyl sulfate, and octyl sulfate, and lauryl sulfate.

35. The composition of any of the preceding claims, the composition comprising a zwitterionic surfactant selected from sultaines and betaines.

36. The composition of any of claim 35, the composition comprising lauramidopropyl hydroxysultaine and/or cocamidopropyl hydroxysultaine.

37. The composition of claim 35, the composition comprising a betaine selected from the group consisting of lauramidopropyl betaine, disodium lauriminodipropionate, octyliminodipropionate, cocamidopropyl betaine, and combinations thereof.

38. The composition of any of the preceding claims, the composition comprising one or more zwitterionic surfactants.

39. The composition of any of the preceding claims, wherein the total proportion of surfactant is at least about 5 wt%, at least about 10 wt%, at

least about 15 wt%, from about 0.1 wt% to about 20 wt%, from about wt% to about 20 wt%, from about 5 wt% to about 20 wt%, or from about 10 wt% to about 20 wt% of the composition.

40. The composition of any of the preceding claims, wherein the composition comprises an inorganic bridging ligand as a viscosity modifier selected from magnesium sulfate, magnesium chloride, sodium chloride, potassium chloride, iron sulfate, iron chloride, and combinations thereof.

41. The composition of any of preceding claims, wherein the composition comprises a foam stabilizer selected from C_4-C_{20} alcohols, C_{12}-C_{18} amines, sorbitan esters, polysorbates, fatty acids, and combinations thereof.

42. The composition of any of the preceding claims, wherein the composition comprises a foam stabilizer selected from the group consisting of fructose, galactose, dextrose, sucrose, maltose, lactose, xylose, glucose, and combinations thereof.

43. The composition of any of the preceding claims, wherein the composition further comprises a preservative.

44. The composition of claim 43, wherein the preservative is a tolytriazole.

45. The composition of any of the preceding claims, wherein the weight ratio of total proportion of biopolymer to surfactant is from about 1:5 to about 1:10 or from about 1:7 to about to about 1:10.

46. The composition of any of the preceding claims, wherein the weight ratio of the total proportion of biopolymer to organic solvent is typically from about 1:0.5 to about 1:1.

47. The composition of any of the preceding claims, wherein the weight ratio of the total proportion of biopolymer to any alcohol component is from about 1:4 to about 1:10 or from about 1:5 to about 1:10.

48. A method for suppressing and/or extinguishing a Class-B fire, the method comprising applying a composition or foam composition of any of the preceding claims either directly or indirectly to or onto a Class-B fire or directly or indirectly to or onto the fuel ahead of a potentially advancing Class-B fire front.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/57562

A. CLASSIFICATION OF SUBJECT MATTER

IPC - A62D 1/02; C08G 77/392; C08G 77/452 (2021.01)

CPC - A62D 1/0071; C08G 77/14; C08G 77/26

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/0138104 A1 (Robinet et al.) 22 May 2014 (22.05.2014) Abstract; para [0001], para [008], para [0010], para [0019], para [0027], claims and entire document	1,5,6/(1,5), 7/6/(1,5)
X	US 2019/0262647 A1 (Tyco Fire Products LP) 29 August 2019 (29.08.2019) Abstract; para [0053], para [00150], para [00127], Table 7, Table 2 Table 3; claims; and entire document	2-4, 6/(2-4), 7/6/(2-4)
A	US 2003/0212177 A1 (Vandersall et al.) 13 November 2003 (13.11.2003) Abstract; para [0014]-[0018], claims	1-7
A	US 5,997,758 A (Barbarin et al.) 7 December 1999 (07.12.1999) Abstract; col 2 ln 15 - col 5 ln 55;	1-7
P/X	WO 2021/191706 A1 (Tyco Fire Products LP) 30 September 2021 (30.09.2021) Abstract; para [0003]-[0010]	1-7

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

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

Date of the actual completion of the international search	Date of mailing of the international search report
6 January 2022	FEB 02 2022
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Kari Rodriquez Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 21/57562

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 8-48
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos..

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.