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(54) **FIRE EXTINGUISHING AEROSOL FORMING MEANS**

AEROSOLBILDENDES FEUERLÖSCHMITTEL

CONSTITUANTS FORMANT UN AEROSOL D'EXTINCTION D'INCENDIE

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(56) References cited:
EP-A- 0 560 095 EP-A- 0 561 035
DE-A- 19 531 130

- **DATABASE WPI Section Ch, Week 199815**
Derwent Publications Ltd., London, GB; Class
A97, AN 1998-167693 XP002122626 & RU 2 086
278 C (LYUBERETS SOYUZ RES PRODN
ASSOC), 10 August 1997 (1997-08-10) cited in
the application
- **DATABASE WPI Section Ch, Week 199823**
Derwent Publications Ltd., London, GB; Class
A97, AN 1998-259575 XP002122627 & RU 2 091
106 C (SOYUZ TECHN CENTRE), 27 September
1997 (1997-09-27) cited in the application
- **DATABASE WPI Section Ch, Week 199841**
Derwent Publications Ltd., London, GB; Class
E37, AN 1998-479537 XP002122628 & RU 2 105
581 C (PAK Z P), 27 February 1998 (1998-02-27)
cited in the application

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Description

Summary of the invention

[0001] The present invention relates to the field of extinguishing a fire, in particular, to a fire extinguishing aerosol forming means (FEAFM).

[0002] Fire extinguishing aerosol forming means have presently wide application as an effective volumetric fire extinguishing means because they are characterized by fast emitting of the fire extinguishing aerosol and fast filling the protected volume therewith, entering even into difficult places, in result the fire will be practically instantly liquidated (PCT/RU 93/00025 of Jan. 28, 1993, A 62D 1/00; EP 0560095 of Jan. 25, 1995, A 62D 1/00).

[0003] Extinguishing a fire with use of FEAFM is based on a principally new mechanism consisting in burning of the means with formation of gaseous and highly dispersed condensed products having inhibiting properties and suppressing the chain reaction of burning and, as result, extinguishing the flame. Aerosol formed at burning of such means has fire extinguishing properties due to the presence of alkaline metals ions therein. Potassium nitrate or a mixture thereof with potassium perchlorate is most frequently used as a source of alkaline metals ions in FEAFM. For the rest, the known FEAFM differ, as a rule, by type of binder and contain of additives of various purpose (Patents RU No.2105581 A 62C 3/00 and No.2091106 A 62D 1/00).

[0004] Variety of types of fire dangerous materials and objects, their dimensions, degree of uptightness and other features of the protected volumes dictate variety of aerosol fire extinguishing devices and as a consequence of this, large enough variety of FEAFM having a set of certain properties which could be relate to the following:

- high fire extinguishing efficiency, that could be expressed in low FEAFM fire extinguishing concentration;
- absence of negative influence on the atmosphere ozone layer and environment, i.e. ecological cleanliness of FEAFM combustion products, their low toxicity;
- reduced temperature of FEAFM combustion products;
- possibility of wide range regulation of burning speed, i.e. speed of emitting of the fire extinguishing aerosol;
- acceptable operational characteristics (mechanical reliability, thermal-resistance, safety etc.).

[0005] The practical application conditions of FEAFM in fire extinguishing devices set forward contradictory requirements to parameters of aerosol forming: fire extinguishing efficiency and aerosol forming speed should be rather high, and temperature of the fire extinguishing aerosol should be low. In practice, high speed of aerosol forming corresponds to increased temperature of the aerosol, and significant reduction of the aerosol temperature results in loss in fire extinguishing efficiency thereof.

[0006] As the majority of FEAFM in industrial application have high temperature of burning and, hence, form a high-temperature aerosol, reduction of temperature of FEAFM combustion products, alongside with increasing of efficiency thereof, with the purpose of creation an economic and highly effective aerosol forming fire extinguishing devices is an actual problem.

[0007] Closest to the claimed technical decision is aerosol forming fire extinguishing composition described in the Patent of the Russian Federation No.2091106, A 62D 1/00, comprising the following components, in mass %:

potassium nitrate	45.0 - 75.0;
carbon	4.0 - 11.0;
centralyte and/or diphenylamine	0.5 - 2.0;
industrial or instrumental oil	0.5 - 2.5;
zinc and/or sodium stearate, or mixture thereof with sulforicinate and gelatin	0.02-0.5;
burning catalyst and/or inhibitor	0.5 - 20.0;
plasticized derivative of cellulose, or mixture thereof with additional binder the rest	

[0008] As the burning catalyst FEAFM comprises compounds chosen from the sequence including oxides of metals of variable valence or metals of the II group (oxides of iron, copper, nickel, cobalt, manganese, chrome and zinc, or mixture thereof), their organic or inorganic compositions or mixture thereof (salicylates, phthalates, acetylacetolates or oxalates of copper, nickel, cobalt, iron, manganese, zinc or calcium; carbonates of these metals, except calcium carbonate).

[0009] As the burning inhibitor FEAFM comprises compounds chosen from the sequence including inorganic and organic phosphor containing compounds, inorganic and organic nitrogen containing compounds, hydroxides, carbonates, basic carbonates, borates of metals or trioxide of aluminum and/or mixtures thereof.

[0010] Introduction in FEAFM inhibitor or a mixture thereof with catalyst even in maximum quantity does not provide

stability of the process conversion flame burning of FEAFM in flameless gasification.

[0011] With increasing of FEAFM weight or obstruction of heat removal the process of flameless gasification changes over in flame burning again, that restricts application of FEAFM in fire extinguishing devices.

[0012] The modern fire extinguishing means based on use of aerosol forming compositions provide, as a rule, presence of various agents ensuring cooling of the fire extinguishing aerosol: cooling liquids (water, water solutions of salts), air ejectors, chemical thermally decomposing powders or compositions.

[0013] In the Patent of the Russian Federation No.2086278 A 62D 1/00 it is described a composition for cooling of the fire extinguishing aerosol, containing as a binder cellulose nitrate, plasticized by a low-volatile plasticizer, diphenylamine, polyvinyl acetate, carbon, iron oxide, as a filler basic manganese carbonate, or ammonium oxalate, or basic magnesium phosphate; and technological additives: industrial or instrumental oil, sodium or zinc stearate, graphite, paraffin and water at the following contents of the components, mass %:

cellulose nitrate	5.0 - 12.5;
low-volatile plasticizer	5.0 - 12.5;
diphenyl amine	0.1 - 0.5;
polyvinyl acetate	0.2 - 1.5;
carbon	0.1 - 0.5;
iron oxide	0.3 - 1.5;
basic manganese carbonate of ammonium oxalate or basic magnesium phosphate	25.0 - 45.0;
industrial or instrumental oil	0.5 - 5.0;
sodium or zinc stearate	0.1 - 3.0;
graphite	0.1 - 1.5;
paraffin	0.1 - 1.5;
water	the rest.

[0014] This composition for cooling of aerosol is insufficiently effective because of low contents of the heat absorbing component (25-45 weight %). Furthermore, rheological, physical and mechanical properties of the composition limit the forms of joint application thereof directly with aerosol forming compositions.

[0015] It is proposed a fire extinguishing aerosol forming means including flame suppressing agent, fuel-binder, source of carbon, stabilizer, modifier of burning and technological additives, and as the flame suppressing agent it contains nitrates of alkaline metals or mixture thereof with complex compositions of alkaline metals, as the source of carbon - carbon as it or aliphatic or aromatic alcohols, or mixture thereof, as the modifier of burning it additionally contains a cooling agent, and as the technological additives it additionally contains compositions chosen from the class of glycoles or glycerin.

[0016] Main ingredients of the means are contained therein in the following ratio, mass parts:

flame suppressing agent	35 - 80;
fuel-binder	12 - 40;
source of carbon	1 - 15;
stabilizer	0.5 - 2.5;
modifier of burning	1 - 250;
technological additives	0.5 - 7.5.

[0017] Nitrates of alkaline metals or mixture thereof with complex compositions of alkaline metals are used as the flame suppressing agent.

[0018] The included in the structure complex compositions of alkaline metals comprise compositions having temperature of chemolysis of approximately 2000°C, that is commensurable with the surface temperature of burning FEAFM. As these compositions it is preferable to use potassium or sodium dipyrocatechol, potassium hexanitrocobaltate, potassium ferrocyanide or potassium ferricyanide, or mixture thereof.

[0019] Products formed at decomposition of the complexes have superfluous energy and are active accelerators of reactions taking place in the surface layer of FEAFM. This results in increasing of completeness of potassium nitrate decomposition. The products of chemolysis of the complex compositions of alkaline metals are also capable to break off the chain reactions of oxidation at burning process and, together with decomposition products of potassium nitrate, form a mixture effectively inhibiting process of burning.

[0020] Furthermore, using of complex compositions of alkaline metals allows to reduce essentially the lower limit of

carbon contents in FEA FM, providing thus reduction of carbon monoxide contents in the products of FEA FM combustion, that, in turn, leads to decreasing toxicity of the fire extinguishing aerosol itself.

[0021] Plasticized derivatives of cellulose or mixture thereof with other binder is used as a fuel-binder. It is preferred to use such compositions, as cellulose ethers, e.g. nitrocellulose, cellulose methyl-, ethylacetates or mixtures thereof.

[0022] As plasticizers of cellulose derivatives there are used ethers of carboxylic or mineral acids and alcohols, e.g., triacetin, diethylene glycol propionate, triethylene glycol dipropionate, dibutyl phthalate, dioctyl sebacate, diethylene glycol dinitrate or triethylene glycol dinitrate or mixture thereof.

[0023] FEA FM can contain polyvinyl acetate, or polyvinyl alcohol, or mixture thereof as an additional binder.

[0024] As a source of carbon the means contains carbon as such, aliphatic or aromatic alcohols (e.g., sorbitol, xylitol, pirocathechol, hydroquinone or α -naphthol) or mixture thereof.

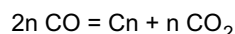
[0025] Centralyte and/or diphenylamine are mostly used as a stabilizer.

[0026] The means contains a catalyst and/or an inhibitor of burning, and a cooling agent as a modifier of burning. It is desirable for regulation of FEA FM burning characteristics to the required level.

[0027] The catalysts of burning are used for increasing of speed of burning and maintenance of burning stability at low pressure. The catalysts accelerate achievement of thermodynamic balance of oxidation reactions, those as $2\text{NO} + 2\text{CO} = 2\text{CO}_2 + \text{N}_2$; $\text{C} + 2\text{NO} = \text{CO}_2 + \text{N}_2$; $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$; etc. resulting in increasing of proportion of products of complete oxidation in FEA FM burning products and decreasing of contents of toxic substances, in particular, carbon and nitrogen monoxides.

[0028] As the catalyst, as a rule, there used compositions of metals of variable valence, e.g., oxides of iron, copper, nickel, cobalt, manganese, chrome; organic or inorganic compositions of same metals or mixtures thereof. The catalysts are added in FEA FM in quantity from 0.5 to 10 mass parts, preferably 1-5 mass parts.

[0029] Inhibitors of burning are added in FEA FM for reduction of their speed of burning, decreasing of temperature of surface burning and flame zone. Damping of chemical reactions of burning is achieved either due to blocking the active centers of flame (gas) reactions by inhibitors or products of their decomposition, or due to intensification of reactions of carbonization, resulting in forming on the surface of burning of dense and hard carbon carcass changing conditions of mass- and heat exchange on the border of gaseous and condensed phases. Due to the reaction



contents of the toxic monoxide in gaseous products is decreased.

[0030] It is reasonable to use as the inhibitor of burning compositions chosen from classes: inorganic and organic phosphor- and/or nitrogen- containing composition, borates or carbonates of metals or hydroxides of metals of the III group or mixtures thereof.

[0031] E.g., from phosphor- and nitrogen- containing inhibitors it is preferable to use phosphates of potassium, calcium, iron of any degree of displacement; triphenyl phosphate; ammonium phosphates, ferric-ammonium phosphate, ammonium oxalate, ferric-ammonium oxalate; amides-carbamide, triazine and its derivatives, dicyanamide; among borates of metals - borates of potassium, sodium, calcium, magnesium, barium, zinc.

[0032] Quantity of entered inhibitor comprises 5-30 mass parts, preferably 15-25 mass parts.

[0033] The cooling agents are added in FEA FM for change of its thermal balance of burning. Additional reduction of temperature on the surface, and cooling of products of burning of FEA FM occurs due to physical removing of heat which is spent on heating of particles of the entered cooling agent, its endothermic decomposition, and also due to shielding of the thermal flow directed from the zone of flame reactions to the burning surface.

[0034] As the cooling agent there are used oxides and hydroxides of metals of the II group, aluminosilicates, nepheline, metal shavings or mixtures thereof, or a heat-absorbing composition.

[0035] Incombustible products of disintegration of the composition dilute products of FEA FM burning in the flame zone of reaction, reduce temperature of the flame and with it decrease return thermal flow to the surface of burning. Interaction of FEA FM combustion products with products of disintegration of the heat-absorbing composition results in "freezing" thereof, possibility of their further interaction is eliminated, in result, it is generated a cooled aerosol. Heat-absorbing composition includes the following ingredients, mass parts:

heat-absorbing component	50-80
binder	10-35,
additives	1-7,

thus, as the heat-absorbing component there are mainly used carbonates or basic carbonates, phosphates of metals of the II group; crystal hydrides thereof, hydroxides of metals of the III group or mixtures thereof; as the binder - deriv-

atives of cellulose, e.g., nitrocellulose, plasticized by a low-volatile plasticizer, e.g., triacetin and/or dibutyl phthalate, and polyvinyl acetate or polyvinyl alcohol; as the additive it is used lubricant oil, potassium or zinc stearate, organosilicon compositions and oleic acid.

[0036] Depending on the purpose and application of FEAFM in a particular fire extinguishing device, quantity of the cooling agent can vary over a wide range from 0.5 to 250 mass parts.

[0037] Lubricant oil, composition chosen from the class of glycoles, or glycerin, salt of a fatty acid, e.g., potassium or zinc stearate or mixture thereof with sulfuricinate and gelatin are used in FEAFM as the technological additives.

[0038] Introduction in FEAFM of compositions from the class of glycoles such as diethylene glycol, triethylene glycol, or glycerin is caused by their lubricating action. Therefore they are used in quantities from 0.1 to 2 mass parts as additional technological additives lowering external friction and the phenomenon of sticking to the technological equipment during manufacturing of FEAFM and processing thereof in various products (aerosol forming elements). The best efficiency is shown with the technological additive including a triple mixture of: lubricant oil, diethylene glycol (triethylene glycol or glycerin) and a salt of a fatty acid.

[0039] Diethylene glycol or triethylene glycol serves simultaneously as a plasticizer for cellulose derivatives, in particular, for nitrocellulose, and as an additive in small quantities (2-5 mass parts) to the base plasticizer it improves process of plasticization of nitrocellulose.

[0040] Manufacturing of FEAFM is carried out by mixing of all components in required proportions in an apparatus having an agitator using a dry method or in water environment (for water insoluble nitrate plasticizers) at temperature 10-55°C with subsequent forming from the received mixture of elements of necessary sizes and configuration at temperature 50-80°C. In case of in-water manufacturing of FEAFM the fire extinguishing agent is added to the mixture pressed out of water. In case of using as the cooling agent of heat-absorbing composition manufacturing thereof and forming of elements is carried out by the same way; in this case FEAFM is produced without cooling agent, and then it is performed mixing thereof or elements are used in layers.

[0041] The main characteristic of FEAFM is its fire extinguishing efficiency (FEE), i.e. minimal weight of FEAFM, ensuring suppression of the fire in 1 m³ of protected volume.

[0042] FEE of FEAFM compositions was extensively examined in laboratory and testing stand conditions at suppression of inflammable liquids (acetone, petrol, ethyl and isopropyl alcohols, mixture of diesel fuel with petrol) and was confirmed by tests of aerosol generators on their basis.

[0043] Laboratory technique of FEE estimation consist in following. In an exhaust hood under a glass cap of 10 l capacity there was placed a burning alcohol-lamp or a melting-pot with inflammable liquid and a certain weight sample of FEAFM, connected with a Nichrome spiral. Using electric current with about 12 V voltage supplied to the Nichrome spiral it was set fire the sample of FEAFM and the process of suppression of the flame of the alcohol-lamp (or inflammable liquid) was observed through the transparent glass of the cap. The result was considered to be positive if the flame was suppressed during period no longer than 5 s after burning away the sample of FEAFM. Minimal fire extinguishing concentration was determined by interpolation on two nearest points. For comparison it was carried out a check experiment on burning an alcohol-lamp (or inflammable liquid in a melting-pot) under the closed cap. Time of natural dying of the alcohol-lamp flame, due to consumption of oxygen of air enclosed under the cap, was 75 s.

[0044] American Standard UL 1058 was laid in base of testing stand technique of examination of FEAFM fire extinguishing efficiency.

[0045] In a chamber of 1 m³ volume (2.08 x 0.8 x 0.6), having a flat screen of 0.25 m width in the middle part on whole height of the chamber, there were placed 5 sources of inflammable liquid (capacities of 75 mm in diameter, 125 mm in height with 500 ml of petrol in each of them), which were placed on four corners of the chamber and one source was placed behind the screen. Above each source of inflammable liquid in the cover of chamber there were formed small windows made of organic glass for visual observation for suppression of the fire.

[0046] The tested sample of FEAFM was placed in a metal housing and was fixed in the central part of the side wall of the chamber. Initiation of ignition of the FEAFM sample was performed using a fuse or a source of electric current located outside of the testing chamber. Petrol or another inflammable liquid in capacities was ignited, the cover of testing chamber was closed. After steady burning of inflammable liquid during 30 s it was initiated ignition of the FEAFM sample. And after 1 more minute the cover of chamber was opened and the chamber was inspected after dispersion of aerosol. Suppression or burning of inflammable liquid was defined with help of decoded oscillogramme records or visually through the windows in the chamber cover.

[0047] The result was considered to be positive in case of suppression of all sources of fire within no longer than one minute after the end of burning of the FEAFM sample. Method of FEAFM manufacturing is illustrated by the following examples, not limiting the scope of the present invention.

Example 1.

[0048] FEAFM has the following structure of components (mass parts):

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Flame suppressing agent:	potassium nitrate	58.0
	potassium dipyrocatechol borate	10.0
Source of carbon:	highly dispersed carbon	2.0
Stabilizer of chemical stability:	centralite	0.3
	diphenyl-amine	0.7
Technological Additives:	diethylene glycol	1.0
	lubricant (industrial) oil	1.0
	sodium (zinc) stearate	0.1
Fuel-binder	nitrocellulose	12.4
	triacetone	9.0
	polyvinyl acetate	2.0
Modifier of burning:		
- catalyst:	ferric oxide	1.5
- cooling agent:	hydrated magnesium oxide	1.0

[0049] All loose components in specified proportions except potassium nitrate and stabilizer are entered in an apparatus of "Beken" type at environment temperature, mixed, and liquid components are added with dissolved centralite and diphenyl amine therein, mixed. At last, for the safety reasons, the apparatus is loaded with potassium nitrate and mixed not less than 30 mins. The obtained mixture is unloaded from the apparatus, is rolled and formed into elements of required sizes on a hydraulic or an auger-press at temperature 60-70°C.

[0050] Fire extinguishing efficiency of FEA FM according to the laboratory method of estimation comprises 10 g/m³ and in testing stand conditions according to the Standard UL 1058 - 25 g/m³.

Example 2.

[0051] FEA FM has the following structure of components (mass parts):

Flame suppressing agent:	potassium nitrate	58.0
	potassium ferrocyanide	10.0
Source of carbon:	highly dispersed carbon	2.0
Stabilizer:	centralite	0.3
	diphenyl-amine	0.7
Technological additives:	diethylene glycol	1.0
	lubricant (industrial) oil	1.0
	sodium stearate	0.1
Fuel-binder	nitrocellulose	11.9
	triacetone	9.0
	polyvinyl acetate	2.0
Modifier of burning:	cobalt acetylacetonate	2.0
	magnesium hydroxide	1.0

[0052] This FEA FM was prepared similarly to example 1. Fire extinguishing efficiency the FEA FM according to the laboratory method of estimation comprises 10 g/m³ and in testing stand conditions according to the Standard UL 1058 - 25 g/m³.

Example 3.

[0053] Preparation of the means was carried out according to the method of example 1.

[0054] Data on structure and efficiency is presented in the table.

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Example 4.

[0055] FEAFM has the following structure of components (mass parts):

5	Flame suppressing agent:	potassium nitrate	50.0
		potassium dipyrocatechol borate	5.0
	Source of carbon:	highly dispersed carbon	4.5
10		sorbitol	5.0
	Stabilizer:	centralite	0.5
		diphenyl-amine	0.5
	Technological Additives:		
15		diethylene glycol	0.5
		lubricant (industrial) oil	1.0
		zinc stearate	0.07
		sulforicinate	0.1
20		gelatin	0.03
	Fuel-binder	nitrocellulose mixture of diethylene glycol dinitrate with triethylene glycol	13.8
		dinitrate (7:3)	16.0
	Modifier of burning:	ferric oxide	2.0
25		hydrated magnesium oxide	1.0

[0056] Mixture of all components, except the flame suppressing agent and sorbitol, is performed in a mixer in a water environment at M 1:5 without additional heating of the equipment. To the mixer it is added nitrocellulose, technological additives (lubricant oil, diethylene glycol, zinc stearate) and. modifiers of burning. It is prepared separately emulsion of mixture of plasticizers with stabilizers of chemical stability (centralite and diphenylamine) with addition of emulsifier - sulforicinate and emulsion stabilizer - gelatin. The emulsion is added into the mixer and contents of the mixer is mixed for 18-24 hours. Then the received mixture is squeezed out of water on a squeezing apparatus up to humidity of 10-16 mass % and further in an apparatus without mechanical mixers is mixed with the flame suppressing agent and sorbitol during 20-30 minutes. The ready mix is rolled and is formed into elements of required size in a hydraulic or an auger-press at temperature 60-80°C.

Examples 5-6.

[0057] Preparation of the means was carried out according to the method of example 1.

[0058] Data on structure and efficiency is presented in the table.

Example 7.

[0059] Structure of FEAFM components, mass parts:

45	Flame suppressing agent:	potassium nitrate	58.0
		potassium dipyrocatechol borate	10.0
	Source of carbon:	carbon	2.0
50	Stabilizer:	centralite	0.5
		diphenyl-amine	0.5
	Technological Additives:		
55		diethylene glycol	1.0
		lubricant industrial) oil	1.0
		zinc stearate	0.1

(continued)

5 10 15 20	Fuel-binder	nitrocellulose		12.4
		triacetine		9.0
		polyvinyl acetate		2.0
	Modifier of burning: - catalyst: - cooling agent:	ferric oxide		1.5
		heat-absorbing composition		
		nitrocellulose	12.0	
		triacetine	9.8	
		polyvinyl acetate	2.0	
		basic magnesium carbonate	67.0	
		lubricant (industrial) oil	2.0	
		sodium stearate oligoethyl dihydride	0.2	
		siloxane	2.7	
		oleic acid	1.3	
		balance water	3.0	

[0060] All components, except the cooling agent, are mixed in the "Beken" type apparatus similar to the used in example 1. The obtained mixture is rolled and is formed into elements or products also similar to example 1. Heat-absorbing composition is prepared separately. Mixing of all components in required proportions is carried out in the "Beken" type apparatus. Basic magnesium carbonate is initially processed by water emulsion of silicon-organic composition, oleic acid is added and mixed during 20-30 minutes, then, obtained emulsion is filtered up to humidity 50-70%. All liquid components are entered into mixing apparatus, mixed not less than 30 minutes.

[0061] The obtained mixture is rolled at temperature 90-120°C and formed on an auger-press into elements of required form and size. The obtained thus components of the means are mixed in the abovementioned ratio. Data on efficiency is specified in the table.

Example 8.

[0062] Preparation of the means was carried out according to the method of example 7.

[0063] Data on structure and efficiency is represented in the table.

The table

Influence of structure of the proposed agent on efficiency thereof									
Contents of the components, mass parts	Structure of the means according to the present examples								
	Russian Patent No. 2091 106	1	2	3	4	5	6	7	8
1	2	3	4	5	6	7	8	9	10
Flame suppressing agent:	45-75								
Potassium nitrate		58	58	53,9	50	54	64	59	40,5
Potassium dipyrrocatechol borate		10			5	10		10	5
potassium ferrocyanide			10						
Potassium hexanitro cobaltate				5					
Source of carbon:	4-11								

The table (continued)

	Influence of structure of the proposed agent on efficiency thereof									
5	Contents of the components, mass parts	Structure of the means according to the present examples								
		Russian Patent No. 2091 106	1	2	3	4	5	6	7	8
10	1	2	3	4	5	6	7	8	9	10
	Carbon		2	2	4	4,5	2	7,5	2	5
	Sorbitol				9	5				
15	1	2	3	4	5	6	7	8	9	10
	Stabilizer:	0.5-2.0								
	Mixture of centralite and diphenyl-amine		1	1	1	1	0,5	1	1	1
20	Technological additives:	0.52 -3.0								
	Diethylene glycol		1	1	0,1	0,5	1	0,5	1	1
	Lubricant oil		1	1	1	1	1	1	1	1
25	Sodium (zinc) stearate		0.1	0.1	0.1	0.2	0.2	0.1	0.1	0,1
	Fuel-binder	12-41,85								
	Nitrocellulose		12.4	11.9	12.4	13,8	12,4	12.4	12.4	12,4
	Triacetine		9 9 9				9	9	9	9
30	Plasticizer LD-70*					16				
	Polyvinyl acetate		2 2 2				2	2	2	2
	Modifier of burning:	0.5-20								
35	catalyst		1.5	2	1.5	2	2	1,5	1.5	3
	inhibitor									20
	cooling agent		1	1	1	1	5	1	100	5
40	Efficiency of the agent, g/m³	15-54	10	10	10	8	20	12	40	35

*LD-70 - mixture of diethylene glycol nitrate with triethylene glycol dinitrate (7:3)

[0064] It is clear from the presented tables, that in comparison with the known art, the lower level of fire extinguishing concentration is reduced, i.e. fire extinguishing efficiency is increased. In variants of FEAFM embodiments, which have fire extinguishing efficiency at the level of the prior art, e.g., sample No.5, the fire extinguishing aerosol is characterized by lowered contents of toxic monoxide owing to the low contents of carbon therein. In embodiments according to samples 8 and 7 FEAFM includes inhibitor and/or cooling agent in sufficient quantity and does not require to use additional cooling means in case of using them in fire extinguishing devices.

[0065] Aerosol forming fire extinguishing composition according to the prior art is used in fire extinguishing devices together with a cooling agent with the purpose of obtaining a cooled flameless aerosol. Use of a cooling agent reduces efficiency (increases fire extinguishing concentration) due to settling of the aerosol in the layer of cooling agent. Fire extinguishing concentration in this case increases till 50-54 g/m³ and more.

[0066] Introduction into proposed FEAFM of an inhibitor or a mixture thereof with a catalyst and/or a cooling agent in quantity more than 20 mass parts provides steady flameless gasification of FEAFM. Gasification character of FEAFM and large potential thereof for operational safety allows to use it as elements with highly developed surface, e.g., in the form of granules, that contributes to intensification of emitting of aerosol and faster filling the protected volume thereby, furthermore it is also economically favorable.

[0067] To eliminate getting through the flame in the FEAFM granules layer it is reasonable to include a cooling agent in FEAFM in form of, e.g., metal shaving or minute elements of heat-absorbing composition, forming a mechanical mixture. The cooling agent in this case promotes formation of more loose structure of FEAFM, facilitating heat dissipation and simultaneously taking away additional amount of heat for self heating.

The cooling agent amount is determined by chemical composition, size of used FEAFM elements, feature of application thereof and a number of other factors.

In FEAFM without inhibitor the cooling agent contents can be high. Depending on the required purpose, e.g., on using of FEAFM in devices intended for explosion and fire protection of objects, it is reasonable to use the generated fire extinguishing aerosol in cold condition, i.e. temperature thereof should be below than temperature of self-ignition of explosive mixtures, therefore quantity of the cooling agent in FEAFM can make up to 250 mass parts. The proposed FEAFM depending on structure and the quantities of the modifier of burning are characterized by wide spectrum of variability of characteristics thereof. By changing the ratio catalyst-inhibitor-cooling agent it is possible to adjust the process of thermal decomposition of FEAFM from flame burning till grading thereof into flameless gasification. As a rule, high-temperature aerosol has the most fine-disperse structure and is characterized by higher fire extinguishing efficiency and speed of aerosol generation. Flameless low-temperature aerosol has in some degree lesser fire extinguishing efficiency and lower speed of aerosol generation. Each of variants has, however, own advantages which could be realized in practice. High speed of aerosol generation promotes fast filling of protected volume and fast creation of fire extinguishing concentration therein, that allows to use fire extinguishing devices on basis of such FEAFM in untight, ventilated or extended objects, e.g., in vehicles engine compartments, cable channels etc. To protect tight volumes, in order to prevent sharp increase of pressure, it is reasonable to use fire extinguishing devices on the basis of FEAFM with lowered speed of aerosol generation. The proposed invention considerably expands area of application of FEAFM due to the possibility of wide regulation of temperature of the generated fire extinguishing aerosol and speed of aerosol generation thereof, and can be used in various fire extinguishing devices, both with application of the cooling agent, and without it, which is a result of creation of FEAFM embodiments with steady flameless gasification not requiring additional cooling of the aerosol.

[0068] The last circumstance considerably simplifies design of the apparatus, makes them less metal containing, simple in production, reliable in use. The aerosol generated by FEAFM, reliably extinguishes fires of various classes, provides retardation of dust-gas-air explosive mixtures.

[0069] Level of the basic characteristics of FEAFM (physicochemical, mechanical, technological etc.) allows to manufacture elements of the various sizes and forms therefrom and to use them in fire extinguishing means.

[0070] The area of application of the proposed FEAFM in fire extinguishing devices is characterized by the widest spectrum: all kinds of automobile-, railroad, aviation-, water transport, underground railway, warehouses of inflammable liquids and fuels and lubricants, enterprises of various branches of industry, including objects with explosive dust-gas-air environment and extended communication network of power supply, ventilation, etc.

[0071] All devices using FEAFM can work in automatic and manual-operating modes, are designed for long service life (up to 10 years and longer), do not require additional service, are always ready to action. The means has low toxic level, is ozone safe, does not cause corrosion of metals, does not have destroying effect to material objects. Thus FEAFM according to the present invention solves the stipulated problems completely.

Claims

1. The fire extinguishing aerosol forming means including a flame suppressing agent, a fuel-binder, a source of carbon, a stabilizer, a modifier of burning and technological additives, said means contains nitrates of alkaline metals or mixture thereof with complex composition of alkaline metals as the flame suppressing agent, carbon as such, aliphatic or aromatic alcohols, or mixture thereof as the source of carbon, **characterised in that**, it contains as the modifier of burning a cooling agent chosen from oxides and hydroxides of metals of the II group, aluminosilicates, nepheline or metal shaving or mixtures thereof or a heat absorbing composition, in combination with compositions chosen from the class of glycoles or glycerin as the technological additives.

2. The means according to claim 1, **characterised in that**, it contains ingredients in the following ratio, mass parts:

flame suppressing agent	40 - 80;
fuel-binder	12 - 40;
source of carbon	1 - 15;
stabilizer	0.5 - 2.5;
modifier of burning	1 - 250;

(continued)

technological additives	0.5 - 7.5.
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3. The means according to claim 1, **characterised in that**, it contains a lubricant oil, a salt of a greasy acid, e.g., sodium or zinc stearate, or a mixture of the salt with sulforicinate and gelatin as the technological additives.
4. The means according to claim 1, **characterised in that**, it contains a catalyst and/or an inhibitor as the modifier of burning and the cooling agent.
5. The means according to claim 4, **characterised in that**, the heat absorbing composition includes a heat-absorbing component, a binder and additives in the following ratio, mass parts:

heat-absorbing component	50 - 80;
binder	10 - 35;
additives	1 - 7.

6. The means according to claim 5, **characterised in that**, it contains a derivative of cellulose, a low-volatile plasticizer and polyvinyl acetate or polyvinyl alcohol as the binder in the following ratio of the ingredients, mass parts:

derivative of cellulose and low-volatile plasticizer	9 - 34;
polyvinyl acetate or polyvinyl alcohol	1 - 5.

7. The means according to claim 5, **characterised in that**, it contains carbonates, basic carbonates or phosphates of metals of the II group, crystal hydrides thereof or hydroxides of metals of the III group or mixtures thereof as the heat absorbing component.
8. The means according to claim 5, **characterised in that**, it contains a lubricant oil, a sodium or zinc stearate, organosilicon compositions, an oleic acid as the additives.
9. The means according to claim 4, **characterised in that**, it contains a composition chosen from the group including oxides of metals of variable valence, their organic or inorganic compositions, or mixture thereof as the catalyst.
10. The means according to claim 4, **characterised in that**, it contains a composition chosen from the group including inorganic and organic phosphorus- and/or nitrogen-containing compositions, hydroxides of metals of the III group, borates or carbonates of metals or mixture thereof as an inhibitor.

Patentansprüche

1. Aerosolbildendes Feuerlöschmittel, umfassend ein flammenerstickendes Mittel, ein Brennstoffbindemittel, eine Kohlenstoffquelle, einen Stabilisator, einen Verbrennungsmodifikator und technologische Zusätze, wobei als flammenerstickendes Mittel Alkalimetallnitrate oder deren Gemisch mit einer komplexen Verbindungen von Alkalimetallen und als Kohlenstoffquelle Kohlenstoff als solcher, aliphatische oder aromatische Alkohole oder deren Gemisch enthalten sind, **dadurch gekennzeichnet, daß** das aerosolbildende Feuerlöschmittel ein Kühlmittel, welches aus Oxiden und Hydroxiden von Metallen der II. Gruppe, Alumosilikaten, Nephelin oder Metallspänen oder deren Gemischen ausgewählt ist, oder eine wärmeaufnehmende Zusammensetzung als Verbrennungsmodifikator enthält in Kombination mit aus der Klasse von Glykolen oder Glycerin ausgewählten Verbindungen als technologischen Zusätzen.
2. Feuerlöschmittel nach Anspruch 1, **dadurch gekennzeichnet, daß** die Bestandteile im folgenden Verhältnis, Gewichtsteile:

Flammenerstickendes Mittel	40 bis 80;
Brennstoffbindemittel	12 bis 40;
Kohlenstoffquelle	1 bis 15;

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(fortgesetzt)

Stabilisator	0,5 bis 2,5;
Brennstoffmodifikator	1 bis 250;
Technologische Zusätze	0,5 bis 7,5

enthalten sind.

3. Feuerlöschmittel nach Anspruch 1, **dadurch gekennzeichnet, daß** es als technologische Zusätze ein Schmieröl, ein Salz einer Fettsäure, z.B. Natrium- oder Zinkstearat, oder ein Gemisch des Salzes mit Sulforizinat und Gelatin enthält.
4. Feuerlöschmittel nach Anspruch 1, **dadurch gekennzeichnet, daß** als Verbrennungsmodifikator es einen Katalysator und/oder einen Inhibitor und ein Kühlmittel enthält.
5. Feuerlöschmittel nach Anspruch 4, **dadurch gekennzeichnet, daß** die wärmeaufnehmende Zusammensetzung eine wärmeaufnehmende Komponente, ein Bindemittel und Zusätze im folgenden Verhältnis, Gewichtsteile:

Wärmeaufnehmende Komponente	50 bis 80;
Bindemittel	10 bis 35;
Zusätze	1 bis 7

enthält.

6. Feuerlöschmittel nach Anspruch 5, **dadurch gekennzeichnet, daß** es als Bindemittel ein Zelulosederivat, einen niedrigflüchtigen Weichmacher und Polyvinylazetat oder Polyvinylalkohol im folgenden Verhältnis, Gewichtsteile:

Zelulosederivat und Niedrigflüchtiger Weichmacher	9 bis 34;
Polyvinylazetat oder Polyvinylalkohol	1 bis 5

enthält.

7. Feuerlöschmittel nach Anspruch 5, **dadurch gekennzeichnet, daß** es basische Karbonate oder Phosphate von Metallen der II. Gruppe, deren Kristallhydrate oder Hydroxide von Metallen der III. Gruppe oder deren Gemische als wärmeaufnehmende Komponente enthält.
8. Feuerlöschmittel nach Anspruch 5, **dadurch gekennzeichnet, daß** es ein Schmieröl, Natrium- oder Zinkstearat, siliziumorganische Verbindungen, Ölsäure als Zusätze enthält.
9. Feuerlöschmittel nach Anspruch 4, **dadurch gekennzeichnet, daß** es als Katalysator eine Verbindungen, ausgewählt aus der Gruppe, bestehend aus Oxiden von Metallen veränderlicher Valenz, deren organischen oder anorganischen Verbindungen oder deren Gemischen, enthält.
10. Feuerlöschmittel nach Anspruch 4, **dadurch gekennzeichnet, daß** es als Inhibitor eine Verbindungen, ausgewählt aus der Gruppe, bestehend aus anorganischen oder organischen phosphor- und/oder stickstoffhaltigen Verbindungen, Hydroxiden von Metallen der III. Gruppe, Boraten oder Karbonaten von Metallen oder deren Gemisch enthält.

Revendications

1. Moyen d'extinction du feu formant l'aérosol comprenant un extincteur de flamme, un combustible-liant, une source de carbone, un stabilisateur, un modificateur de combustion et des additifs technologiques, ledit moyen comprend comme extincteur de flamme des nitrates des métaux alcalins ou leur mélange avec composition complexe des métaux alcalins, comme source de carbone le carbone comme tel, des alcools aliphatiques ou aromatiques ou leur mélange, **caractérisé en ce que** comme modificateur de combustion il comprend un agent de refroidissement

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choisi parmi des oxydes ou des hydroxydes des métaux du groupe II, des aluminosilicates, la néphéline ou la paille de fer ou leurs mélanges ou bien une composition thermoabsorbante, en combinaison avec compositions choisies parmi des glycols ou la glycérine comme additifs technologiques.

- 5 2. Moyen selon la revendication 1, **caractérisé en ce qu'il** contient les ingrédients dans les proportions suivantes, parties en masse:

extincteur de flamme	40 - 80
combustible - liant	12 - 40
source de carbone	1 - 5
modificateur de combustion	1 - 250
additifs technologiques	0,5 - 7,5

- 15 3. Moyen selon la revendication 1, **caractérisé en ce que** comme additifs technologiques il contient l'huile de graissage, un sel de l'acide gras, par exemple, le stéarate de sodium ou de zinc, ou bien un mélange du sel avec le sulforicinate et la gélatine.

- 20 4. Moyen selon la revendication 1, **caractérisé en ce que** comme modificateur de combustion il contient un catalyseur et/ ou un inhibiteur et un agent de refroidissement.

5. Moyen selon la revendication 4, **caractérisé en ce que** la composition thermoabsorbante comprend un composant thermoabsorbant, un liant et des additifs dans les proportions suivantes, parties en masse:

composant thermoabsorbant	50 - 80
liant	10 - 35
additifs	1 - 7

- 30 6. Moyen selon la revendication 5, **caractérisé en ce que** comme liant il comprend un dérivé de la cellulose, un plastifiant peu volatil et un polyvinylacétate ou un alcool polyvinylique dans les proportions suivantes, parties en masse:

dérivé de la cellulose et plastifiant peu volatil	9 - 34
polyvinylacétate ou alcool polyvinylique	1 - 5

- 40 7. Moyen selon la revendication 5, **caractérisé en ce que** comme composant thermoabsorbant il contient des carbonates, des carbonates de la base et des phosphates des métaux du groupe II, leurs hydrates cristallisés ou bien des hydroxydes des métaux du groupe III ou leurs mélanges.

8. Moyen selon la revendication 5, **caractérisé en ce que** comme additif il contient l'huile de graissage, le stéarate de sodium ou de zinc, des silicones, l'acide oléique.

- 45 9. Moyen selon la revendication 4, **caractérisé en ce que** comme catalyseur il contient une composition choisie du groupe incluant des oxydes des métaux à valence variable, leurs compositions organiques ou minérales ou leurs mélanges.

- 50 10. Moyen selon la revendication 4, **caractérisé en ce que** comme inhibiteur il contient une matière choisie du groupe incluant des compositions minérales et organiques phosphorées et/ ou azotées, des hydroxydes des métaux du groupe III, des borates ou des carbonates des métaux ou leurs mélanges.