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(54) **AEROSOL-FORMING COMPOSITION FOR FIRE SUPPRESSION**

(57) An aerosol-forming composition for fire suppression contains alkali metal nitrate as an oxidant, a novolac-type phenol formaldehyde resin and an epoxide resin as a fuel/binder, a mixture of sodium carbonate and at least one alkali metal salt and carbonic acid as an additional fuel that simultaneously fulfills the function of a coolant, a gas-forming buffer component and a steam-regulating component, a mixture of magnesium hexacyanoferrate (II) ($\text{Mg}_2[\text{Fe}(\text{CN})_6]$) with cobalt (II) ni-

trate ($\text{Co}(\text{NO}_3)_2$) and with promoting additives of aluminum oxide and copper oxide as a combustion modifier. The proposed composition makes it possible to reduce the concentration of toxic substances in its combustion products, and also provides high thermodynamic stability and, as a result, heat resistance, impact resistance, moisture resistance and safety of use of the composition, including under severe climatic conditions.

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Description**Technical Field**

[0001] The invention relates to aerosol-forming compositions for volume fire-extinguishing and may be used to suppress fire at its seat in enclosed or partially enclosed spaces, as well as to prevent highly flammable liquid, combustible substance and material steam and aerosuspension combustion and explosion. Aerosol-forming compositions are widely used due to their high fire extinguishing efficiency at minimum fire extinguishing concentrations. Fire-extinguishing aerosol-based equipment, such as fire extinguishing generators, does not require continuous maintenance, may be mobile or fixed, are readily available for use, and retain their properties over a long time.

Background

[0002] All types of fire-extinguishing aerosol-forming compositions have in common the following components: an oxidant, a fuel/binder, an additional fuel, a coolant, catalysts, combustion modifiers, and various process additives. Pyrotechnic mixture combustion produces inhibitors in gaseous state and a disperse solid condensed phase containing salts, oxides, such as those of alkali and alkali-earth metals. When in a fire area, surface heterogeneous relaxation of excited flame atoms and molecules on the surface of these components' particles causes these components to act as combustion inhibitors, thus disrupting the chain reaction of reactive radical formation in the flame spread area.

[0003] The main issue with aerosol-based fire extinguishing systems is that aerosol-forming composition combustion products contain toxic gases, such as carbon oxide CO and ammonia NH₃, as well as high temperatures of pyrotechnic mixture aerosol products both inside and outside the generator. The compositions are essentially required to provide such performance characteristics as moisture and thermal resistance, charge strength, etc.

[0004] Aerosol-forming compositions for fire extinguishing have been known. For example, Patent US-B-7832493 (published 16.11.2010) describes an aerosol-forming fire-extinguishing composition comprising 62 to 72 wt.% of potassium nitrate as an oxidant, 8 to 12 wt.% of phenol formaldehyde resin as a fuel/binder, dicyandiamide as an additional fuel and a coolant to cool a gas/aerosol mixture during AFC burning.

[0005] However, a high toxicity level of combustion products of the composition described in Patent US-B-7832493 renders it unsuitable for fire extinguishing in enclosed spaces in the presence of people.

[0006] International Application WO2012/112037 A1 (published 23.08.2012) discloses a fire-extinguishing composition comprising an oxidant, an additional fuel and phenol formaldehyde resins, wherein the phenol formaldehyde resin molecule contains 3 or more aromatic ring structures. As such, the applicants state that, to achieve a low toxicity level, the phenol formaldehyde resin should contain more than 3 aromatic ring structures. However, the invention specification does not provide any experimental evidence of that. Gaseous phase composition was not measured either in a combustion chamber or at its outlet. Low levels of condensed phase toxicity in Example 3 in the International Application WO2012/112037 Specification were obtained by an experiment done with the composition placed in a fire-extinguishing generator containing no cooling elements; the combustion products were finally combusted under atmospheric conditions with the temperature of 1100°C and excess oxygen. High temperatures downstream of the fire-extinguishing generator discharge orifice or nozzle restrict the generator application areas. By using a polymeric fuel of high aromaticity level, carbon content in the composition is increased, resin thermal and temperature resistance is increased, coke formation is increased, thus increasing the carbon oxide content in thermal decomposition products (V. V. Korshak, Khimicheskoye stroenie i temperaturnye kharakteristiki polimerov (Chemical Constitution and Thermal Behavior of Polymers), M. Nauka, 1970, pages 295-308).

[0007] Patent RU2091106 (published 27.09.1997) discloses an aerosol-forming fire-extinguishing compound comprising (in wt.%): 45 to 75 of potassium nitrate, 4 to 11 of carbon, 0.5 to 2.0 of centralite and/or diphenylamine, 0.5 to 2.5 of industrial or instrument oil, zinc stearate and/or sodium stearate, or 0.02 to 0.5 of salts mixed with sulphonated castor oil and gelatin, 0.5 to 20.0 of a catalyst and/or a combustion inhibitor, and a plasticized cellulose derivative or a mixture thereof with a supplementary binding agent making up the balance. With the main ingredient of the composition being a plasticized cellulose derivative, including cellulose nitrate, explosive safety of the composition is substantially compromised. Furthermore, the combustion inhibitors cause the combustion products' coking residue to increase, thus reducing the fire extinguishing efficiency.

[0008] Patent RU2477163 (published 10.03.2013) discloses an aerosol-forming composition comprising (in wt.%): 1.5 to 18 of iditol as a fuel/binder, 3 to 25 of dicyandiamide (DCD) as a secondary fuel, 5.5 to 25 of full oxidation agents (iron oxide and copper oxide), and potassium nitrate as an oxidant making up the balance. It is stated that low toxicity characteristics were obtained upon combustion of a 1g caseless charge in the form of pellets under atmospheric conditions. Secondary redox reactions with atmospheric oxygen cause carbon oxide afterburning and increase the flame temperature: $2\text{CO} + \text{O}_2 = 2\text{CO}_2 + \text{Q}$. However, experiments show that the composition of Patent RU2477163 does not meet either Russian or international regulatory performance requirements, such as to thermal and moisture resistance,

due to the absence of thermally resistant or moisture repellent compositions in the formulation.

[0009] Patent RU2193429 (published 27.11.2002) discloses a composition comprising a finely dispersed coolant selected from the following range: aluminium hydroxide, and/or activated alumina, and/or activated aluminosilicate, and/or a mixture thereof, and/or a mixture thereof with clay or other inorganic binders. Mixing ratio (wt.%): 1.5 to 18.0 of fuel/binder, 3.0 to 25.0 of secondary fuel, 1.5 to 60.0 of coolant, 0.5 to 10.0 of additives, and an oxidant making up the balance. The secondary fuel is selected from the following range: guanidine, urea, dicyandiamide, melon, melem, melamine, urotropin, azobisformamide, semicarbazide, dihydro-glyoxime, tetrazole, di-tetrazole, derivatives or salts thereof. Oxidant: metal or ammonium nitrates or perchlorates, or mixtures thereof. Fuel/binder: polymers, resins, rubbers and/or mixtures thereof. Additives: metals, such as aluminum and/or magnesium, as individual components, or mixtures thereof, or alloys thereof. A redox catalyst in an amount of 0.05 to 5.00 wt.% is included into the coolant. The compositions referred to in Patent RU2193429 are manufactured to relevant specifications not described in the patent. However, preparing the composition includes mixing of its constituting components.

[0010] The beneficial results of reducing the toxicity of gases released upon the AFC combustion were accomplished by the inventors through using a finely dispersed coolant selected from the following range: aluminium hydroxide, and/or activated alumina, and/or activated aluminosilicate, and/or a mixture thereof and/or a mixture thereof with clay or other inorganic binders. However, the reduced toxicity level, accomplished as the result, is not sufficient; furthermore, such cooling system substantially reduces the fire extinguishing efficiency due to a high gas dynamic drag of the coolant finely dispersed particles and loss of a substantial portion of aerosol on them, as well as due to an increased amount of slag residue in the combustion chamber.

[0011] Prior art closest to the composition of the present Application is an aerosol-forming composition (AFC) for fire extinguishing disclosed in Patent RU2648081 (published 22.03.2018). The composition comprises an alkali metal nitrate as an oxidant, a novolac-type phenol formaldehyde resin and an epoxy resin as a fuel/binder, an alkali metal carboxylate as an additional fuel, also acting as a coolant, and a cobalt(II) nitrate as a combustion modifier, with an aluminium oxide and a copper oxide as promoting additives. The composition is produced by staged mixing of individual components: mixing of the oxidant with the additional fuel-coolant to produce a 1st mixture, separately mixing the cobalt nitrate with the aluminium oxide to produce a 2nd mixture, and separately preparing the epoxy resin by adding a solvent thereto and mixing it with a curing agent until a 3rd mixture is produced, then mixing together the 1st and 2nd mixture, followed by adding thereto the 3rd mixture; the mass so produced is mixed with the phenol formaldehyde resin and, simultaneously, with the copper oxide and dried at such a temperature as to cause the epoxy resin polymerization and to remove the solvent. The result of the invention is that concentrations of toxic substances in pyrotechnic composition combustion products may be reduced. However, due to increasingly stringent requirements to fire-extinguishing systems, there is a need for enhancing environmental performance and efficiency of aerosol-forming compositions.

Summary

[0012] Formation of toxic substances, mainly carbon dioxide and ammonia, in combustion products is due, primarily, to incomplete combustion of an aerosol-forming composition attributable to various factors associated with both the nature of the composition components and combustion conditions, the latter being affected by insufficient oxidant content in reaction zones, short presence of fuel in those zones, poorly burning carbonized layer formation on the composition surface, heat leakage to the environment.

[0013] The present invention is aimed at solving the technical problem of reducing toxic substances in combustion products of an aerosol-forming composition (AFC) for fire extinguishing in the AFC burning zone and, thus, downstream the nozzle exit (discharge orifice) of a fire-extinguishing aerosol generator comprising a coolant unit, to a level below immediately life-threatening concentrations, through modifying the combustion processes by acting on the mechanisms of phase interactions between chemical components both in the fuel oxidation reaction zone and in the fire-extinguishing aerosol generator coolant unit's region where gas phase reactions and catalytic processes occur.

[0014] The above problem is solved by providing an aerosol-forming composition for fire extinguishing, comprising an alkali metal nitrate as an oxidant, a novolac-type phenol formaldehyde resin and an epoxy resin as a fuel/binder, an additional fuel, and a combustion modifier, the composition *according to the present invention*, comprising, as an additional fuel, a mixture of sodium carbonate and an alkali metal carboxylate which also acts as a coolant, a gas-forming buffer component and a steam-regulating component, and comprising, as a combustion modifier, a mixture of magnesium hexacyanoferrate(II) ($\text{Mg}_2[\text{Fe}(\text{CN})_6]$) and cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2$), with an aluminium oxide and a copper oxide as promoting additives, at the following mixing ratio (wt.%):

fuel/binder 4 - 11,

additional fuel/coolant 6 - 12,

combustion modifier 6- 16,
oxidant to balance.

[0015] More specifically, the mixing ratio (wt.%) of the present composition is as follows:

fuel/binder 4 - 11,
alkali metal carboxylate 5 - 11,
sodium carbonate 1 - 3
magnesium hexacyanoferrate 1 - 5
cobalt nitrate 1 - 5,
aluminium oxide 1 - 3,
copper oxide 1 - 3,
oxidant to balance.

[0016] As the alkali metal nitrate, the composition comprises: lithium nitrate, or sodium nitrate, or potassium nitrate, preferably potassium nitrate; as the alkali metal carboxylate, it comprises, for example, potassium fumarate, or potassium phthalate, or potassium benzoate, or a mixture thereof in any combination; as the hard novolac-type phenol formaldehyde resin, it comprises, for example, an SF-0112, and, as the epoxy resin, it comprises, for example, ED-20 or D.E.R.-331.

[0017] The method for producing the composition of the present invention is similar to the multistage method for producing the aerosol-forming composition for fire extinguishing as described in Patent RU2648081, except that a mixture of sodium carbonate and an alkali metal carboxylate is used to produce the 1st mixture as an additional fuel and, to produce the 2nd mixture, cobalt nitrate is mixed with the aluminium oxide and magnesium hexacyanoferrate.

[0018] A solvent, for example, ethanol, or acetone, or ethyl acetate, or a mixture of acetone and ethyl acetate, was used as the process additives, and the epoxy resin was mixed with the solvent at a ratio of approximately 10:1.

[0019] In particular embodiments, the phenol formaldehyde resin (PFR) and the epoxy resin (ER) were used at a ratio between 1:1 and 1:3.

[0020] The essence of the invention is that a reduced ammonia content upon AFC combustion is accomplished by including sodium carbonate into the secondary fuel, while a reduced toxic gas concentration is accomplished by including magnesium hexacyanoferrate into the combustion modifier, thus enhancing, as compared to the prior art composition, the modifying effect on combustion not only directly in the reaction zone, but also in the fire-extinguishing generator cooler location region.

[0021] Experiments proved that, with a magnesium hexacyanoferrate content of less than 1 wt.% in the composition, carbon monoxide concentration substantially increases, such as by more than 40%, while with a concentration of more than 5 wt.%, ammonia concentration in combustion products increases up to 65%. This data is given in Table 1 as Examples 11, 12. A minimum ammonia concentration in combustion products is achieved with a sodium carbonate content in the composition of 1 to 3 wt.%. Higher sodium carbonate contents degrade the compositions' performance characteristics, for example, increase its hygroscopicity, while lower contents do not allow accomplishing the required result, i.e. reduced ammonia concentration.

[0022] Another beneficial effect on the present composition's properties is further provided by that the epoxy resin reacts with the novolac-type phenol formaldehyde resin during mixing to produce a homogenous self-curing system that contains a co-oligomerization product (epoxy/novolac block copolymer) and confers high thermal and moisture resistance properties to the composition.

[0023] The technical result provided by the present invention consists in a more stable combustion rate, reduced toxic gas concentration downstream the fire-extinguishing aerosol generator nozzle exit, reduced temperature in the active burning zone and, therefore, that of the aerosol spray, increased thermal resistance and gas formation properties of the composition, and, thereby, enhanced fire extinguishing efficiency and performance characteristics of the aerosol-forming composition (AFC).

[0024] The aerosol-forming composition of the present invention, while providing substantially reduced combustion product toxicity and enhanced fire extinguishing efficiency, features high thermodynamic stability and, thereby, high thermal resistance, impact resistance, moisture resistance and operational safety even in severe climatic conditions.

[0025] The invention will be better understood from the following specific examples of producing an aerosol-forming composition for fire extinguishing according to the present invention.

Detailed Description of Example Embodiments

[0026] The composition of the present invention is produced by using:

- lithium nitrate (CAS 7790-69-4), sodium nitrate (CAS 7631-99-4), potassium nitrate (CAS 7757-79-1) as an oxidant;
- phenol formaldehyde resin (hereinafter the 'PFR') SF-0112 (to GOST 18694- 80) or CAS 103-16-20 as a fuel/binder;
- epoxy diane resin type ED-20 (to GOST 10587-84) or D.E.R.-331 (CAS 25068-38-6) - as a fuel/binder;
- potassium fumarate (CAS 7704-72-5), or potassium phthalate (CAS 877-24-7), or potassium benzoate ($\text{KC}_7\text{H}_5\text{O}_2$) (CAS 582-25-2), or a mixture thereof in any combination, and sodium carbonate Na_2CO_3 (CAS 497-19-8), as an additional fuel/buffer gas forming component and a steam methane reforming inhibitor;
- cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2$) (CAS 10026-22-9) and magnesium hexacyanoferrate(II) (CAS 38192-52-8) as a modifier;
- aluminium oxide (Al_2O_3) (CAS 1344-28-1) as a promoting additive;
- copper oxide (CuO) (CAS 1317-38-0) as a promoting additive;
- ethyl acetate (CAS 141-78-6), or acetone (CAS 67-64-1), ethanol (CAS 64-17-5), or a mixture of acetone and ethyl acetate may be used, as a process additive, i.e. an epoxy resin solvent.

[0027] The aerosol-forming composition for fire extinguishing according to the present invention is produced as follows:

Stage 1: lithium nitrate, or sodium nitrate, or potassium nitrate are mixed dry with sodium carbonate and then with potassium benzoate, or potassium fumarate, or potassium phthalate until a homogenous mixture is produced (a 1st mixture);

Stage 2: separately, cobalt nitrate $\text{Co}(\text{NO}_3)_2$ is mixed dry with aluminium oxide Al_2O_3 and with magnesium hexacyanoferrate until a mixture of uniform color is produced (a 2nd mixture);

Stage 3: epoxy and phenol formaldehyde resins are mixed and a solvent is added until a homogenous mass is produced (a 3rd mixture);

Stage 4: the masses produced at Stages 1, 2, 3 are mixed together and, simultaneously, with copper oxide;

Stage 5: the mass produced at Stage 4 is dried at such a temperature as to cause copolymerization of the epoxy resin with the phenol formaldehyde resin and residual solvent removal to produce, upon the system self-curing, a co-oligomerization product (an epoxy/novolac block copolymer) which is the composition of the present invention.

[0028] To use the composition of the present invention in a fire-extinguishing aerosol generator (a fire-extinguishing generator), granules are formed from the mass so produced, which are then formed into pellets of such shape, density and sizes as to suite the thermodynamic, intraballistic and gas dynamic parameters of the fire-extinguishing aerosol generator into which they will be charged, as well as the technical requirements to the use of that generator. The latter is due to the fact that the pellet shape (for example, round, romboid, starlike, etc.) determines the total surface area of the aerosol-forming composition, which, together with its chemical composition, pellet density and the generator design parameters, determine, in accordance with the burning law, the composition thermal decomposition rate and, therefore, the gas discharge, aerosol spray pressure, temperature and rate of aerosol spray outflow from the generator, thereby influencing the generator's fire extinguishing capabilities.

[0029] In view of the above, at Stage 6, granules are formed from the mass produced at Stage 5, for example, by passing the mass through a screen with a predetermined aperture size, for example, 0.5 to 4.0 mm.

[0030] At Stage 7, products are formed, for example, by compressing the granules into pellets of predetermined shape, density and strength on which the required performance characteristics of the subject fire-extinguishing generator and

thermal and gas dynamic parameters in its combustion chamber depend.

[0031] Example 1. An aerosol-forming composition of the present invention was produced by using 72 g of potassium nitrate, 2 g of sodium carbonate, 2 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED-20, 10 g of potassium benzoate, 3 g of cobalt(II) nitrate, 2 g of aluminium oxide, 4 g of magnesium hexacyanoferrate, 1 g of copper oxide, 0.4 g of ethyl acetate.

[0032] Said components in said quantities were mixed in a staged manner as follows:

First (Stage 1), potassium nitrate, sodium carbonate and potassium benzoate were mixed dry until a homogenous mixture was produced (the 1st mixture). Then (Stage 2), cobalt nitrate was mixed dry with aluminium oxide and magnesium hexacyanoferrate until a homogenous mixture was produced (the 2nd mixture). Following that (Stage 3), epoxy and phenol formaldehyde resins were mixed with a solvent until a homogenous mass was produced (the 3rd mixture). Then (Stage 4), the masses produced at Stages 1, 2 and 3 were mixed together and, simultaneously, with copper oxide. The mass produced at Stage 4 was dried (Stage 5) at 70°C to cause copolymerization of the mixture and to remove residual solvent. As the result, a mass with the weight of 100 g was produced. To improve process (for example, flowing) properties of the composition, granules were formed (Stage 6) from the mass produced at Stage 5, for example, by passing the mass through a screen with a predetermined aperture size, specifically, 1.0 mm, from which (Stage 7) pellets were formed, specifically, by compressing them by a press at a unit pressure of 900 kg/cm².

[0033] Combustion products of the aerosol-forming composition of the present invention were tested for toxic gas, such as carbon oxide CO and ammonia NH₃, content in Fire-Extinguishing Generators FP-100S (<http://www.fire-pro.hu/en/products/small-to-medium-units/fp-100s>, Russian Certificate of Conformity No. C-CY ПБ04.B.0260). The generator design enables using an aerosol-forming product in an amount of about 100g and provides for a coolant unit charged with a coolant comprising sphere-shaped elements 5 to 7 mm in diameter made of CB-6 aluminium oxide (manufactured by Zibo Zhengsen Chemical Co., Ltd) in an amount of about 125 g.

[0034] The tests were done at a test facility, in a chamber with an approximate volume of 1m³. Toxic gas concentrations were measured using a Dräger Tubes Measurement System Gas Detector, an Accuro Pump, Detection Tubes 0.3%B (CH 29901) for carbon dioxide and 5/a (CH 20501) for ammonia.

[0035] Carbon dioxide and ammonia concentrations were further analyzed using a Dräger X-am 7000 detector with CATEX (catalytic) sensors and EC (electrochemical) sensors.

[0036] The compositions' physical and mechanical properties were analyzed by standard methods: thermal resistance under EN 60068-2, hygroscopicity under Standard MIL-STD-286C (Method 503.1.3), hardness under Standard EN ISO 2039-1.

[0037] The obtained toxic gas concentrations are given in Table 1 under Number 1. Comparative physical and mechanical properties of the composition according to Example 1 are given in Table 2.

[0038] Example 2. An aerosol-forming composition of the present invention was produced by using 70 g of potassium nitrate, 3 g of sodium carbonate, 3 g of phenol formaldehyde resin SF-0112, 5 g of diene resin ED-20, 8 g of potassium fumarate (CAS 582-25-2), 2 g of cobalt(II) nitrate, 3 g of aluminium oxide, 1 g of copper oxide, 5 g of magnesium hexacyanoferrate, 0.5 g of ethyl acetate. The composition was prepared as described in Example 1, except for Stage 1, wherein potassium nitrate was mixed with sodium carbonate and potassium fumarate. Finally, a mass with the weight of 100 g was produced. Toxic gas concentrations upon combustion of the claimed composition were tested as described in Example 1. The obtained results are given in Table 1 under Number 2.

[0039] Example 3. An aerosol-forming product composed in accordance with the present invention was produced by using 73 g of potassium nitrate, 3 g of sodium carbonate, 3 g of phenol formaldehyde resin SF-0112, 5 g of diene resin ED-20, 8 g of potassium phthalate, 1 g of cobalt(II) nitrate, 2 g of aluminium oxide, 3 g of magnesium hexacyanoferrate, 2 g of copper oxide, 0.5 g of ethyl acetate. The composition was prepared as described in Example 1, except for Stage 1, wherein potassium nitrate was mixed with sodium carbonate and potassium phthalate. Finally, a mass with the weight of 100 g was produced. Toxic gas concentrations upon combustion of the claimed composition were tested as described in Example 1. The obtained results are given in Table 1 under Number 3.

[0040] Example 4. An aerosol-forming product composed in accordance with the present invention was produced by using 68 g of potassium nitrate, 2 g of sodium carbonate, 4 g of phenol formaldehyde resin SF-0112, 7 g of diene resin ED-20, 10 g of potassium benzoate, 4 g of cobalt(II) nitrate, 2 g of aluminium oxide, 1 g of magnesium hexacyanoferrate, 2 g of copper oxide, 0.7 g of ethyl acetate. The composition was prepared as described in Example 1, except for Stage 1, wherein potassium nitrate was mixed with sodium carbonate and potassium benzoate. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the produced composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 4.

[0041] Example 5. An aerosol-forming product composed in accordance with the present invention was produced by using 75 g of potassium nitrate, 1 g of sodium carbonate, 4 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED-20, 8 g of potassium benzoate, 3 g of cobalt(II) nitrate, 2 g of aluminium oxide, 2 g of magnesium hexacyanoferrate, 1 g of copper oxide, 0.4 g of ethyl acetate. The composition was prepared as described in Example 1, except for Stage

1, wherein potassium nitrate was mixed with sodium carbonate and potassium benzoate. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 5.

[0042] Example 6. To test physical and mechanical properties of a prior art composition, a composition was produced in accordance with that described in Example 1 of the invention of RF Patent 2468081 (the 'prior art composition'), comprising 72 g of potassium nitrate, 3 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED-20, 12 g of potassium benzoate, 5 g of cobalt(II) nitrate, 2 g of aluminium oxide and 2 g of copper oxide.

[0043] It was produced by using 72 g of potassium nitrate, 3 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED-20, 12 g of potassium benzoate, 5 g of cobalt(II) nitrate, 2 g of aluminium oxide, 2 g of copper oxide; 4 g of ethyl acetate and 0.4 g of triethylene tetramine (TETA).

[0044] Said components in said quantities were mixed in a staged manner entirely in accordance with the technique described in Example 1 of RU 2468081 Patent Invention Specification.

[0045] Physical and mechanical properties of the above composition, same as those of the claimed composition of Example 1, were analyzed by standard methods: thermal resistance under EN 60068-2, hygroscopicity under Standard MIL-STD-286C (Method 503.1.3), hardness under Standard EN ISO 2039-1

[0046] Comparative physical and mechanical properties of the composition according to Example 6 are given in Table 2.

[0047] Furthermore, Table 1 provides, under Number 6, the results related to the prior art composition (Patent RU2468081) in terms of the toxic gas content upon combustion of the prior art AFC, as given under Number 71 in a table of Patent RU2468081, and those corresponding to the composition described in Example 1 of the invention of said patent (prior art composition) and containing 72 g of potassium nitrate, 3 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED-20, 12 g of potassium benzoate, 5 g of cobalt(II) nitrate, 2 g of aluminium oxide and 2 g of copper oxide.

[0048] Example 7. An aerosol-forming composition of the present invention was produced by using 74 g of potassium nitrate, 1 g of sodium carbonate, 2 g of phenol formaldehyde resin SF-0112, 4 g of diene resin ED- 20, 11 g of potassium benzoate, 2.5 g of cobalt(II) nitrate, 1 g of aluminium oxide, 1.5 g of copper oxide, 3 g of magnesium hexacyanoferrate, 0.4 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 7.

[0049] Example 8. An aerosol-forming composition of the present invention was produced by using 75 g of potassium nitrate, 2 g of sodium carbonate, 3 g of phenol formaldehyde resin SF-0112, 5 g of diene resin ED- 20, 9 g of potassium benzoate, 2 g of cobalt(II) nitrate, 1 g of aluminium oxide, 1 g of copper oxide, 2 g of magnesium hexacyanoferrate, 0.4 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition according to this Example was tested as described in Example 1. The obtained results are given in Table 1 under Number 8

[0050] Example 9. An aerosol-forming composition of the present invention was produced by using 70 g of potassium nitrate, 2 g of sodium carbonate, 2 g of phenol formaldehyde resin SF-0112, 2 g of diene resin ED- 20, 8 g of potassium benzoate, 5 g of cobalt(II) nitrate, 3 g of aluminium oxide, 3 g of copper oxide, 5 g of magnesium hexacyanoferrate, 0.2 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition according to Example 9 was tested as described in Example 1. The obtained results are given in Table 1 under Number 9.

[0051] Table 2 provides certain physical and mechanical properties of the composition produced in accordance with Example 9, which are typical for the claimed composition. By way of comparison, there are also provided the physical and mechanical properties of the prior art composition (Example 6). The measuring methods are given in Example 1.

[0052] Example 10. An aerosol-forming composition of the present invention was produced by using 73 g of potassium nitrate, 2 g of sodium carbonate, 4 g of phenol formaldehyde resin SF-0112, 7 g of diene resin ED- 20, 5 g of potassium benzoate, 5 g of cobalt(II) nitrate, 3 g of aluminium oxide, 3 g of copper oxide, 4 g of magnesium hexacyanoferrate, 0.7 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 10.

[0053] Example 11. An aerosol-forming composition was produced by using 75 g of potassium nitrate, 8 g of potassium benzoate, 0.5 g of magnesium hexacyanoferrate, 2 g of sodium carbonate, 3 g of phenol formaldehyde resin SF-0112, 1 g of diene resin ED-20, 4.5 g of cobalt(II) nitrate, 3 g of aluminium oxide, 3 g of copper oxide, 0.1 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic gas content upon combustion of the composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 11.

[0054] Example 12. An aerosol-forming composition was produced by using 70 g of potassium nitrate, 7 g of potassium benzoate, 6 g of magnesium hexacyanoferrate, 2 g of sodium carbonate, 3 g of phenol formaldehyde resin SF-0112, 1 g of diene resin ED-20, 5 g of cobalt(II) nitrate, 3 g of aluminium oxide, 3 g of copper oxide, 0.1 g of ethyl acetate. The composition was prepared as described in Example 1. Finally, a mass with the weight of 100 g was produced. Toxic

gas content upon combustion of the composition was tested as described in Example 1. The obtained results are given in Table 1 under Number 12.

Industrial Applicability

[0055] The provided specific example embodiments demonstrate that the present invention can be carried out and can provide the stated result, i.e. reducing, by more than 2 times as compared with the prior art composition, the ammonia and carbon oxide content in aerosol-forming composition combustion products in the environment downstream the nozzle exit (discharge orifice) of a fire-extinguishing generator.

[0056] According to the present invention, the efficient toxic gas concentration reduction is accomplished by the inventors by combining cobalt(II) nitrate with magnesium hexacyanoferrate and promoting additives, i.e. aluminium oxide and copper oxide, thereby enhancing their modifying effect on combustion processes not only directly in the reaction zone, but also in the fire-extinguishing aerosol generator cooler location region, and, as a result, promoting the processes of direct oxidation and carbon oxide conversion to dioxide.

[0057] The composition of the present invention comprising a novel combustion modifier composition, a novel secondary fuel composition which also acts as a coolant and a buffer gas forming component, a modified fuel/binder with characteristics of a block copolymer, while providing reduced combustion product toxicity and enhanced fire extinguishing efficiency, features high thermodynamic stability and, thereby, high thermal resistance, impact resistance, moisture resistance and operational safety even in severe climatic conditions.

TABLE 1. Results of Toxic Gas Concentration Measurements in Aerosol-Forming Composition Combustion Products

Composition No.	Aerosol-Forming Composition Components (wt.%)										Toxic Gases (ppm)	
	Potassium nitrate	Potassium benzoate	Potassium fumarate	Potassium phthalate	Mg ₂ [Fe(CN) ₆]	Na ₂ CO ₃	Co(N ₂ O ₃) ₂	CuO	Al ₂ O ₃	PFR+ER	CO,	NH ₃ ,
1	2	3	4	5	6	7	8	9	10	11	12	13
1	72	10			4	2	3	1	2	6	850	45
2	70		8		5	3	2	1	3	8	800	40
3	73			8	3	3	1	2	2	8	880	42
4	68	10			1	2	4	2	2	11	980	45
5	75	8			2	1	3	1	2	8	910	50
6	72	12					5	2	2	7	2500	100
7	74	11			3	1	2.5	1.5	1	6	880	51
8	75	9			2	2	2	1	1	8	910	46
9	70	8			5	2	5	3	3	4	800	43
10	73	5			4	1	3	1	2	11	850	50
11	75	8			0.5	2	4.5	3	3	4	1100	43
12	70	7			6	2	5	3	3	4	830	65
* Immediately life-threatening concentrations of toxic gases (ppm)											3000	5000
Table Legend: PFR is Phenol Formaldehyde Resin, ER is Epoxy Resin *Vrednye veshchestva v promyshlennosti. Spravochnik dlya khimikov, inzhenerov i vrachey. Tom III. Neorganicheskie i elementoorganicheskie soedineniya (Harmful Substances in Industrial Environments. A Reference Book for Chemical Industry Workers, Engineers and Physicians. Volume III. Inorganic and Organoelement Compounds). Leningrad, Khimiya, 1997. https://de.wikipedia.org/wiki/Ammoniak												

TABLE 2. Comparative Physical and Mechanical Properties of Aerosol-Forming Compositions

Properties	Thermal Resistance,	Hygroscopicity (%)	Brinell Hardness (kg/mm ²)
Measured parameters and experimental conditions	EN 60068-2 Standard Weight loss (%), 504 h, 60°C	MIL-STD-286C Standard, Method 503.1.3 Temperature 54°C, 240 h, Relative humidity 95%	EN ISO 2039-1 Standard Temperature 20C°
Claimed composition Example 1	0.03	0.1	30
Example 9	0.04	0.12	28
Example 6 Composition of Example 1 described in Patent RU2468081 (prior art composition)	0.15	0.9	13

Claims

1. An aerosol-forming composition for fire extinguishing, comprising an alkali metal nitrate as an oxidant, a novolac-type phenol formaldehyde resin and an epoxy resin as a fuel/binder, an additional fuel, and a combustion modifier, **characterized in that** it comprises, as a additional fuel, a mixture of sodium carbonate and an alkali metal carboxylate which also acts as a coolant, a gas-forming buffer component and a steam-regulating component, and comprising, as a combustion modifier, a mixture of magnesium hexacyanoferrate (II) ($Mg_2[Fe(CN)_6]$) and cobalt(II) nitrate ($Co(NO_3)_2$), with an aluminium oxide and a copper oxide as promoting additives, at the following mixing ratio (wt.%):

fuel/binder 4 - 11,
additional fuel 6 - 12,
combustion modifier 6 - 16,
oxidant to balance.
2. The aerosol-forming composition of Claim 1, **characterized in that** it comprises components at the following ratio (wt.%):

fuel/binder 4 - 11,
alkali metal carboxylate 5 - 11,
sodium carbonate 1 - 3,
magnesium hexacyanoferrate 1 - 5,
cobalt nitrate 1 - 5,
aluminium oxide 1 - 3,
copper oxide 1 - 3,
oxidant to balance.
3. The aerosol-forming composition of Claim 1, **characterized in that** it comprises, as the alkali metal nitrate, lithium nitrate, or sodium nitrate, preferably potassium nitrate.
4. The aerosol-forming composition of Claim 1, **characterized in that** it comprises, as the alkali metal carboxylate, for example, potassium fumarate, or potassium phthalate, or potassium benzoate, or a mixture thereof in any combination.
5. The aerosol-forming composition of Claim 1, **characterized in that** it comprises, as the novolac-type phenol formaldehyde resin, for example, SF-0112, and comprises, as the epoxy resin, for example, ED-20 or D.E.R.-331.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/RU 2019/000435

5	A. CLASSIFICATION OF SUBJECT MATTER		
	A62D1/06 (2006.01)		
	According to International Patent Classification (IPC) or to both national classification and IPC		
	B. FIELDS SEARCHED		
10	Minimum documentation searched (classification system followed by classification symbols)		
	A62 D1/00, A62D 1/06, C06D 5/00, C06D 5/06		
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
	EAPATIS, ESPACENET, PatSearch (RUPTO internal), Information Retrieval System of FIPS, USPTO, PATENTSCOPE, Google Patents		
	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
20	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	A, D	RU 2648081 C1 (SELANOVA LIMITED) 22.03.2018	1-5
25	A	RU 2101054 C1 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "TEKHNO-TM") 10.01.1998	1-5
	A	RU 2248233 C1 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "TEKHNO-TM") 20.03.2005	1-5
30	A	EA 199800774 A1 (ZAKRYTOE AKTSIONERNOE OBSHCHESTVO "SANSAR") 24.06.1999	1-5
	A	WO 2000/048683 A1 (PRIMEX AEROSPACE COMPANY et al.) 24.08.2000	1-5
35			
40	<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> 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 "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		
50	Date of the actual completion of the international search		Date of mailing of the international search report
	28 January 2020 (28.01.2020)		19 March 2020 (19.03.2020)
	Name and mailing address of the ISA/ RU		Authorized officer
55	Facsimile No.		Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 7832493 B [0004] [0005]
- WO 2012112037 A1 [0006]
- WO 2012112037 A [0006]
- RU 2091106 [0007]
- RU 2477163 [0008]
- RU 2193429 [0009]
- RU 2648081 [0011] [0017]
- RU 2468081 [0042] [0044] [0047] [0057]

Non-patent literature cited in the description

- **V. V. KORSHAK.** Khimicheskoye stroenie i temperaturnye kharakteristiki polimerov (Chemical Constitution and Thermal Behavior of Polymers). 1970, 295-308 [0006]
- **CHEMICAL ABSTRACTS**, 7790-69-4 [0026]
- **CHEMICAL ABSTRACTS**, 7631-99-4 [0026]
- **CHEMICAL ABSTRACTS**, 7757-79-1 [0026]
- **CHEMICAL ABSTRACTS**, 103-16-20 [0026]
- **CHEMICAL ABSTRACTS**, 25068-38-6 [0026]
- **CHEMICAL ABSTRACTS**, 7704-72-5 [0026]
- **CHEMICAL ABSTRACTS**, 877-24-7 [0026]
- **CHEMICAL ABSTRACTS**, 582-25-2 [0026] [0038]
- **CHEMICAL ABSTRACTS**, 497-19-8 [0026]
- **CHEMICAL ABSTRACTS**, 10026-22-9 [0026]
- **CHEMICAL ABSTRACTS**, 38192-52-8 [0026]
- **CHEMICAL ABSTRACTS**, 1344-28-1 [0026]
- **CHEMICAL ABSTRACTS**, 1317-38-0 [0026]
- **CHEMICAL ABSTRACTS**, 141-78-6 [0026]
- **CHEMICAL ABSTRACTS**, 67-64-1 [0026]
- **CHEMICAL ABSTRACTS**, 64-17-5 [0026]
- Vrednye veshchestva v promyshlennosti. *Spravochnik dlya khimikov, inzhenerov i vrachey. Tom III. Neorganicheskie i elementoorganicheskie soedinenia*, vol. III [0057]
- Harmful Substances in Industrial Environments. A Reference Book for Chemical Industry Workers, Engineers and Physicians. Volume III. Inorganic and Organoelement Compounds. vol. III [0057]
- **LENINGRAD.** *Khimiya*, 1997, <https://de.wikipedia.org/wiki/Ammoniak> [0057]