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MODIFICATION OF PYROTECHNIC COMPOSITION TO EFFECTIVELY NEUTRALIZE ACIDIC AND CHEMICALLY HAZARDOUS ATMOSPHERIC PRECIPITATION

In this article the problem of reducing environmental hazards of the region from acid rain and emissions of chlorine and phosgene in emergency situations of anthropogenic nature has been solved. For this purpose, a new composition of the pyrotechnic charge capable under certain conditions to initiate precipitation and to neutralize their acidity has been developed. Various modifications of the developed composition lead to active sedimentation of both supercooled clouds and clouds with a temperature above 12 °C. The main pyrotechnic properties of the developed composition have been checked experimentally. It is shown that additive of cellulose allows to obtain an additional amount of alkali in the combustion component of pyrotechnic composition and to an increase in the degree of neutralization of the acidity of the sediments. For the purpose to increase the degree of neutralization of highly toxic gases – chlorine and phosgene, modification of pyrotechnic composition with sodium hydroxide addition is offered. A method is proposed for neutralizing chlorine and phosgene by inoculating the zone of contamination with sodium alkali using light aviation.

Keywords: atmospheric precipitation, pyrotechnic composition, acid rain, chemical neutralization, the initiation of precipitation.

Problem statement. At emergence of scale technogenic accidents the huge amount of dangerous chemicals gets to the atmosphere. The structure and physical and chemical properties of these substances depend by nature and a history of technogenic accidents. Thus, large natural and technogenic catastrophes are the reason of larger damages and the human victims and the environmental degradation situation in the region.

Atmospheric precipitation over the pollution territory significantly accelerates process of the atmosphere cleaning. There is a need to increase intensity of process cleaning. It can be carried out due to introduction to the atmosphere of express chemical reagents which increase the speed of a sorption of dangerous particles drops of a rain or neutralize their negative impact. Because various poisoning and radioactive substances significantly differ on the physical and chemical properties, chemical reagents efficiently can influence only a particular class of pollutants with similar properties. As a result of the major natural and technogenic fire the widest range of various dangerous substances gets to the atmosphere. Therefore, development of express pyrotechnic compositions which are capable to simulated initiation of precipitation and to neutralization of negative effect of pollutants is a topical task.

Analysis of the recent researches and publications. The qualitative and quantitative structure of combustion gases significantly depends on a type of combustible substance and combustion conditions (temperature, concentration of an oxidizer and a reducer). Principal components of combustion gases are CO_2, CO, NO, NO_2, SO_2, soot and ashes [1-3]. It is known that an atmospheric precipitation is capable to occlude efficiently dangerous chemical and radioactive substances. Also, an precipitation can besiege these substances from the atmosphere [4–6]. Intensity of cleaning of the atmosphere with settlings depends on intensity of precipitation and physical and chemical properties of the besieged substances [7, 8]. Various reagents are used for simulated initiation of precipitation. Use of pyrotechnic compositions in the form of aerosol generators or pyros [9] is the most efficient solution of delivery and dispersion of reagents. However, the existing structures of pyros cannot be used for neutralization of negative effect of pollutants.

Statement of the problem and its solution. The purpose of work is development of the pyrotechnic composition having properties of initiation of an atmospheric precipitation and neutralizations of their acidity and the contained toxiferous components.

Among light-end products of combustion CO, NO, NO_2, SO_2 have the greatest reactivity. At hit in the atmosphere these combustion gases react with atmospheric gases. The lower troposphere, except H_2O, O_2 and rather inert CO_2 and N_2, contains highly active radicals – hydroxyl $HO^{\bullet}$, gydro-peroxide $HO_2^{\bullet}$ and NO_3 [10] nitrate ions. Such radicals appear in the atmosphere under the influence of an ultra-violet radiation, and, therefore, their concentration increases with height. However due to the high activity they have significant effect on chemical processes and in the lower troposphere. Reactive components of combustion gases react with radicals according to the following schemes:

$$CO + HO^{\bullet} \rightarrow CO_2 + H^{\bullet}; \quad (1)$$

$$CO + HO_2^{\bullet} \rightarrow CO_2 + HO^{\bullet}; \quad (2)$$

$$NO + HO^{\bullet} \rightarrow NO_2 + H^{\bullet}; \quad (3)$$

$$NO + HO_2^{\bullet} \rightarrow NO_2 + HO^{\bullet}; \quad (4)$$

$$NO_2 + HO^{\bullet} \overrightarrow{\leftarrow} HNO_3; \quad (5)$$

$$NO_2 + NO_3^{-} \overrightarrow{\leftarrow} N_2O_5; \quad (6)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3; \quad (7)$$

$$SO_2 + HO^{\bullet} \rightarrow HSO_3^{\bullet}; \quad (8)$$

$$HSO_3^{\bullet} + O_2 \rightarrow SO_3 + HO_2^{\bullet}; \quad (9)$$

$$SO_3 + H_2O \rightleftarrows H_2SO_4. \quad (10)$$

Apparently from the equations of reactions (1)–(10), as a result of chemical transformations of NO, NO_2, SO_2 in the atmosphere nitric and sulfuric acids have been formed. These acids are occluded by water microdrops. Aqueous solutions drops of acids prolapses out at particular weather conditions that does essential harm to crops and other vegetation. Proceeding from it the acid removal method until its hit on the Earth's surface due to dispersion of finely divided alkali has been offered one of methods of fight against acid settlings. Introduction to the atmosphere of finely divided alkali can be carried out due to use of pyrotechnic compositions [11].

The most available alkalis are oxyhydroxides of sodium and a potassium (NaOH, KOH). Besides, these alkalis are well dissolved in water and decaying on ions. That results in their high activity at neutralization of water acid baths. As the principal combustible components of pyrotechnic composition for dispersion of alkali finely divided powders of aluminum and a magnesium (ASD-4, MPF-4), nitrate of potassium (KNO_3) as an oxidizer and organic pitch (CKH 26) as binding are chosen. Composition of PS-1-0: MPF-4 – 7 %; ASD-4 – 4 %; KNO_3 – 79 %; SKN of 26 – 10 %.

Composition is formed as the cylindrical extended sword by a diameter d = 20 mm and long l = 150 mm. Lighting of pyrotechnic composition takes place an electric spark method.

Finely divided alkalis (NaON, KOH) do not take part in combustion process. As a result of explosive charge combustion of a particle of alkali are sprayed and contacted to acid atmospheric creation and neutralize them on reactions (11)–(14):

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O; \quad (11)$$

$$H_2SO_4 + 2KOH = K_2SO_4 + 2H_2O; \quad (12)$$

$$HNO_3 + NaOH = NaNO_3 + H_2O; \quad (13)$$

$$HNO_3 + KOH = KNO_3 + H_2O. \quad (14)$$

As, the specified alkalis have rather low boiling point (T_{boil} (NaON) – 1676 K; T_{boil} (KOH) – 1600 K), at combustion of an explosive charge occurs their sublimation that leads to a padding dispersion of particles of alkali. The padding amount of alkali can be formed as a result of combustion reaction of metals with potassium nitrate on the following equations:

$$Mg + 2KNO_3 + H_2O = \\ = MgO\downarrow + 2KOH + 2NO_2\uparrow, \quad (15)$$

$$Mg + 2KNO_3 + 2H_2O = \\ = Mg(OH)_2\downarrow + 2KOH + 2NO_2\uparrow. \quad (16)$$

Apparently from the equations (15)–(16), additional creation of potassium hydroxide requires presence of molecules of water. In spite of the fact that at the atmosphere constantly there is a moisture, at the expense of a powerful stream superheated reaction products hit of molecules of water in a reaction zone of combustion explosive charge is extremely complicated.

Ensuring reactionary volume with water introduction of combustible hydrogenous components immediately in an explosive charge allows to solve a problem. Organic compounds can be such components. From the technological point of view organic matters for formation of an explosive charge have to be in solidity under normal conditions. As such additive it is possible to use cellulose. Combustion of an explosive charge on a molecular scale happens to cellulose additive according to the scheme:

$$Mg + KNO_3 + C_6H_{10}O_5 \rightarrow \\ \rightarrow MgO + CO_2\uparrow + KOH + NO\uparrow. \quad (17)$$

At the same time practically all atoms of a potassium participating in process of combustion form potash alkali. It in addition increases intensity of neutralization of acid atmospheric creation at combustion of pyrotechnic mix.

After the choice of components of a pyrotechnic composition it is necessary to decide on mass composition.

Definition of efficient mass composition was carried out experimentally by measurement of burn speed and combustion temperature. An experiment was conducted in the isolated chamber (figure 1).

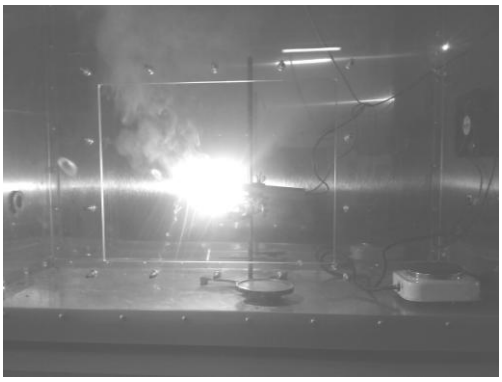

Figure 1 – Experimental research of pyrotechnic composition burning parameters

As a result of experiments it was determined a low probability of ignition of the electric-spark method. This negative phenomenon is also associated with the presence of the oxide film, which prevents the initiation of the combustion process. The melting temperature for MgO film is much higher than for the oxide film of aluminum, which, apparently, affects the low probability of ignition compositions with magnesium. To eliminate this drawback it is proposed to use a two-layer structure of a charge, with a thin layer of the initiating composition based on potassium perchlorate and graphite ($KClO_4$ + C) in the area of ignition and the main working part with the use of potassium nitrate and metals (figure 2).

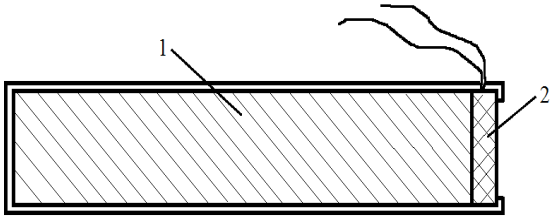

Figure 2 – Structure of two-layer pyrotechnic composition: 1 – main composition; 2 - initiator burning composition

The test results of the two-layer compositions show that the introduced changes do not affect the burning intensity within the measurement error, but the probability of ignition in all series was 100 %.

On pyrotechnic properties pyrotechnic composition, in addition to the chemical nature of the combustible mixture, significantly influences the polydispersity of fuel relative to the oxidizer and the total dispersion.

Results of the experimental research are presented in tables 1 and 2. In the beginning the structure with addition only of potash alkali as main neutralizer of acidity has been investigated.

Table 1 – Main combustion parameters of pyrotechnic compositions for deacidizing without cellulose addition

Composition	Content KOH, % mass	Burn Speed, 10^3 m·s^{-1}	Burn temperature, K
PC-1-0	0	3,3 ± 0,1	1870 ± 20
PC-1-1	10	3,1 ± 0,1	1850 ± 20
PC-1-2	20	3,1 ± 0,1	1820 ± 20
PC-1-3	30	2,9 ± 0,1	1820 ± 20
PC-1-4	40	2,7 ± 0,1	1810 ± 20
PC-1-5	50	2,6 ± 0,1	1800 ± 20
PC-1-6	60	2,3 ± 0,1	1780 ± 20
PC-1-7	70	~ 2,1 (blowout)	1750 ± 20
PC-1-8	80	~ 2,0 (blowout)	1720 ± 20

Table 2 – Main combustion parameters of pyrotechnic compositions for deacidizing with cellulose addition

Composition	Content KOH, % mass	Content cellulose, % mass	Burn Speed, 10^3 m·s^{-1}	Burn temperature, K
PC-1-51	50	5	2,4 ± 0,1	1790 ± 20
PC-1-52	50	10	2,4 ± 0,1	1780 ± 20
PC-1-53	50	15	2,4 ± 0,1	1760 ± 20
PC-1-61	60	5	2,1 ± 0,1	1750 ± 20
PC-1-62	60	10	(blowout)	1720 ± 20
PC-1-63	60	15	(blowout)	1710 ± 20
PC-1-71	70	5	(blowout)	1700 ± 20

Results of an experiment showed that addition of potash alkali to 60–65 % (mass) allows to keep steady combustion of pyrotechnic composition. Cellulose addition reduces combustible properties of an explosive charge as a result of quantity replacement of the active combustible components with cellulose a little. However the structure of PC-1-61 from 60 % the KOH and 5 % of cellulose possesses steady combustion and can be used at neutralization of acid precipitation. Besides, the magnesias formed at combustion and aluminum are the centers of teardrop that leads to padding initiation of process of sludge formation.

In addition it is possible to accelerate sludge formation process due to introduction to pyrostructure of AgI or NaCl from calculation that the total of the modifying additives should not exceed 65 % mass.

Use of the offered structure for simulated sludge formation allows to initiate settlings over a zone of the major natural and technogenic fire that leads to a deposition from the atmosphere of harmful combustion gases and prevents formation of an acid atmospheric precipitation by their neutralization.

The separate group of toxic substances is made by chlorine and phosgene. Unlike ammonia, chlorine (Cl_2) and phosgene ($COCl_2$) have extremely low water solubility. The main physical and chemical properties of these gases are given in table 3.

Low solubility of chlorine and phosgene in water testifies to low intensity of a deposition of these gases an atmospheric precipitation. Therefore, for increase in cleaning speed of the atmosphere in aquacondensate it is necessary to include neutralizers in addition.

Table 3 – Some physical and chemical properties of chlorine and phosgene neutralizers

Gases	Boiling temperature, K	Decomposition temperature, K	Water solubility at 273 K, g/100 g
Cl_2	239	~1680	1,5
$COCl_2$	282	~1075	0,9

The most active neutralizer of chlorine is sodium thiosulfatum:

$$Na_2S_2O_3 + 4Cl_2 + 5H_2O = \\ = 2H_2SO_4 + 2NaCl + 6HCl \quad (18)$$

According to (18) neutralization of 1 ton of chlorine requires about 0,5 ton of $Na_2S_2O_3$. Apparently from (18), reaction proceeds in aqueous solutions. It is necessary to consider however that Sodium thiosulfatum is combustible and explosive substance – when heating to 220 °C it decompose according to the scheme:

$$4Na_2S_2O_3 \xrightarrow{t} 3Na_2SO_4 + Na_2S + 4S\downarrow . \quad (19)$$

Proceeding from it, use of $Na_2S_2O_3$ as additives in explosive charges is strictly forbidden.

Efficient neutralizer of chlorine is sodium hydroxide:

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O . \quad (20)$$

Neutralization of 1 ton of chlorine requires 1,2 ton of NaOH. Hydroxide of sodium is well dissolved in water. Therefore in practice of decontamination usually use aqueous solutions. Apparently from (20), at chlorine neutralization alkali in addition forms salts which desublimated in water-absorbing crystals, and water. Formation of such reaction products (water-absorbing crystals) positively influences sludge formation process.

Not less dangerous substance getting to the atmosphere at technogenic accidents (especially at large fire), is phosgene ($COCl_2$). In express literature phosgene carries the name «carbonyl dichloride». In the nature phosgene does not exist and was widely adopted in chemical industry where it is used as the intermediate product by production, in particular, of dyes, pesticides, pharmaceuticals, polymers, pitches and hardeners. Annual world production makes about 5 million tons. Phosgene is formed at thermal decomposition or a photo-oxidation of chlorinated solvents, and also at combustion of polyvinylchloride.

In spite of the fact that phosgene has low water solubility (table 3), but as well as chlorine is actively neutralized by sodium hydroxide:

$$COCl_2 + 4NaOH \rightarrow \\ \rightarrow Na_2CO_3 + 2NaCl + 2H_2O . \quad (21)$$

Follows from the equation of reaction (20) that is necessary for neutralization of 1 ton of phosgene for 1,6 ton of sodium alkali or 16 ton of its 10 % aqueous solution.

Pyrotechnic compositions with additives of alkalis have been considered earlier. Similar properties of potassium and sodium alkalis allow to replace them as a part of an explosive charge without essential changes of combustion parameters. So, by analogy with structure of PC-1-6 whereas non-combustible addition agent there are 60 % the KOH, properties of composition PC-1-61 from 60 % of NaOH have been investigated. As a result of the experimental researches it is established that this structure has burn speed $(2,4\pm0,1)\ 10^{-3}$ m s^{-1} and combustion temperature (1790±20) K. At limit of permissible error these parameters correspond to parameters of combustion composition PS-1-6.

In case of adverse weather conditions for simulated initiation of precipitation use of a method of dispersion of finely divided reagent (NaOH) with light piloted and unmanned aerial vehicles is in the pneumatic method expedient.

Considering that the molar mass of chlorine and phosgene is more than molar mass of air, the greatest concentration of these dangerous gases is localized in a ground layer of the atmosphere. It gives the chance to efficiently use light aircraft for cloud seeding of chlorine or phosgene. It allows to lower significantly the material costs at irritation liquidation.

Conclusions. In article the pyrotechnic composition of dual purpose is developed: for simulated initiation of precipitation and for efficient deacidizing of the rains and fogs formed at the scale natural and technogenic fires. Mass contains pyrotechnic composition to 65 %. The KOH and also cellulose which promotes additional creation of alkali in reaction of combustion charge explosive. Modification of the developed composition with use of NaON allows to neutralize efficiently such dangerous gases as chlorine and phosgene.

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МОДИФІКАЦІЯ ПІРОТЕХНІЧНИХ СКЛАДІВ ДЛЯ ЕФЕКТИВНОЇ НЕЙТРАЛІЗАЦІЇ КИСЛОТНИХ ТА ХІМІЧНО НЕБЕЗПЕЧНИХ АТМОСФЕРНИХ ОПАДІВ

В роботі вирішується завдання зниження екологічної небезпеки регіону від кислотних опадів і викидів хлору та фосгену при виникненні надзвичайної ситуації техногенного характеру. З цією метою розроблено новий склад піротехнічного заряду, здатний за певних умов ініціювати атмосферні опади та нейтралізувати їх надмірну кислотність. Різні модифікації розробленого складу призводять до активного опадоутворення, як переохолоджених хмар, так і хмар з температурою вище 12 ºС. Основні піротехнічні властивості розробленого складу перевірені експериментально. Показано, що введення целюлози в цей склад сприяє генерації додаткової кількості лугу (в результаті горіння компонент пірозарядом) та підвищення ступеня нейтралізації кислотності опадів. З метою підвищення ступеня нейтралізації високотоксичних газів – хлору та фосгену, запропонована модифікація піротехнічного складу з додаванням гідроксиду натрію. Запропоновано метод нейтралізації хлору та фосгену шляхом засіву зони забруднення натрієвим лугом з використанням легкоматорної авіації.

Ключові слова: атмосферні опади, піротехнічний склад, кислотні дощі, хімічна нейтралізація, ініціювання опадів.

М. В. Кустов, В. Д. Калугин

МОДИФИКАЦИЯ ПИРОТЕХНИЧЕСКИХ СОСТАВОВ ДЛЯ ЭФФЕКТИВНОЙ НЕЙТРАЛИЗАЦИИ КИСЛОТНЫХ И ХИМИЧЕСКИ ОПАСНЫХ АТМОСФЕРНЫХ ОСАДКОВ

В работе решается задача снижения экологической опасности региона от кислотных осадков и выбросов хлора и фосгена при возникновении чрезвычайной ситуации техногенного характера. С этой целью разработан новый состав пиротехнического заряда, способный при определенных условиях инициировать атмосферные осадки и нейтрализовать их избыточную кислотность. Различные модификации разработанного состава приводят к активному осадкообразованию, как переохлажденных облаков, так и облаков с температурой выше 12 ºС. Основные пиротехнические свойства разработанного состава проверены экспериментально. Показано, что введение целлюлозы в этот состав способствует генерации дополнительного количества щелочи (в результате горения компонент пирозаряда) и повышению степени нейтрализации кислотности осадков. С целью повышения степени нейтрализации высокотоксичных газов – хлора и фосгена, предложена модификация пиротехнического состава с добавлением гидроксида натрия. Предложен метод нейтрализации хлора и фосгена путем засева зоны загрязнения натриевой щелочью с использованием легкоматорной авиации.

Ключевые слова: атмосферные осадки, пиротехнический состав, кислотные дожди, химическая нейтрализация, инициирование осадков.