

Review of the Environmental Characteristics of Fire Extinguishing Substances of Different Composition used for Fires Extinguishing of Various Classes

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Abstract: The study shows the environmental characteristics of various substances used for the fires extinguishing. It is specified there is a negative impact on the environment of synthetic foam agents containing the fluorine, the absence of environmentally non-hazardous foam agents. The presence in the environment of a significant amount of decomposition products of fluorine-containing film-forming foams is marked. Some of them belong to persistent organic pollutants and the properties of the most compounds have not been investigated yet. There is a departure from the use of gaseous fire extinguishing agents with ozone-depleting properties-chlorofluorocarbons and the ambiguity of the environmental characteristics of the compounds replacing them. For a number of fire-extinguishing compounds informative environmental data are presented a little. And there is search in progress for more environmentally non-hazardous fire-extinguishing compounds. Analysis of the environmental requirements for fire extinguishing substances in a number of countries has shown that for most developed countries there is a trend away from the use of environmentally hazardous fire extinguishing agents which are used for the fires extinguishing of various classes. There is no one universal approach to determining the environmental parameters of fire extinguishing compounds.

Key words: Fire extinguishing agent, fire, fire fighting foam, fire extinguishing powder, halon, environmental characteristic, environment

INTRODUCTION

Anthropogenic activities are currently the main source of environmental pollution. A threat can be represented both by mineral production and further production by emitting pollutants and waste (Semko *et al.*, 2014; Malhijlongi *et al.*, 2019). The processing of minerals, the use of the obtained products, industrial production can also be the reason for penetrating uncharacteristic compounds into the environment (Tregubov and Miroshnichenko, 2005; Kondratenko *et al.*, 2015; Prokhorenko *et al.*, 2015; Thiruvenkatasamy and Rahman, 2018).

Various emergencies that may occur during these activities pose a threat to all components of ecosystems.

Fires are one of the common types of such situations. Due to a number of factors their timely liquidation is not always ensured including the use of fire retardants by firefighters (Kovalov *et al.*, 2018). The fires expanding a large number of harmful and hazardous substances escape into the environment.

A large number of reports (Isaeva, 2001; Vasiliev *et al.*, 2014; Semko *et al.*, 2016; Martin *et al.*, 2016; Belkova *et al.*, 2016; Chen *et al.*, 2017; Timofeeva *et al.*, 2017; Plaza-Alvarez *et al.*, 2019) are devoted to the environmental impact of both fires and combustion products (Zhu *et al.*, 2018). Actually, the fires cause significant material and economic damage. They have a negative impact on natural and anthropogenic ecosystems of various levels polluting adjacent and

remote areas with combustion products. In the case of burning a liquid material additional danger to any ecosystem including biotic is also spilling (Klymenko and Zalessky, 2017). Thus, fires associated with the burning of flammable liquids, apart from damaging equipment and reservoirs (Abramov *et al.*, 2018) can also be accompanied by leaking these liquids into the ground and the water (Vyalyshev *et al.*, 2012; Bondarets *et al.*, 2014) which makes an additional contribution to environmental pollution.

Another factor that can affect the atmosphere, hydrosphere, lithosphere and biota is substances used for fires extinguishing (Holemann, 1994; Isaeva, 2001; Modovsky, 2007; Martin *et al.*, 2016).

Considering the above mentioned, an important component of environmental protection and as a result one of the urgent tasks for today, apart from identifying emergencies related to the localization of the fires of combustible substances (Andronov *et al.*, 2017a, b; Dubinin *et al.*, 2017; Migalenko *et al.*, 2018; Loboichenko and Strelec, 2018) using the technical means for extinguishing fires and their prevention (Pospelov *et al.*, 2017a, b; 2018) is the use of non-hazardous fire extinguishing agents.

According to the international classification there are 5 main types of the fires: A-F (Anonymous, 2007) which are defined in accordance with the burning material. Thus, the fires of class A are the burning of solid materials, class B is the burning of liquid materials, class C is the burning of gaseous materials, class D is the burning of metal, class F is combustible materials such as vegetable and animal oils and fats used for cooking. In different states, these classifications may vary somewhat. For example, in Russia there are such classes of the fires: fires of solid combustible substances and materials fires of flammable liquids or melting solids and materials fires of gases metal fires fires of combustible substances and materials of electrical installations under voltage and fires of nuclear materials, radioactive waste and radioactive substances (Anonymous, 2008a, b). In the USA, the standard NFPA 10 (NFPA., 2018) is in force according to which fires are divided into classes is as follows: class A is the fires with the involvement of conventional combustible materials; class B is the fires involving flammable liquids, burnable liquids, etc., class C is the fires with the involvement of existing electrical equipment; class D is the fires involving flammable metals; class K is the fires of the equipment used for cooking meals involving flammable materials such as vegetable and animal oils and fats.

Various factors or their complex interaction can contribute to the ignition of the materials themselves (Pospelov *et al.*, 2017a, b).

Depending on the type and the category of the fire, various equipment and substances are used for extinguishing the fire (Abduragimov *et al.*, 1980; Andronov *et al.*, 2017a, b; Dubinin *et al.*, 2018a, b).

In turn, the substances extinguishing the fire can have a different nature and effect on the source of the fire and be also used for protecting the firefighters (Kostenko *et al.*, 2017). They can be used in solid, liquid or gaseous form. The most common and long known fire extinguishing agent is water (Baratov and Ivanov, 1979) including water and salt solutions (Tyner, 1941; Tarancev and Chashin, 2015).

The further development of approaches to extinguish the fire has led to the working-out and use of fire extinguishing foams, gases, powders (VNIPO., 1997; Korolchenko and Korolchenko, 2004), gel systems (Abramov and Kireev, 2015; Dadashov *et al.*, 2016; Dadashov, 2018) and hydrogels (Hajiyev *et al.*, 2014, Ivanov *et al.*, 2017).

In the study of fire extinguishing substances comprehensive approach is applied they can be considered as separate chemical compounds with certain properties and as substances that ensure the ceasing the combustion. Recently, another direction has emerged the environmental characteristics of fire extinguishing agents which are used.

So, in 1994 the International Association for the Science of Fire Safety noted there was the negative impact both the fire itself and the fire extinguishing agents such as water, gases, powders and foams on the living organisms and the environment as a whole (Bondarets *et al.*, 2014).

The global tendency is to reduce the negative anthropogenic impact on the environment. In connection with the ratification in 2004 of the UN Stockholm Convention on Persistent Organic Pollutants (Anonymous, 2000) the countries participants committed themselves to stop or in some cases, limit the use of a number of organic substances that adversely affect the environment and human health including through food products (INFOSAN., 2007). In 2009 the organic substances (Anonymous, 2009a-c) such as Perfluorooctane sulfonic acid (PFOC), its salts and perfluorooctane sulfonyl fluoride were added to the accepted additions to Stockholm Convention about organic substances. Perfluorooctane sulfonyl fluoride is a precursor of perfluorooctane sulfonic acid (Anonymous, 2015a, b). The further report of the committee about research into persistent organic pollutants within the framework of the United Nations (UN) activities led to the fact that in 2015 the European Union (EU) and its member states proposed to include Perfluorooctanoic Acid

(PFOA), its salts and PFOA related compounds in annexes A-C to Stockholm Convention (Anonymous, 2017a-c). Although, it is proposed to consider as an exception, options for its use in some industries including fire extinguishing foams (Anonymous, 2017a-c; Anonymous, 2018a-e). These substances are decomposition products of foam agents based on fluorine and have a significant negative impact on the environment. They have bioaccumulation properties and are not biodegradable (Seow, 2013). In turn, this limited sharply the use of foam agents containing fluorine for extinguishing the fire.

According to the report by European Regional Office of World Health Organization (WHO) (WHO., 2015) in 2015 “more than 80% of European states which are members of WHO made an official commitment to comply with international agreements on chemical safety” including Stockholm Convention. They also, legally confirmed their consent to work under the EU regulation on registration, evaluation, resolution and restriction of chemicals (REACH., 2006) which also, toughened the use of persistent organic pollutants or compounds producing them.

The USA, China, Canada are also, actively involved in researching into the field of the environment and human health funded by the European Union (WHO., 2015). The positive changes related to environmental tendencies which have been included, since, 1970s in various aspects of the activities of the European Union countries are specified in the report of European Environment Agency “Europe’s Environment: Condition and Prospects -201” (EEA., 2015). It is also noted the complex problems have yet to be tackled at various levels.

At the same time in China (Wang, 2018) there is a lack of supporting the foundations and grants to study in detailed way the environmental and ecotoxicological properties and the effects of the foams, based on water and the extinguishing agents on the environment.

In the information document, presented by the Special Working Group on the Implementation of the Environmental Action Program for Central and Eastern Europe and the Organization for Economic Cooperation and Development the attitude of a number of the states to the environmental issues is analyzed. In particular, the faults or advantages in the environmental field are noted.

All above mentioned information indicates the relevance of the scientific task of reducing the environmental risk of the fire extinguishing agents that are used for extinguishing the fires. To accomplish this task,

first of all, it is necessary to review the environmental characteristics of the fire extinguishing compositions of various compounds used for extinguishing the fires of various classes. Below is an overview of the fire extinguishing agents used for extinguishing the fires of flammable substances.

Literature review

Review of the environmental characteristics of fire extinguishing substances

Review of the environmental characteristics of fire fighting foams:

The most common extinguishing agent is water. The emergence and significant development of chemical, oil and gas and a number of other industrial sectors contributed to the emergence of a variety of combustible compounds of which the ceasing of the fire with the water was difficult or impossible. A similar situation contributed to the search into new means for extinguishing them and led to the appearance of foams. They are used for extinguishing the solid and liquid materials. Physicochemical methods are used to determine their characteristics stability, multiplicity, dispersion, etc. To determine their environmental and ecotoxicological characteristics their effects on living organisms are studied by using bioindication. Foams are essentially aqueous solutions of surfactants. The fires of class B (oil and oil products) being extinguished, the aqueous foams, containing the fluorine and forming the film are especially in demand. In addition, to synthetic agents, the film forming foams made on the basis of natural protein are used for fires extinguishing (Anonymous, 1996, 1999; Anonymous, 2012).

In the case of the fire extinguishing with the help of environmental foam either the foam itself or their decomposition products may be unsafe (Turekova and Balog, 2010; Turekova *et al.*, 2012; Sontake and Wagh, 2014). Their negative impact is assessed mainly on aquatic and semi-aquatic environments there is an impact on other components of the biosphere, though (Adams and Simmons, 1999a, b).

The researchers (Goto *et al.*, 2015) investigate the toxic mechanism of sodium alkyl sulfonates with different length of carbon chain that are part of fire fighting foams. As a criterion for the reliability of the results obtained, the necessity to use natural aqueous solutions rather than experimental laboratory media is noted.

The advantages of using soaps (surfactants based on oleates, stearates) as foaming agent for the fire extinguishing are described in the reports (Mizuki *et al.*, 2007; Kawahara *et al.*, 2016).

The foams based on plants (soap root and hop) (Taysumov, 2012a, b; Chirkina *et al.*, 2017) or beer are

proposed in the studies. The researchers mention the fire-extinguishing characteristics of such foams are environmentally safe.

The film forming foams, based on fluorine has proven to be an effective fire extinguishing agent for the fires extinguishing of class B (flammable liquids) (Korolchenko and Volkov, 2017). However, from an environmental point of view there is a significant negative impact on the environment because of decomposition products (Skutlarek *et al.*, 2006; Bocharov and Raevskaya, 2013).

In particular, a large number of the study deal with the environmental impact of PFOS and PFOA (Liu *et al.*, 2016). Thus, the researchers note the presence of PFOA within a radius of 4 km from the polluted part of the Dong Julong River, China. Long chained Perfluoroalkyl Acids (PFAA) fall into the surface water of the river with waste disposal their concentration in groundwater strongly correlates with the concentration in the surface water.

PFOA and PFOS available in the surface run off water which is eight urban basins and in the tap water in Korea are analyzed (Kim *et al.*, 2011). The tap water reflected the nature and levels of pollution in the respective water basins. Although, the hazardous levels for public health are recorded only for PFOA, the authors state the necessity for both additional purification the tap water and reducing the wastes of PFOA into the water.

Surveys of soil and groundwater samples carried out in the metropolitan region of the United States (Xiao *et al.*, 2015) also, showed the migration of PFOA and PFOS from the soil surface to the aqueous layer their sorption on solid particles in the aqueous layer.

According to Liu *et al.* (2017) the data 10% of the total amount of PFOA and PFOS wasted into the environment in eastern and central China is caused by the use of the agents containing fluorine. Among other sources of pollution of the soil, surface and groundwater are industrial and domestic wastewater, landfill leakage. The need to control these contaminants is emphasized.

Studies by Japanese scientists Nakayama *et al.* (2005) showed a significant variation in the concentrations of PFOA and PFOS in the surface water of Japan. Their carcinogenic effects on people and animals as well as their reproductive, neuro and hepatotoxicity are noted. They note the presence of higher concentrations of perfluorochemicals in aquatic environment in Taiwan compared to other countries and the need to reduce the release of these compounds including PFOS into the aquatic environment (Lin *et al.*, 2010).

In the study, Xiao (2017) speaks about the danger of the presence in the environment of a large number of

various perfluoroalkyl compounds with fluorinated hydrocarbons in addition, to the known PFOS and perfluoroalkyl acids from 2009-2017 the researcher identified 455 new compounds that were found in natural water, fish, sediments, wastewater, activated sludge, soils, commercial fluoropolymer surfactants. These compounds can also lead to forming PFOS and PFAA which have become a global problem today due to their bioaccumulation and toxic properties.

Another aspect of the negative impact of the decomposition products of film foams containing the fluorine is shown by recent detailed studies of samples of concrete and soil collected on the fire training ground where various fluorine containing foams have been used for several decades. It is shown that they contain more than 60 chemicals not being previously identified and controlled in the environment. It is noted that of these new per-and polyfluoroalkyl substances might be mobile in the groundwater and in the soil (Baduel *et al.*, 2017).

The search for environmentally safe foams goes in different directions. Thus, the use of saline solutions based on ammonium chloride with perfluorinated surfactants for extinguishing petroleum products increases the frost resistance of the composition, although, there is a need to increase more than twice the minimum specific consumption of the foaming agent to extinguish the flames compared to common aqueous solutions of perfluorinated surfactants (Vlasov and Eremina, 2017).

Some researchers Sharovarnikov *et al.* (2014) propose to use a foaming agent for extinguishing multicomponent mixed fuels which in addition to perfluorinated surfactants also include polymeric components (polysaccharides). However, despite the choice of the optimal ratio of components, the environmental characteristics of such composition are not considered.

It is also proposed to use environmentally safe short chained carbons (Cortina and Korzeniowski, 2008) based on fluorine or even softer surfactants based on alkyl sulfates, sodium oleinsulfonates (Bocharov and Raevskaya, 2016) to obtain the foaming agent. However, this may have a negative or uncertain effect on living organisms due to a large amount of foams getting into the environment (Bezrodnyy, 2013).

As manufacturers of foams in particular Oil Technics Ltd (Scotland), note today there is no unified standard at the international level (Anonymous, 2019a-c) for studying the biodegradability of foams. That is there is no uniform methodology regarding approaches to the study of this parameter both in European standards and in US standards and the information available

may be contradictory. An exception is the US standard MIL-F 24385 which requires the ratio of biological oxygen consumption to chemical oxygen consumption (BOD/COD) at least 50% which is believed to be an indication that the chemical is easy to biodegrade. Most manufacturers of fire extinguishing agents test the fire-fighting foam concentrate for biodegradability rather than the actual foam that enters the environment (usually 1-3% vs. 100%). In addition, combinations of BOD results are often reported by 5, 20, 28 days or indefinite duration and measured by using total organic carbon. The obtained results are indicated by manufacturers in the accompanying documents for the foaming agent (Anonymous, 2015a, b).

Thus, a review of the environmental characteristics of fire fighting foams confirmed the negative environmental impact of fluorinated synthetic foams. To date there are no environmentally safe foams and a unified methodology for obtaining their environmental characteristics.

Review of the environmental characteristics of fire extinguishing powders: Another group of substances that belong to fire extinguishing agents are fire extinguishing powders. They are a mixture of inorganic compounds with a certain content of phosphates, hydrophosphates, dihydrophosphates or carbonates (Kazakov *et al.*, 1977) and can be used for extinguishing fires of various classes including oil products.

In addition to the abovementioned, fire extinguishing powders, based on chlorides, sulfates and other compounds are used (Baratov and Wogman, 1982). Urea, betonite, pumice, etc. can be added to them. The composition of the powders can be very diverse and there are a large number of variations (Zhartovsky *et al.*, 1997; Mokeyev *et al.*, 2006; Baratov, 2012). The aerosol mixtures of powders and inert gases are also used in the fire fighting (Balanyuk *et al.*, 2016).

The ecological and ecotoxicological properties of this group of compounds are not considered separately they are certified as inorganic chemical compounds, taking into account the risk of their effects on humans and the environment according to the Globally Harmonized System of Classification and Labeling of Chemicals (Globally Harmonized Chemical Systems) (Anonymous, 2013a, b). In this case, a safety data sheet is issued for the product. However, despite the fact that the safety data sheets prepared by various manufacturers (Anonymous, 2012; Anonymous, 2016a-e) there is an impact on various aquatic organisms, the impact on the soil in them is practically not considered.

Thus, ecological and ecotoxicological properties are not fully represented in the certificates for fire extinguishing powders.

Review of the environmental characteristics of fire extinguishing gases: Some gases or gas compositions can also have a fire extinguishing effect. Gas fire extinguishing products are used for the fires extinguishing of petroleum products as well as the fires of class A and C, i.e., combustible solid and gaseous materials (Korolchenko and Shilina, 2016).

Gas fire extinguishing is based on the inhibition of fire by reducing the rate of oxidation reactions in the flame or by reducing the oxygen content in the combustion zone. At the same time, halohydrocarbons can be used as inhibitors while a decrease in the oxygen concentration is achieved by supplying inert gases to the combustion zone-carbon dioxide, argon, nitrogen, etc. (Yelansky *et al.*, 2005; Anonymous, 1984).

And if in the case of inert gases, it is possible to speak of their relatively small negative environmental impact, then the use of inhibiting gaseous substances cannot always be justified from an environmental point of view. Thus, bromo-, fluoro- or chlorine-containing halohydrocarbons such as heptafluoropropane, fluoroketone C-6, freons (halons) of various modifications can be used as inhibiting compounds (Korolchenko *et al.*, 2015).

However, it was discovered in 1987 that halogenated hydrocarbons destroyed the ozone layer. As part of the research of the United Nations, the Montreal Protocol on substances that deplete the ozone layer was developed, the countries which signed it, committed themselves to abandon the use and production of a number of halogenated hydrocarbons which at the time were also used in fire fighting CFCl_3 (XΦY-11), CF_2Cl_2 (XΦY-12), $\text{C}_2\text{F}_3\text{Cl}$ (XΦY-113), $\text{C}_2\text{F}_4\text{Cl}$ (XΦY-114), $\text{C}_2\text{F}_5\text{Cl}$ (XΦY-115), CF_2BrCl (halon-1211), CF_3Br (halon-1301), $\text{C}_2\text{F}_4\text{Br}_2$ (halon-2402) (Anonymous, 1987). The adoption of Montreal Protocol led to a gradual decrease in growing halons in the atmosphere despite their long period of being there (Butler *et al.*, 1992). To date, more than 190 countries have ratified this document.

Halons are fully halogenated chemical compounds that have a relatively long lifetime in the atmosphere (Anonymous, 2018). Halon 1301 (CF_3Br) is the most dangerous for the environment as it destroys the ozone layer as much as possible. It should be noted that they do not stop using halons completely. Thus, according to a report by the association of fire protection of Australia for 2018, the use of halons continues in areas where they cannot be dispensed with. In other cases, the most

popular replacement for halons is C_3HF_7 compound (FM 200). Thus, it reached about 80% of the global market for replacing halons in fire extinguishing systems. At the same time, FM 200 contributes to global warming which is a negative environmental impact factor (Anonymous, 2018).

The competitor FM 200 is a fire extinguishing agent Novec 1230 manufactured by 3M which has a smaller global warming potential compared to FM 200 and is safe for the ozone layer (Ziemba, 2007). Many states have taken measures to reduce the use of halons. For example, the United States Environmental Protection Agency has adopted the Halons Program (Anonymous, 2019a-c) which provides for the prohibition and reduction of emissions of halons and their mixtures, although, it stipulates certain permissible cases of their use. Canada (Anonymous, 2016b) has Federal Regulations on Ozone-Depleting Substances which regulate the production, import and export of these substances including prohibiting the production of new halons and stipulate certain cases of their acceptable use.

In research of Al-Awad *et al.* (2018) it is noted the need to comply with the requirements of Montreal Protocol (Anonymous, 1987) while ensuring that it is possible to meet the demand for halons in the main areas of their application until an affordable alternative appears. In turn, the issue of environmental safety of fire extinguishing gases, offered instead of ozone-depleting gallons, remains open. In particular their contribution to global warming is noted (Johnson *et al.*, 1997; Banks *et al.*, 1998). The creation of fire extinguishing gases, capable of replacing halons (Hurley *et al.*, 2015; Rajput and Saikia, 2018) is also complicated by the large number of different criteria: global warming potential, depletion potential of the ozone layer (Ziemba, 2007) no-adverse effect level (Hurley *et al.*, 2015), total gas hazard index (Anonymous, 2005).

Thus, there is no unified approach to assessing the environmental impact of gaseous extinguishing agents which makes it difficult to effectively comply with the requirements of Montreal Protocol.

Review of the environmental characteristics of other fire extinguishing agents: The search into environmentally safe fire extinguishing agents has led to the emergence of a number of other compounds that can be used for extinguishing flammable substances. A group of mineral-based gel-forming systems has been proposed which can be used for extinguishing class A and B fires including systems with foamed silicon dioxide (Borisov *et al.*, 2005; Abramov and Kireev, 2015;

Dadashov *et al.*, 2016; Dadashov, 2018). They both from an economic point of view and in terms of their impact on living organisms are safe enough for the environment (Dadashov *et al.*, 2018a, b).

Abduragimov *et al.*, 2016 developed quick-hardening foams based on silica for extinguishing forest fires and more. The researchers point out the high environmental characteristics of these fire extinguishing mixtures. It is convenient to evaluate the environmental impact of those groups of fire extinguishing substances by common methods of analysis including the methods of “green chemistry” by using the conductivity and the coefficient of identification (Loboichenko *et al.*, 2016; Vasyukov *et al.*, 2016; Loboichenko *et al.*, 2018a, b).

It is proposed to use hydrogels with carbon nanostructures (Hajiyev *et al.*, 2014, Ivanov *et al.*, 2017) for the fires extinguishing, including oil products. These hydrogels are structured by homogeneous colloidal systems filled with liquid of which the framework is formed by particles of high molecular weight compounds. However, their ecological properties are not considered by the researchers.

Speaking about the environmental hazards of both fluorine-free and fluorinated foams, Klein suggests alternative options for the fires extinguishing class A and B such as water, mist or fog, compressed air foam systems (CAFS), hydrophilic gels or free-radical chain-breaking powders (Klein, 2008).

Thus, there is a versatile tendency in the development of new fire extinguishing agents. Ecological properties of the proposed compounds are not always considered.

ECOLOGICAL REQUIREMENTS FOR FIRE EXTINGUISHING SUBSTANCES IN VARIOUS COUNTRIES

In the study “EU Hazard concept, approaches and Principles for the treatment of chemicals” developed in the framework of the project “Building capacity in Northwestern Russia to manage hazardous substances” FKZ 380 01 188 (2008-2010) (Reihlen, 2010) reviewed European hazard concept of chemical mixes.

To date, the hazard criteria of a substance are stipulated in European document Reach (REACH., 2006). This document considers the hazard of a substance from the point of view of effect on human or environment. Hazard criteria are persistence, accumulation, toxicity, effects on the human body.

The water framework directive (Anonymous, 2000) also distinguishes between hazardous substances which

penetration into the environment must be stopped and the priority hazardous substances which penetration into the environment must be completely stopped.

In Europe, there is a series of standards EN 1568 parts 1-3 which regulates the test methods for foam concentrates of high, medium and low expansion for application to water-immiscible liquids and water-miscible liquids (Part 4) (Anonymous, 2019a-c). These test methods do not suggest a study of environmental characteristics, although, viscosity, pH, sedimentation, etc. are determined. Similar information is not available for powdered extinguishing agents in the EN 615 standard "Fire extinguishing media specifications" (Anonymous, 2009a-c). The existing series of international standards ISO 7203 regarding requirements for foam concentrates of various expansion for using with water-immiscible liquids (ISO., 2011) do not regulate their environmental requirements. At the same time, such characteristics as viscosity, temperature, expansion, etc. are noted. A similar situation holds true for powder fire extinguishing agents. In ISO 7202 (Anonymous, 2018a-d), parameters such as humidity, electrical insulation, toxicity of fire extinguishing powders are specified but environmental characteristics are also not given.

The world's largest European chemical concern BASF which has divisions around the world, manufactures products for various sectors of the national economy, including the means for passive and active protection against fire. The latter include foams and powders for extinguishing fires of classes A-F. In the product line there are fluorine-containing and fluorine-free foams. Among European manufacturers of fire extinguishing agents, Dafo Fomtec AB, headquartered in Stockholm (Sweden) is also known. It is engaged in the production of powder and foam fire extinguishing agents to extinguish the fires of classes A-D. Company Dr. Sthamer Hamburg (Germany) produces various synthetic and protein foams, both containing fluorine and non-fluorine. Sabo Foam S.R.L (Italy), similar to Dr. Sthamer Hamburg also produces various foam concentrates. At the same time, Sabo Foam S.R.L., focusing also on Foreign consumers, warns about the peculiarities of US legislation regarding the use of fluorine-containing foams.

Thus in the EU, the assessment of the degree of environmental hazard of fire extinguishing substances which is determined by the harm inflicted on the environment or human does not rely on test methods for foam concentrates of various multiplicity and fire extinguishing powders to fight the fire. As a result, environmental requirements for foam concentrates of various expansion and powder fire extinguishing substances are not regulated.

According to the report by Reihlen *et al.* (2010), carried out in the framework of the project "Building capacity in northwestern Russia to manage hazardous substances" FKZ 380 01 188 (2008-2010), Russia has its own system of chemical hazard assessment, taking into account hygienic norms and toxicological, ecotoxicological criteria and stability. Such quality parameters as BOD, the content of ammonium ions, nitrates, microorganisms, etc. are used.

As part of this project ("Building capacity in northwestern Russia to manage hazardous substances" FKZ 380 01 188 (2008-2010)), it was shown (Reihlen *et al.*, 2010) that unlike the European approaches in assessing the effects of chemicals on the environment in Russia does not have a working mechanism for comparing the system of priorities and determining actions; decisions about resolving the presence of chemicals in the environment are taken individually in each case, often without complying with environmental requirements.

In Russia, the parameters of biodegradability and phytotoxicity are also used to study and evaluate the environmental characteristics of fire extinguishing substances in particular, foam formers (Anonymous, 2013a, b; Anonymous, 2016a-e).

Thus Anonymous (2002), the biodegradability of foams is only mentioned in the "The procedure for the use of foam for extinguishing fire" (Anonymous, 1996) according to which the foams are biologically "soft" or "hard", it is necessary to clean the soil when using the last or refuse to use them. GOST R 50588 "Foaming agents for fire extinguishing. General technical requirements and test methods" (Anonymous, 2012) and GOST R 53280.2 "Automatic fire extinguishing systems. Fire extinguishing media. Part 2. Foam concentrates for subsurface extinguishing of fires of oil and petroleum production tanks. General technical requirements and test methods" (Anonymous, 2010) do not provide for the determination of the environmental characteristics of foams. Standards for test methods of gas fire extinguishing substances (Anonymous, 2009a-e) also do not contain requirements for the environmental characteristics of these compounds but only the requirements for their fire safety. The international standards of the ISO 7202-7203 on the methods for testing foaming agents and fire extinguishing powders (ISO., 2011; Anonymous, 2011a, b; Anonymous, 2018b) that are active in the Russian Federation as already mentioned above do not contain information on the determination of their environmental characteristics.

Thus, in the Russian Federation in the regulatory documents, environmental requirements for fire extinguishing substances are either absent or unclear. In the US, huge attention is paid to the composition and

environmental impact of fire extinguishing agents. In 2003, the US Environmental Protection Agency (EPA) formed a fluorosulfonant working group which concluded that fluorosulfonants with a carbon chain length greater than C6 could potentially decompose and form PFOA, i.e. can be toxic to the environment whereas fluorosulfonants with a smaller or similar long carbon chain cannot decompose to PFOA. As a result in 2005, the EPA organized PFOA Stewardship Program (Anonymous, 2006a, b). According to the requirements of this program all manufacturers should voluntarily change the compositions of foaming agents using short-chained fluorocarbon compounds and double-check their characteristics for compliance with international standards. This program has been supported by many national and Foreign manufacturers of foams and as a result, the availability of long-chained fluorine-containing frothers has significantly decreased.

In the United States, the internationally recognized standard NFPA 11: 2016, "The US Standard for Low, Medium and High-Expansion Foams" (NFPA., 2016) introduced by the National Fire Protection Agency (NFPA) (NFPA., 2019) operates. This standard regulates the design, installation, operation, testing and maintenance of low, medium and high expansion foam systems for fire protection. It also, refers to the environmental impact of fluorine-containing foams and foams with long chain fluorocarbon compounds and environmental risks.

Manufacturers of fire extinguishing agents in the United States inform the public about new environmental regulatory requirements for fluorinated foams and articulate the advantages of existing foaming agents (Anonymous, 2017a-c; 2016a-e).

There are a lot of such manufacturers of fire extinguishing substances in the USA that work on the domestic and international market. One of the largest in the world is the chemical company DuPont. Its product line contains the FM 200 extinguishing gas which is often used in fire extinguishing systems.

It can be noted Amerex, badger fire protection. They are engaged both directly in the production of a whole range of extinguishing agents (foams, powders, equipment, etc.) and in their sale from other manufacturers. As a division of Amerex you can specify a major producer of Solberg foams which positions itself as an environmentally conscious producer. Known manufacturers include the company ANSUL which is engaged in the production of foam, solid and gaseous fire extinguishing substances as well as fire equipment. The manufacturer of the well-known fire-extinguishing substance Novec 1230 is a multi-industry investment and

production company 3M. Many of these companies note in their safety data sheets for fire extinguishing substances information on compliance with the REACH regulation.

Thus, in the United States there is a tightening of legal requirements for finding perfluorooctanoic acid, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in the environment as well as as a result for the production, packaging and storage conditions of fluorine-containing foams.

Active studies of the impact of human activity on the Chinese environment are relatively short-lived. Only in the last decade a trend has emerged in China not only towards the development of an industrial component but also towards an environmental one with support at the state level. It is noted the need to develop the environmental protection industry and increase investment in this direction. At the same time, Chinese experts note the retardation of China in comparison with other developed countries (Anonymous, 2011a, b).

As mentioned above (Wang, 2015) as of today, a detailed study of the Chinese environment is complicated by rather weak funding. However, it should be noted that recently there have appeared quite a lot of works devoted to the influence of industry, urbanization as well as fire fighting and other components on the state of water, soil, atmospheric air and biota. This includes the spread of PFOC and PFOS in the environment.

The researchers by Lim *et al.* (2011) note an increase in the concentration of PFOS in the Chinese environment compared with other countries. However, the lack of a reliable methodology for inventorying PFOA discharges significantly complicates the identification of all its sources. According to the research conducted by many scientists (Lim *et al.*, 2011; Xie *et al.*, 2013) one of the priority sources of PFOS in addition to metallurgy study production, textile industry in the environment of China are fluorine-containing foams.

The content of a group of perfluorinated compounds in water and bottom sediments of one of the largest sources of drinking water in China, Lake Taihu is determined (Pan *et al.*, 2014). It is noted that PFOS exhibits a greater affinity for sediment while short-chained perfluorinated compounds predominate in water. Although, drinking water did not directly affect public health, the researchers note the potential risk to human and animal health in the long term as well as the need to take into account the relationship between their distribution in water and sediments, bioaccumulation, concentration and toxicity when developing water standards for perfluorinated compounds. Researches carried out by another group of scientists (Guo *et al.*,

2015) for the same lake showed that the main source of perfluorinated acids and salts in it is urban runoff and bottom sediments, containing these substances can act as potential sources of pollution in the adjacent territory.

The main sources Chen *et al.* (2012) of PFOC and PFOS in wastewater are also referred to industrial and municipal wastewater with PFOS in wastewater almost 30 times higher than in seawater. According to the studies (Chen *et al.*, 2016), perfluorinated compounds can migrate from industrialized areas to nearby rural areas and pollute the soil, surface and groundwater.

It should be noted that the presence of perfluorinated compounds in the environment is often compared by Chinese experts with Foreign standards or they use Foreign approaches to assess various environmental parameters which indirectly confirms the fact of imperfection of Chinese environmental legislation (Chen *et al.*, 2012; Guo *et al.*, 2015).

The researchers themselves state a poorly developed assessment of the environmental risk of perfluoroalkyl acids in China (Wang *et al.*, 2015) including PFOA, provided that these compounds are widely distributed in water, soil, plants and even living organisms including humans, especially in industrialized regions.

The requirements of the Chinese standards for powder fire extinguishing agents (Anonymous, 2017a) merely state that their production process must comply with national legislation on health, safety and the environment and the requirements for water-based foams and extinguishing agents are not mentioned at all (GB 17835, 2008). Ecological characteristics are also absent among the necessary components of new water-based fire extinguishing agents being developed (Anonymous, 2006; Huang, *et al.*, 2012).

The researchers Liu *et al.* (2017) state that China has become the largest source of pollution in the world and the most important center for the production and consumption of PFOS and PFOA in the world. At the same time there is a lack of a systematic analysis of the ways of getting into various components of the environment and their quantitative assessment.

The main manufacturers of fire extinguishing agents in China Jiangsu Suolong Fire Science and Technology Co., Ltd can be emphasised which are mainly engaged in the production of synthetic and protein-based fire extinguishing foams for extinguishing the fires of various classes for more than 30 countries in Asia, the Middle East, Africa and Europe; Luoyang Langchao Fire Technology Co., Ltd which produces foams and powders to extinguish various classes of fires and several others.

Thus, Foreign standards and methods are used for assessing the environmental parameters of perfluorinated compounds in the environment in China. Ecological characteristics among the newly developed extinguishing agents are absent.

In Ukraine, regulatory documents do not clearly specify environmental requirements for fire extinguishing compounds. In particular, DSTU 3789 “Fire safety. General designation foam concentrates for fire extinguishing. General specifications and test methods” declares at least 80% of biodegradability of foam formers and Ukraine’s commitment to the requirements of Montreal Protocol in accordance with national legislation (Anonymous, 2016).

As part of the implementation of European legislation in Ukraine, there is a series of international standards DSTU EN 1568, parts 1-4 regarding the requirements for foaming agents of various multiplicities and various liquids applicable to extinguishing as well as the standard DSTU EN 615 “Fire protection-Fire extinguishing media- Specifications for powders (other than class D powders)”. However, as mentioned above, they have no requirements for the environmental safety of these compounds (Anonymous, 2017, 2018a-e).

Thus, in Ukraine today there are no uniform approaches to the assessment of the environmental characteristics of fire extinguishing substances. The fire-extinguishing characteristics of the compounds are determined first.

The Republic of Azerbaijan as a state with large reserves of natural complex hydrocarbons in the form of oil and associated gases is faced with environmental threats associated primarily with their extraction and processing. One of such threats may be the occurrence of fires in the oil and gas industry and the oil refining industry, followed by environmental pollution. As a result, the environmental characteristics of substances used for extinguishing the fires of class B are particularly relevant in order to minimize these contaminations in the Azerbaijan Republic.

The regulatory documents of the Republic of Azerbaijan is largely based on the documents developed in Russian Federation. In particular, the “Guidelines for extinguishing oil and petroleum products in tanks and tank farms», GOST R 50588-2012 “Foaming agents for fire extinguishing. General technical requirements and test methods” are applied (Anonymous, 1999, 2012).

The regulatory documents of the Republic of Azerbaijan do not take into account the impact of fire extinguishing agents on the environment. Although, like a number of other states, the Republic of Azerbaijan in 2003 joined Stockholm Convention of May 22, 2001 “On

Persistent Organic Pollutants” (Anonymous, 2003) which include decomposition products of long-chained fluorinated hydrocarbons that are part of the foaming agents that are often used for extinguishing the fires of petroleum products (class B). The existing regulatory document “Resolution of the Cabinet of Ministers of the Republic of Azerbaijan”. Application of payments for emissions of natural resources, discharges of polluting substances into the natural environment and use of funds received as a result of these payments does not regulate compensation for environmental pollution by fire extinguishing chemicals or its calculation (Anonymous, 2008a, b).

The production of fire extinguishing substances in the Republic of Azerbaijan today is not industrially developed, the necessary products are purchased from Foreign manufacturers. However, research is being conducted on the development of domestic foams, taking into account the specifics of the extraction and production of petroleum products in the field. The papers of such scientists as Abbasov, Ismailov, Abdullayev, associated with the development of a foaming agent based on aminoacid complexes of petroleum acids (Abbasov *et al.*, 2008, 2010) are known in this direction. Dyshdurova and Mammedkhanova study the preparation of a foaming agent based on synthetic oil-acid salts (Dyshdurova and Khanova, 2017). However, the environmental properties of the developed foams are not considered in these studies.

Thus, in the regulatory documents of many developed countries, the environmental requirements for substances used in extinguishing fires are not specified or spelled out unclearly.

CONCLUSION

There is a global tendency to abandon the use of environmentally hazardous fire extinguishing agents used for extinguishing the fires of various classes including the prohibition of their production. Ecological parameters of fire extinguishing compounds do not have unified criteria for their determination.

A review of the environmental characteristics of fire-extinguishing foams confirmed the negative impact on the environment of fluorine-containing synthetic foams, the absence of environmentally safe foams and a unified methodology for obtaining their environmental characteristics. The certification documentation for fire extinguishing powders contains insufficient information on their environmental and ecotoxicological properties. To the assessment of environmental exposure to gaseous extinguishing agents is not a unified approach

which makes it difficult to effectively comply with the requirements of Montreal Protocol. There is a diverse tendency in the development of new fire extinguishing agents. Ecological properties of the proposed compounds are not always considered.

In the regulatory documents of many developed countries, the environmental requirements for substances that are used for extinguishing fires are not specified or spelled ambiguously. In EU, the assessment of the environmental hazard of fire extinguishing substances which is determined by the harm they cause to the environment or a human does not rely on test methods for foam concentrates of various expansion and fire extinguishing powders for fire fighting. As a result, environmental requirements for foam concentrates of various multiplicities and powder fire extinguishing substances are not regulated. In Russian Federation and in the Republic of Azerbaijan, environmental regulations for fire extinguishing substances are either absent or unclear in regulatory documents. In the US, there is a tightening of legal requirements for finding perfluorooctanoic acid, perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride in the environment and also as a result for the production, packaging and storage conditions of fluorine-containing foams. To assess the environmental parameters of perfluorinated compounds in the environment in China, Foreign standards and methods are used and environmental characteristics are not available among new fire extinguishing agents. In Ukraine today there are also no common approaches to assessing the environmental characteristics of fire extinguishing substances, first of all the fire extinguishing characteristics of the compounds are determined.

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