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New Types, Halogen-Free, Eco-Safe, Inexpensive Fire-Extinguishing and Fire-Protective Materials

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Abstract

The aim of the presented investigation is the development of technology for production of novel, halogen-free, environmentally safe, highly efficient fire-extinguishing powders based on local mineral raw materials and elaboration of new types, environmentally safe, fire-protective materials on the basis of such fire-extinguishing powders, which in composite materials are functioning, as efficient inert flame retardants. The technology for production of these materials differs from the conventional production. Fire-extinguishing powders will be produced by mechanical blending of local mineral raw materials, which do not require modification with expensive halogen-containing hydrofobizing additives, making the extinguishing materials far cheaper than imported analogues. Experimental data confirm that the developed fire-extinguishing powders are characterized by high inhibition properties and fire-extinguishing ability similarly to flame retardants. Here it should be noted, that obtained powders similarly to inert flame retardants, don't participate in the process of polymer preparation, their mechanical mixing with polymeric binders is possible in the course of processing, and in contrast to them are characterized by high performance properties. That's why fire-extinguishing powders of our preparation in fire-protective materials are functioning, as efficient inert flame retardants. Therefore fire-protective materials are manufactured only by mechanical mixing of binders-Polyurethane resins and fillers-High-dispersed fire-extinguishing powders of our preparation, does not need addition of expensive flame retardants. It on the one hand simplifies technological process of production and on the other hand decreases cost prices of protective materials. Experimental data confirm that the developed fire-protective materials by fire-resistance are qualified as hardly combustible materials and their performance properties are not worse than performance properties of the standard protective materials of common production. Thus, they are fulfilling completely requirements posed by normative documentation to the materials used in building processes.

Keywords: Fire-extinguishing powders; Fire-extinguishing capacity; Inhibition properties; Fire-protective materials; Fire-resistance

Introduction

In the conditions of building and retention of underground tunnels of transport, civil and military function, as well as of social and storehouse buildings, the fire is a very important problem. Within the recent years, the amount of fires increased progressively, while the damage done is comparable to the consequences of terrorist activities. Rapid growth of the damage caused by fires is embarrassing and comprises tens of billions of dollars annually. Injury and poisoning of people is often caused not only by combustion products, but also by toxicity of the utilized preventing measures. Therefore before the whole world sharply arises a problem of fire localization, suppression and development of such preventing measures, which will provide inhibition of burning processes in the zone of inflammation and elimination of toxic materials emission. Among these measures, the most topical is the use of environmentally safe, highly effective fire-extinguishing and fire-protective means. The existing statistics shows that the currently used conventional fire-extinguishing substances (CO_2, water and foam), are comparatively expensive, neither universal, not environmentally safe and have a quite low efficiency. Nowadays, fire-extinguishing powders are considered to be the most efficient fire-extinguishing agents due to their universality and high efficiency [1-3].

As is known, the commonly produced and used fire-extinguishing powders are the finely dispersed mineral salts with different additives, which improve the performance properties of salts, in particular, the unwanted tendency for consolidation and caking. All they are rather complicated multicomponent heterogeneous systems, and their fire-extinguishing capacity (as well as other performance properties) is mainly determined by the chemical composition. In order to improve performance properties (mainly, to decrease the caking capacity) water absorbing additives are used for hydrophobization of powders. Halogen containing organic hydrophobizers is mainly used as additives. Thus, most of them are containing halogen and do not satisfy the contemporary demands for environmentally safe, non-toxic and universal fire-distinguishing agents. It is unambiguously stated that when halogen gets into atmosphere it causes the disturbance of ozone layer [3,4]. Therefore, development of halogen free, nontoxic, environmentally safe fire-extinguishing powders is currently a very important problem.

Protection of material against fire means a decrease of fire-hazard by their special treatment, in which surface treatment of material as well as their impregnation by fire-protective compounds is meant

[5,6]. Protection against fire by the use of impregnating compounds is quite costly process, isn't universal and isn't used for materials of all type. Along with it, every so often, in performance process an elution of impregnating compounds takes place [7,8]. Therefore, at present surface treatment of materials is considered as one of the most important method. For surface treatment the surface protective compounds are used. It is well known, that the main components of surface protective compounds are: binders, flame retardants and fillers. Organic as well as inorganic compounds are used as binders. Inorganic binders are characterized with low performance properties. Therefore organic polymeric compounds: polyethers, polyvinylacetates, phenol-formaldehyde, polyurethane and polycarbamide resins are used as binder every so often. As a rule, organic compounds are qualified as easily combustible compounds and for decrease of their combustibility an addition of efficient flame retardants is necessary. Phosphorous and halogen-containing organic and inorganic compounds are the most efficient flame retardants. According to whether they interact with polymers or with initial monomers, flame retardants of inert or reactive type are found. The use of inert flame retardants aren't associated directly with polymer production, it mixes mechanically with polymer in the course of its processing, which simplify and expand, to some extent, the possibilities of preparation of new fire-resistant compounds. But, along with it, they are characterized by a number of disadvantages (migration at materials surface, elution ability by water and other washing means and etc.), such as effect on physical-mechanical properties of polymeric compounds. Therefore, at present, the demand for the use of reactive flame retardants increases more and more. Reactive flame retardants -chloro-and phosphoroganic monomers participate directly in the processes of polymerization and polycondensation and form co-polymers by high fire-resistance, but every so often by low performance properties. Along with it, it is well-known, that chlorine and phosphorous content enhances smoke formation ability and toxicity of polymeric material. It should be also noted, that the use of reactive flame retardants is associated with quite expensive and complex processes which are not studied completely yet. In this case low-molecular polymers are mainly prepared, which do not satisfy the contemporary demands for effective, nontoxic, environmentally safe and universal fire-protective materials [7-10]. Therefore, elaboration of halogen-free, nontoxic, environmentally safe, inexpensive fire-protective materials is currently a very important problem. On the basis of above-mentioned problems in our work we describe the ways of development of technology for production of novel, halogen-free, environmentally safe, highly efficient fire-extinguishing powders based on local mineral raw materials and elaboration of new types, environmentally safe fire-protective materials on the basis of such fire-extinguishing powders, which in composite materials are functioning as efficient inert flame retardants.

Materials and Methods

The technology for production of proposed fire-extinguishing powders and fire-protective materials is simple and differs from the conventional production. According to this technology, fire-extinguishing powders are prepared using only mechanical treatment (grinding, screening up to 250 μm dispersity, drying at 700-1000°C) and mixing of raw materials. It does not require any additional chemical processing and modification using expensive halogen containing hydrophobizing additives (Figure 1). Due to the developed technology, production processes are simplified and costs are reduced.

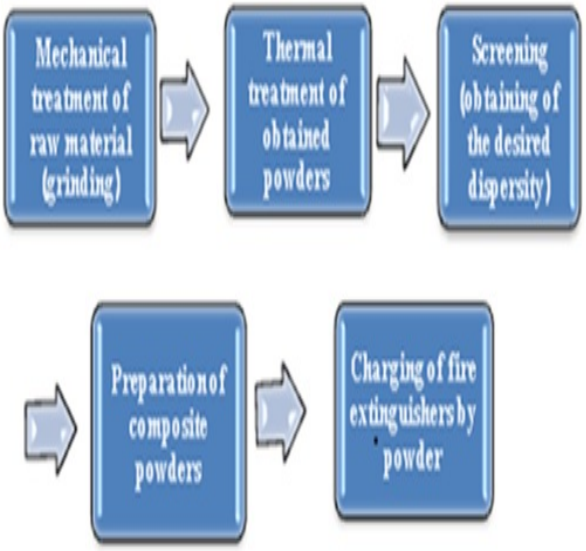

Figure 1: Flow Chart showing Technology for production of proposed fire-extinguishing powders.

Raw materials -zeolite, clay shale and perlite–are chosen due to their high performance properties and ability to suppress the combustion and burning processes, which can be predicted using the results of chemical and thermal gravimetric analysis of raw materials. Mineralogical composition of utilized materials, presented in Table 1, show that they are silicate origin and contain alkali and alkaline-earth metal carbonates, bicarbonates, silicates also iron, aluminium, alkali metal hydroxides and crystallization water. Therefore, at high temperatures these raw materials are characterized with emission of incombustible gases, water steam and metal oxides which dilute combustible products, creating protective film and coke layer on the surface of material. The investigation and estimation of these processes are done with thermogravimetric analysis [11]. On the basis of thermogravimetric analysis it is stated, that at the first stage adsorption and crystallization water separation happen. At the next stages while at higher temperatures (700°C and more) there happens the formation of metal oxides protective film and coke layer. The liberated incombustible gases and water steam in flame zone are functioning as phlegmatizer and in surface zone are causing the formation of swelled layer. The latter, protective film of metal oxides swelled and coke layer cause a strong "fire-limiting" effect. This indicates the fact that these materials can reveal the properties similar to highly effective homogeneous inhibitors. Along with it, it should be noted that high-dispersed composite powders of zeolites, perlites and clay shales are characterized by high heterogenous inhibition effect, which implies heterogeneous recombination of reaction active centers on the surface of solid particles of the powder. Oxygen atom is one of the leading active centers of burning reactions. Therefore, the coefficient of atomic oxygen recombination -γ_0 was selected as one of the main characteristics of heterogenous inhibition effect of powder [12]. Using Electro Paramagnetic Resonance (EPR) methods, we determined the coefficient of recombination of atomic oxygen on the surface of solid particles of the zeolites, perlites and clay shales, which ranged between

$\gamma_0=2.6\times10^{-6}\div6.5\times10^{-3}$ The comparison of the received results with the published data [12] showed, that the studied materials according to this parameter are considerably better than quartz and sulfates ($\gamma0\sim10^{-4}$). On the other hand, γ_0 values are close to the coefficients of heterogeneous recombination of oxygen atoms on the surfaces of carbonates and chlorides ($\gamma0\sim10^{-3}$). This shows that such raw materials are characterized by high heterogenous inhibition properties.

Hence, mentioned fire-extinguishing powders on flame zone perform homogenous as well as heterogenous inhibition of combustion process and in surface zone they form protective layer, which hinders heat transfer to combustive material and excludes direct contact of combustive material with air. This is indicating to the fact, that fire-extinguishing powders of our preparation similarly to efficient flame retardants are characterized by high inhibition properties and in contrast to them are halogen-free, non-toxic, environmentally safe and far cheaper. Here it should be noted, that obtained powders similarly to inert flame retardants, don't participate in the process of polymer preparation, their mechanical mixing with polymeric binders is possible in the course of processing, and in contrast to them are characterized by high performance properties: they have low caking capacity, are practically insoluble, resistant against atmospheric and chemical action and their elution and migration at materials surface doesn't takes place. Thus, such composite powders in fire-protective materials are functioning, in itself, as efficient inert flame retardants.

Therefore Fire-protective materials are manufactured only by mechanical mixing of binders -organic polymeric compounds and fillers-high-dispersed fire-extinguishing powders of our preparation, does not require additional of expensive, phosphorous and halogen-containing flame retardants, which, for its part, will be reflected in low price cost of fire-protective materials in comparison with imported analogues. Polyurethane resins were selected as binders, popularity of which is due to low price and simole technological process of production – at mechanical mixing of initial products; liquid isothyanate and polyol components of various viscosities by definite ratio, at conventional temperature polymerization occurs by high degree and high rate. The surface hardens completely during 60-180 sec. Along with it, polyurethane resins, in comparison with binders, used in series, have a number of advantages: environmentally -safety, low combustibility, high adhesion strength practically with material of all type (wood, metal, concrete, asphalt and etc.); high water proof and anticorrosive properties; heat-and frost-resistance. Estimation of fire-resistance of fire-protective materials is performed by the complex of fire-technical characteristics (combustibility, ignition flame proportion, smoke formation and toxicity), selecting of which is carried out in accordance with materials function and fields of application [9]. Fire-protective materials not only should effectively protect materials surface against fire, but they should retain their properties as well, the variation of which reduces materials efficiency. This parameter is determined not only by their inhibition properties and fire-resistance ability, but also by their performance properties, among which the most important are: adhesion strength, impact strength, hygroscopisity, heat-and frost-resistance and artificial ageing.

Experimental researches were carried out for wood materials for preparation of fire-protective materials. Polyurethane resins and sodium polymetaphospates were used as binders and as filler-composite fire-extinguishing powders of our preparation.

In order to study performance properties of fire-protective materials laboratory standard methods [9,13] are used:

-adhesion strength F(MPa) -force which is necessary for chipping of protective cover from sample surface;

- impact resistance S(cm) -maximum height from which a fall of a load of definite weight on sample surface doesn't cause visible failure of protective cover;

- hygroscopicity B (%) -ability of moisture absorption by protective cover, which is calculated by formula:

where, Б -sample mass after testing (after moisture absorption), gr;

A -sample mass before testing, gr.

-artificial ageing -ability of retaining of cover efficiency at the action of high temper.

Experimental results of performance factors are given in Table 1.

Fire-technical characteristics can be determined by various standard methods of fire testing.

Main characteristics of combustibility:

-time of independent combustion -tcr (sec);

-degree of material failure (mass loss) -(%) which is calculated by formula:

$$S_m = \frac{m_1 - m_2}{m_1} \cdot 100$$

where: m_1 -sample mass before testing, gr.

M_2 -mass after testing, gr.

- degree of failure lengthwise-S_L% , which is calculated by formula:

$$S_L = \frac{S_1 - S_2}{S_1} \cdot 100$$

where: S_1 -sample length before testing, cm;

S_2-length of damage sample, cm.

In the course of studying combustibility of materials in an initial stage it is established combustible group by the method of "fire tube", which is exploited for building materials for establishing of combustibility group. Classifying of materials by combustibility is carried by the following manner: incombustible material -mass loss <9%; hardly combustible material -mass loss 9-20%: combustible material -mass loss >20% [14].

Experimental results show, that fire-protective materials, prepared on the basis of polymetaphosphutes, are characterized with high fire-resistance in comparison with fire-protective materials, prepared on the basis of polyurethane resins, but by their performance properties are very low and do not satisfy the completely requirements posed by normative documentation to the materials used in building processes. Fire-protective materials, prepared on the basis of polymetaphosphutes by fire-resistance are qualified as hardly combustible materials and their performance properties are not worse than performance properties of the standard protective materials of common production. At the same time we have established, that by increase of filler content in polyurethane resins fire-resistance sharply enhances and performance properties changes insignificantly. Therefore we can surmise, that obtained fire-protective materials with their performance properties and fire-resistance are fulfill completely requirements posed

by normative documentation to the materials used in building processes. The results of experimental researches are given in Table 2.

Results

1. The newly developed fire-extinguishing powders will be produced by mechanical treatment and mixing of local mineral raw materials: zeolite, clay shale and perlite, does not require any additional chemical processing and modification with expensive, halogen containing hydrofobizers. Thus, the technology for production of these powders differs from the serial production technology. It is simple and is not associated with significant economic costs.
2. Fire-extinguishing powders of our preparation are halogen-free, environmentally safe, highly efficient, universal and significantly cheaper (1.2-2 times cheaper) than the imported analogues.
3. Obtained powders are characterized by high inhibition properties and fire-extinguishing ability similarly to efficient flame retardants. Thus, in composite materials they play the role of efficient flame retardants.
4. Obtained powders similarly to inert flame retardants, don't participate in the process of polymer preparation, their mechanical mixing with polymeric binders is possible in the course of processing, and in contrast to them are characterized by high performance properties. Thus, the received powders can be effectively used as fillers, which in fire-protective materials are functioning as efficient inert flame retardants.
5. Developed fire-protective materials will be prepared by mechanical mixing of binders -polyurethane resins and fillers – fire-extinguishing powders of our preparation, does not need addition of expensive, phosphorous and halogen-containing flame retardants, which, for its part, will be reflected in low price cost of fire-protective materials in comparison with imported analogues. Thus, the technology for production of these fire-protective materials is simple and differs from the common production technologies.
6. Obtained fire-protective materials are new types, environmentally safe, very effective and significantly cheaper than imported analogues. Thus, they fulfill completely requirements posed by normative documentation to the materials used in building processes, thus they can be used to protect building materials and constructions of any type from fire.

S.No	Fire-protective materials	Hygroscopisity %	Adhesion strength, Pa	Impact strength, sm	Artificial ageing
1	Composite powders – 40% Polyurethane resins -60%	0.1	1.4	75	Resistant against atmospheric action
2	Composite powders -50% Polyurethane resins -50%	0.11	1.3	73	Resistant against atmospheric action
3	Composite powders -60% Polyurethane resins -40%	0.12	1.2	72	Resistant against atmospheric action
4	Composite powders -40% Sodium polymetaphospates -60%	0.2	0.9	65	Not resistant against atmospheric action
5	Composite powders -50% Sodium polymetaphospates -50%	0.25	0.85	62	Not resistant against atmospheric action
6	Composite powders -60% Sodium polymetaphospates -40%	0.3	0.8	60	Not resistant against atmospheric action

Table 1: Performance properties of fire-protective materials.

S. No	Fire-protective materials	Hygroscopisity %	Adhesion strength, MPa	Impact strength, sm	Artificial ageing
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2	Composite powders -50% Polyurethane resins -50%	0.11	1.3	73	Resistant against atmospheric action
3	Composite powders -60% Polyurethane resins -40%	0.12	1.2	72	Resistant against atmospheric action
4	Composite powders -40% Sodium polymetaphospates -60%	0.2	0.9	65	Not resistant against atmospheric action
5	Composite powders -50% Sodium polymetaphospates -50%	0.25	0.85	62	Not resistant against atmospheric action

6	Composite powders -60% Sodium polymetaphospates -40%	0.3	0.8	60	Not resistant against atmospheric action

Table 2: Fire-resistance of fire-protective materials.

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