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Gurchumelia Lali
Chemist, PhD, Senior Researcher, Laboratory of Theoretical Research,
TSU Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia

Tsarakhov Murman
Chemist, PhD, Senior Researcher, N. Landia Laboratory of Thermochemistry,
TSU Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia

Machaladze Tengiz
Chemist, Doctor, Head of N. Landia Laboratory of Thermochemistry,
TSU Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia

Dzanashvili Dali
Chemist, PhD, Senior Researcher Laboratory of Physical-chemical Analysis,
TSU Rafael Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia

Bezhanov Feliks
PhD in Engineering, Specialist, Laboratory of Rock,
Construction Material Properties and Quality Control, G.Tsulukidze Mining Institute, Georgia

Chudakova Olga
MSc in Economic Geography, Coordinator of Scientific Projects,
Department of Scientific Programs, G.Tsulukidze Mining Institute, Georgia

PRODUCING OF NEW TYPES, FIRE-PROTECTIVE COATINGS BY THE USE OF HIGH DISPERSED COMPOSITE POWDERS OF LOCAL MINERAL RAW MATERIALS

Abstract. The aim of this research is the fabrication of new types, environmentally safe, highly efficient and inexpensive fire-protective coatings by the use of high-dispersed composite powders
(with high inhibitory properties) of local mineral raw materials, which in fire-protective coatings will play the role as binders as well as efficient inert flame retardants.

Fire-protective coating was prepared only by mechanical mixing of binders and fillers, does not require addition of expensive phosphorus and halogen-containing flame retardants. On the one hand it simplifies technological process of production of materials and on the other hand decreases price cost of fire-protective coatings.

Polyurethane resins were selected as binders, popularity of which is due to low price and simple technological process of production, high performance properties and low combustion capacity (in comparison with binders, used in series). High-dispersed composite powders of local mineral raw materials: zeolites, perlites, dolomites and clay shales are used as fillers, which are characterized by high inhibition properties and fire-extinguishing ability.

Thus, produced coatings will be environmentally safe and much cheaper compared to imported analogues. Due to their performance properties and fire resistance, they will fully meet the requirements set by the normative documentation for building materials.

The performance properties of the obtained fire-protective coatings were determined by laboratory standard methods. Thermogravimetric analysis method allows us to study the thermal stability of the material and determine the relative combustion capacity of the material. The effectiveness of the obtained coating was evaluated by the determine the relative combustion capacity - Oxygen Index (OI) and by of studying combustibility of materials. In the course of studying combustibility of materials in an initial stage was established combustible group by the method of "fire tube" - ГОСТ 1708-71.

Keywords: environmentally safe, highly efficient, inexpensive, fire-protective coatings.

Introduction

Protection of building materials and constructions against fire is a major problem. It is a technical measure that provides fire hazard reduction through their special treatment: surface treatment of material and construction or their impregnation by fire-protective compounds. Impregnating compounds present the aqueous solutions of various salts (flame retardants). Protection against fire by the use of impregnating compounds is quite costly process, requires large consumption of impregnating compound and isn’t universal [1- 4].

Therefore, at present surface treatment of materials and constructions is considered as one of the most important methods. For surface treatment the surface protective compounds are used, which reduce combustibility of the material, hinder
the flame propagation on material surface and increase fire-resistance of construction. 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 by lesser performance properties. Therefore, organic compounds are used as binder every so often. As a rule, organic compounds are qualified as easily combustible materials and for decrease of their combustibility an addition of efficient flame retardants is necessary. Flame retardants are substances that inhibit combustion processes and reduce the combustibility of the material. The most effective flame retardants are: inorganic salts, metal oxides, hydroxides, phosphorus and halogen-containing organic substances [4,5].

The effect of chemical and thermal inhibition with inorganic salt particles of the combustion process was theoretically studied [6 – 8]. It is stated, that chemical inhibition of the combustion reaction is of special importance when inhibiting flame with inorganic salt particles. Chemical inhibition implies homogeneous and heterogeneous chemical factors. Homogeneous effect involves heating, evaporation and destruction of particles when incombustible gases, water steam and metal oxides are separated. Thus, a quantitative measure of the effectiveness of homogeneous inhibition is the ratio of the reaction velocities \( \omega_{(homo)} \) with the participation of inhibitory molecules in the gaseous phase due to the excitation of particles in the flame to the velocity \( \omega_{branch} \) of the branching of the reaction chains. Based on the kinetic studies of these processes has been established, that at flame extinguishing by small-size particles \( (d<20 \mu m) \) the homogenous inhibition may efficiently compete with important gas-phase reactions in the moderate and high-temperature regions of the flame \( (T>500K) \). While flame extinguishing by the coarse-size particles \( (d > 20 \mu m) \) much attention must be also given to the heterogeneous inhibition in the low-temperature region of the flame \( (T<500K) \), which implies the heterogeneous removal of the leading active centers of the reaction on the surface of solid particle [6,7]. Heat is spent on heating, destroying and evaporating particles of inorganic salts, which reduces the temperature of the condensed phase. The released non-combustible gases dilute the combustible gases
in the combustion zone and reduce the flame temperature. Protective film of metal oxides and coke layer hinders oxygen feeding to reaction zone and reduce the heat flow to the surface of the combustible material, which causes cooling the combustion zone. The heat generation velocities \((w_+ \) in the flame zone and the heat transfer velocities \((w_-)\) on solid particles has been theoretically calculated (Simpson rule). Based on the results obtained, it was established, that the cooling effect (heat inhibition) of the combustion zone by solid particles of inorganic salts can actually make a significant contribution to the overall combustion reaction inhibition process [8].

Depending on how the flame retardants interact with the polymers there are inert and reactive types. The use of inert flame retardants isn’t associated directly with polymer production; it mixes mechanically with polymer in the course of its processing, which somewhat simplifies the possibilities of obtaining new fire-retardant materials. But, along with it, they are characterized by a number of disadvantages. Such as effect on physical-mechanical properties of polymeric compounds, migration at materials surface, elution ability by water and other washing means and etc. Therefore, at present the demand for the use of reactive flame retardants increases more and more. Chlor and phosphororganic monomers are mainly classified as reactive flame retardants, which participate in the reactions of polymerization and form co-polymers by high fire-resistant 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 don’t fulfill modern requirement, primarily from the viewpoint of efficient, non-toxic and universal use [3,9,10].

Therefore, one of the most important problems to increase fire safety building materials and constructions is the use of environmentally safe, non-toxic flame retardants for production of fire-protective materials. For this purpose, it is very important to select environmentally safe inorganic substances and to study flame inhibition processes by them.
On the basis of above-mentioned problems, we propose the ways of elaboration of new types (two components), environmentally safe, highly efficient and inexpensive fire-protective coatings by the use of high-dispersed composite powders (with high inhibitory properties) of mineral raw materials, which in protective coatings will play the role of binders as well as efficient inert flame retardants.

The aim of this research is the elaboration of new types, environmentally safe, highly efficient and inexpensive fire-protective coatings by the use of high-dispersed composite powders (with high inhibitory properties) of local mineral raw materials, which in fire-protective coatings will play the role as binders as well as efficient inert flame retardants.

**Materials and Methods**

The technology for production of proposed fire-protective coatings is simple and differs from the conventional production. According to this technology, fire-protective coating is prepared only by mechanical mixing of binders and fillers, does not require addition of expensive phosphorus and halogen-containing flame retardants (Fig.1). On the one hand it simplifies technological process of production of materials and on the other hand decreases price cost of fire-protective coatings.

![Technological process for production of fire-protective covers](image)

**Fig.1. Technological process for production of fire-protective covers**

Polyurethane resins were selected as binders, popularity of which is due to low price, simple technological process of production, high performance properties and low combustion capacity (in comparison with binders, used in series) [11]. High-dispersed
composite powders of local mineral raw materials: zeolites, perlites, dolomites and clay shales are used as fillers. Such raw materials are silicate origin and containing alkaline-earth metal hydroxides, carbonates, bicarbonates, silicates and crystallization water. At their intensive heating incombustible gases, water steam and metal oxides are separated. The values of their heterogeneous recombination coefficients of atomic oxygen (which is basic characteristic of heterogeneous inhibition) are close to the values of the coefficients of heterogeneous recombination of oxygen atoms on the surfaces carbonates and chlorides. Also, they are characterized by high fire-extinguishing ability [12-13]. Therefore, we can assume, that similarly to inorganic salts, they will have the ability both chemical as well as heat inhibition. Incombustible gases and water steam in the high temperature zone will inhibit homogeneous gas-phase reactions. In the low-temperature zone heterogeneous recombination of the active centers of the reaction on the surface of the powder particles will take place. Metal oxides form an insulating protective layer on the surface of the combustible material, which prevents heat transfer to the combustible material and cools the flame. This is indicative of the fact, that such powders, similarly to flame retardants, will inhibit combustion processes, reduce material combustion and increase their fire resistance. Along with it, it should be noted that mentioned fillers, similarly to inert flame retardants, don’t participate in the process of polymer preparation, their mechanical mixing with polymeric binder is possible in the course of processing, and in contrast to them are characterized by high performance properties: they are environmentally safe, resistant to the atmospheric and chemical action, their migration at material surface and elution doesn’t take place [14].

Fire-protective coatings not only should effectively protect materials surface against fire, but they should retain their properties as well, the variation of which reduces coating 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, hygroscopicity, heat- and frost-resistance and artificial ageing.

Experimental researches were carried out for wood materials for preparation of fire-protective coatings, which we prepared only by mechanical mixing of binders -
polyurethane resins and fillers - high-dispersed composite powders: zeolites, clay shales, perlites and dolomites.

Performance properties of fire-protective coatings were studied by standard laboratory methods [15].

The results of experimental researches are given in Table 1.

### Table 1

**Performance properties of fire-protective materials**

<table>
<thead>
<tr>
<th>#</th>
<th>Fire-protective materials</th>
<th>Hygroscopicity, %</th>
<th>Adhesion strength, MPa</th>
<th>Impact strength, cm</th>
<th>Artificial ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High-dispersed composite fire-extinguishing powders - 30% Polyurethane resins - 70%</td>
<td>0.09</td>
<td>1.41</td>
<td>76</td>
<td>resistant against atmospheric</td>
</tr>
<tr>
<td>2</td>
<td>High-dispersed composite fire-extinguishing powders - 40% Polyurethane resins - 60%</td>
<td>0.1</td>
<td>1.4</td>
<td>74</td>
<td>resistant against atmospheric</td>
</tr>
<tr>
<td>3</td>
<td>High-dispersed composite fire-extinguishing powders - 50% Polyurethane resins - 50%</td>
<td>0.11</td>
<td>1.37</td>
<td>72</td>
<td>resistant against atmospheric</td>
</tr>
<tr>
<td>4</td>
<td>High-dispersed composite fire-extinguishing powders - 60% Polyurethane resins - 40%</td>
<td>0.14</td>
<td>1.25</td>
<td>68</td>
<td>resistant against atmospheric</td>
</tr>
</tbody>
</table>

The effectiveness of the obtained coating was evaluated by the determine the relative combustion capacity - Oxygen Index (OI) and by of studying combustibility of materials.

Thermogravimetric analysis method will be used to identify materials and assess fire safety. This method allows us to study the thermal stability of the material, to carry continuously recording of mass change with respect to temperature and time under conditions of intensive heating of the material, to determine the mass of coke waste of thermal destruction (CW) and calculate the relative combustion capacity of the material - Oxygen Index (OI). The thermal gravimetric analyses are performed using a Thermogravimetric Analyzer - NETSCH STA -2500 Regulus. Relative combustion capacity (OI) is determined by the well-known Van Krevelen formula (calculation method) [16]:

The relative combustion capacity of material is the most reproducible and responsive for changes in material composition. According to this, it quickly allows to investigate the effect of obtained powders on the combustion capacity of polymeric materials.

In the course of studying combustibility of materials in an initial stage it is established combustible group by the method of "fire tube" - ГОСТ 1708-71.

Main characteristics of combustibility: time of independent combustion - $t_{cr}$ (sec); degree of material failure (mass loss) - $S_m$ (%) 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.

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%.

The results of experimental researches are given in Table 2

**Fire-resistance of fire-protective materials**

<table>
<thead>
<tr>
<th>#</th>
<th>Fire-protective materials</th>
<th>Combustibility OI (%)</th>
<th>Mass loss $S_m$ (%)</th>
<th>Degree of failure lengthwise $S_L$ %</th>
<th>Time of independent combustion $t_{cr}$ (sec)</th>
<th>Combustible group</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>High-dispersed composite fire-extinguishing powders 30% Polyurethane resins - 70%</td>
<td>23</td>
<td>14</td>
<td>$\leq 60$</td>
<td>$&lt; 30$</td>
<td>hardly combustible</td>
</tr>
</tbody>
</table>

$$OI = 17.5 + 0.4 CW$$
Table continuation 2

<table>
<thead>
<tr>
<th></th>
<th>High-dispersed composite fire-extinguishing powders – 40% Polyurethane resins – 60%</th>
<th>26</th>
<th>12.5</th>
<th>≤ 56</th>
<th>&lt; 22</th>
<th>hardly combustible</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>High-dispersed composite fire-extinguishing powders – 50% Polyurethane resins – 50%</td>
<td>30</td>
<td>10.2</td>
<td>≤ 45</td>
<td>&lt; 16</td>
<td>hardly combustible</td>
</tr>
<tr>
<td>4</td>
<td>High-dispersed composite fire-extinguishing powders – 60% Polyurethane resins – 50%</td>
<td>34</td>
<td>9.4</td>
<td>≤ 25</td>
<td>&lt; 9</td>
<td>hardly combustible</td>
</tr>
</tbody>
</table>

Experimental results show, that fire-protective materials of our preparation are characterized by higher performance properties (which are not worse than the performance properties of the standard protective materials of common production) and by fire-resistance are qualified as hardly combustible materials. Moreover, we have established that by increase of filler content in polyurethane resins their combustibility significantly decreases (OI increases from 23% to 34%). The fire-resistance sharply enhances and performance properties vary slightly. On the bases of experimental researches for polyurethane resins were selected optimal amount of mentioned fillers (50%), in the case addition of which fire-protective coatings by high performance properties and by high fire-resistance are obtained.

Here should be noted, that zeolites as strong adsorbents are characterized by a high ability of selective ion-exchange and absorption of toxic substances, that is due to its specific frame structure. Frame structure characteristics are caused by existence of channels regular system, in which are placed metal cations and water molecules, called "zeolitic water". They are weakly connected to the frame and can be replaced with an ion-exchange or removed with dehydratation without rupture of structure. This on the one hand causes the formation of swelled layer on the surface of materials (which hinders heat transfer to combustive materials), and on the other hand, in their structure emptiness of various forms of caves and channels are formed, which easily adsorbs a set of toxic substances [17]. We can therefore assume that our protective coatings will not only effectively protect the surface of
the material from the effects of fire, but they will also have the ability to significantly reduce the concentration of smoke and toxic substances emitted from flickering hotspots in the fire zone. It significantly increases the environmental safety of the protective coating.

Thus produced coatings are environmentally safe and much cheaper compared to imported analogues. Due to their performance properties and fire resistance, they fulfill completely requirements posed by normative documentation to the materials used in building processes. We can therefore assume that they will be close to the real demands of the market.

**Conclusions**

– Developed fire-protective coatings are manufactured only by mechanical mixing of binders- polyurethane resins and fillers - high-dispersed composite powders of mineral raw materials, does not need addition of expensive, phosphorous and halogen-containing flame retardants, which are reflected in low price cost of fire- protective materials in comparison with imported analogues.

– The technology for production of these fire-protective coatings differs from the serial production technology. It is simple and is not associated with significant economic costs.

– Obtained fire-protective coatings 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.

**References:**


