Fireproof Composition Based on Liquid Glass and Mechanically Activated Aluminum Oxide

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Abstract

The composition of a fireproof formulation based on liquid glass and alumina and a method for its preparation have been developed. Mechanical activation of alumina changes the phase composition, the structure, and reactivity of the oxide powder and has a favorable effect on the properties of the composition. A flow chart for the production of the composition is suggested.

INTRODUCTION

Fire-protective treatment of constructions is now employed as one of the most common means of fire-prevention maintenance. The compositions in use, after being applied to the surface of combustible materials, enhance their fire retarding quality; for metals, they slow down heating-up and development of plastic deformations at the fire spot. The fireproof properties are ensured by the formation of a porous heat-shielding layer, by the evolution of nonflammable gases that localize flame, and by endothermic processes, lowering the surface temperature.

In practice, preference is given to compositions based on organic binders possessing enhanced technical properties [1]. At the same time, their universal currency is hindered by the poor ecological properties and rather low service life.

The compositions involving liquid glass (LG) hold promise in the group of compositions based on mineral binders. When exposed to elevated temperatures, liquid glass forms a foamy coating; with special additives, it ensures fireproof properties. However, using LG in fireproof compositions is complicated by the specific sensitivity of the processes to external conditions and medium composition, including filling powders. LG hardening as a topochemical process is accompanied by continuous changes in phase composition and structure. Crystallization changes the degree of polymerization, the chemical composition, and the sequence of alternating functional groups. Prospects for using disperse powders produced by mechanical activation (MA) may involve microlevel control over LG hardening processes.

The purpose of this work is to study the physical and chemical processes that take place in mixtures based on liquid glass and mechanically activated powder and to develop an optimally formulated fireproof composition and a production method providing properties sufficient for application in fire-protective treatment of constructions.

EXPERIMENTAL

Sodium liquid glass (GOST 13078) with a silica modulus of 2.8 and density 1.4 g/cm^3 was used for making a composition. Aluminum oxide (alumina of G-00 grade, GOST 30559, content of α-Al_2O_3 25 mass %, the rest being

γ-Al_2O_3) and aluminum hydroxide (GOST 11841) were subjected to heat treatment at 500–1000 °C. According to its reactivity in LG medium, aluminum oxide belongs to the group of most inactive fillers, which ensure high viability of the composition.

Oxide powders were mechanically activated in a planetary centrifugal mill (PCM) in rubber-lined drums with corundum spheres (material/spheres = 1/3, acceleration of drum rotation 18 *g*). Air and water were chosen as dispersion media, differing in energy redistribution between the structural fragments of the powder [2]. Compared to MA in air, destruction of particles in water, accompanied by an increase in specific surface, is significantly faster than accumulation of structural defects. At the same time, formation of aggregates is substantially suppressed.

To study these processes, we measured film adhesion to a wooden substrate. Being an integrated analytical method, adhesion provides data on the entire set of state parameters of a film. The finished composition obtained by mixing liquid glass with filler was applied to a wooden sample of standard size. The layer was 0.5 mm thick, which provided maximum adhesion. The sample was thoroughly dried and then torn up to determine the stretching of a calibrated spring at the moment of coating separation. The relative error of measurement did not exceed 5 % at 0.95 confidence probability and for at least two repeated measurements. X-ray phase analysis (XRPA) was performed on a DRON-3M diffractometer with CuK_α radiation.

RESULTS AND DISCUSSION

The dependence of adhesion and fireproof properties of a LG composition with aluminum oxide and hydroxide on the following parameters has been investigated: «ageing» time of the composition, background and quantity of the filler, time and medium of mechanical activation, and phase composition of aluminum oxide and hydroxide.

«Ageing» of compositions with Al_2O_3 led to increased adhesion (Fig. 1, curves *1* and *2*),

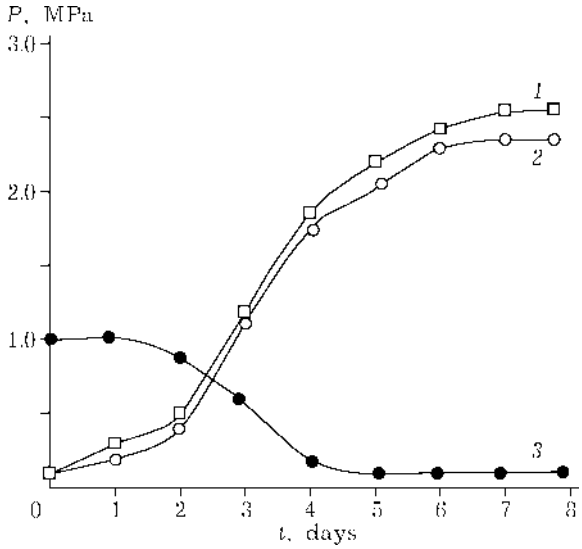

Fig. 1. Effect of composition "ageing" on adhesion: *1* – Al_2O_3, MA for 30 min in water and LG; *2* – the same, MA in air; *3* – $Al(OH)_3$ and LG.

typically occurring when the surface of the filler particles is wetted with silicate ions [3]. After 7 days, adhesion increased by a factor of more than five. The composition with $Al(OH)_3$ decomposed on "ageing" (see Fig. 1, curve *3*). Like aluminum salts, aluminum hydroxide is a more active chemical form, which is likely to form sparingly soluble sodium aluminosilicates, causing medium stratification [4].

Vigorous powdering in water (XRPA data) decreases the height of reflections on the diffractograms. A similar effect is observed when all structural fragments of particles including microcrystals and ACS are crushed simultaneously [2]. When MA is carried out in air, the mechanically unstable phase (γ-Al_2O_3) disperses similarly to MA of powders in water. For α-Al_2O_3, the reflections do not decrease in intensity, which generally suggests that defects form on the surface of microcrystals. Pronged activation forming aggregates even increases the intensity, *i.e.* microcrystals are ordered in the structure of an aggregate, and the off-orientation angle of the crystal planes decreases. Powder reduction, according to BET, occurs actively during 30 min of MA. The specific surface of the powder mechanically activated in water is 7.2 m^2/g, while air activation gives 2.5 m^2/g. When the time of air treatment increases to 40 min, S_{sp} reduces to 2.1 m^2/g due

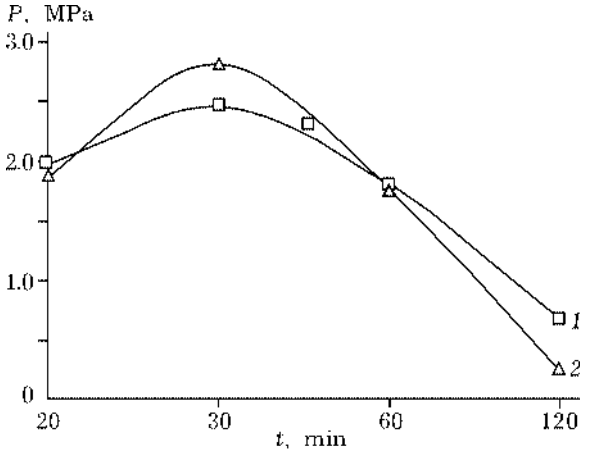

Fig. 2. Effect of MA time of Al_2O_3 in water *(1)* and in air *(2)* on adhesion.

to the formation of dense aggregates. Packing of aggregates in water is noticeable until MA time has reached 60 min; $S_{sp} = 5.9$ m^2/g.

Mechanical activation of Al_2O_3 particles up to the point of aggregation increases adhesion (Fig. 2). Prolonged activation accompanied by aggregation sharply decreases adhesion. Minimum adhesion is observed for aggregated

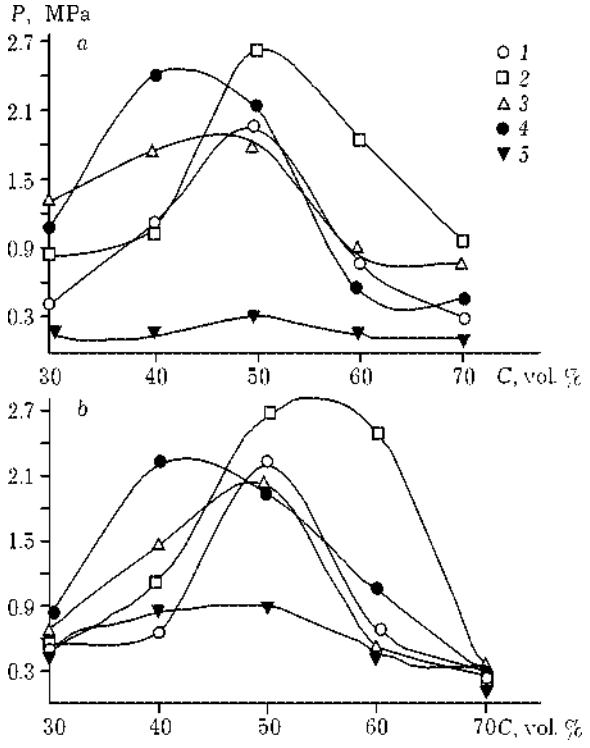

Fig. 3. Influence of the content of the filler (C) on adhesion: a and b – air and water MA of Al_2O_3, respectively; time of MA, min: 20 *(1)*, 30 *(2)*, *(3)* 60 *(3)*, 90 *(4)*, 120 *(5)*.

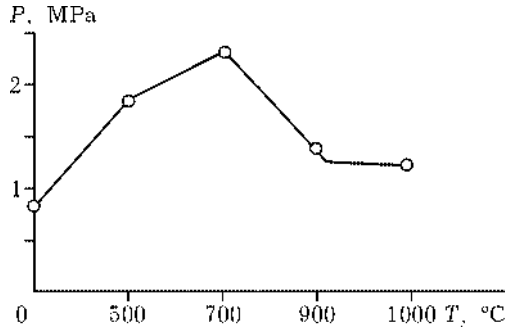

Fig. 4. Temperature effect of annealing of $Al(OH)_3$ on adhesion of the composition.

particles with structurally ordered microcrystals. The influence of the activation time is most pronounced for powders mechanically activated in air (see Fig. 2, curve *2*).

The dependence of adhesion on the filler content reveals that the cohesive type of film destruction at low concentrations changes to the adhesive type at a concentration of 52 vol. % (Fig. 3, *a*, *b*) [3]. Generation and evolution of cracks during cohesion failure occurs in the interparticle space of an LG crystal. Adhesion failure develops in the near-surface layer, in the contact region between LG and the particle. Low strength of LG in the solid state is the reason for low film adhesion at low concentrations of powder. In compositions with increased powder contents, a decrease in strength stems from the loss of connection strength caused by deficit of LG on the surface.

Compared to initial $Al(OH)_3$, annealing of hydroxide eliminates medium coagulation, thus increasing adhesion substantially (Fig. 4). Maximum adhesion coincides with the start of γ-Al_2O_3 and α-Al_2O_3 crystalline phase formation at 700 °C, and with practically complete decomposition of $Al(OH)_3$ (Fig. 5). Annealing at higher temperatures increases the content of Al_2O_3 crystalline phases, which decreases adhesion of the composition. Comparison of X-ray diffractograms of annealed $Al(OH)_3$ and mechanically activated G-00 alumina reveals that the structural states of the γ-Al_2O_3 phase are similar (Fig. 6). In Al_2O_3 powders obtained by prolonged MA and in $Al(OH)_3$ powder annealed at 700 °C, the profiles of γ-phase reflections coincide to the greatest extent. In

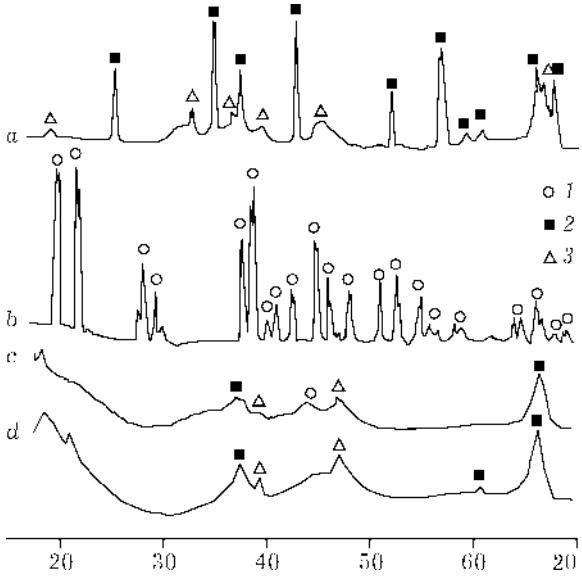

Fig. 5. Phase composition of annealed $Al(OH)_3$: *a* – Al_2O_3, no MA; *b*–*d* – $Al(OH)_3$ at 500, 700, 1000 °C, respectively; *1* – $Al(OH)_3$, *2* – α-Al_2O_3, *3* – γ-Al_2O_3.

oxide and in the product of annealing, the reflection from the plane with low occupancy and with d = 4.56 Å and I_{ann} = 12 % is extinct.

For LG compositions with mechanically activated (in water and air) and nonactivated oxides, both fresh and after 7 days of "ageing", XRPA data confirm that γ-Al_2O_3 affects the "ageing" process (see Fig. 6). Stable chemisorption bonds, which are peculiar to the chemical mechanism of adhesion, are likely to form between γ-Al_2O_3 and the silicate ions of LG [5]. These bonds can involve atoms from the plane with d = 4.56 Å of γ-Al_2O_3 for nonactivated Al_2O_3, moving from their equilibrium positions (see Fig. 6, *a*, *b*). Mechanical activation of oxide (especially in air), as well as annealing of hydroxide at 700 °C, accelerates the formation of chemisorption bonds, since the reflection of γ-Al_2O_3 vanishes even at the stage of powder preparation (see Figs. 5 and 6). The difference in behavior of powders with different backgrounds lies in the fact that an active structure of γ-Al_2O_3 is formed during annealing owing to thermal decomposition of $Al(OH)_3$ prior to the beginning of structural stabilization of oxide phases, and during MA, the relatively ordered γ-Al_2O_3 phase of alumina particles converts into an active state due to structural disordering. We have found the concentration dependence of adhesion on the mechanically activated oxide content in the filler (Fig. 7). To increase the stability of the composition, 12 % fraction of mechanically activated powder in the nonactivated powder is enough.

Fire retardants and bloating agents as functional additives ensure the fireproof properties of the composition [6]. Boric acid (GOST 18704) and carbamide (GOST 6691) were chosen in our work in view of their compatibility and availability (commercial scale of production). The optimum contents of additives were determined in a complete factorial experiment [7].

Film adhesion and fireproof efficiency of the coating were chosen as response functions. To determine the fireproof efficiency,

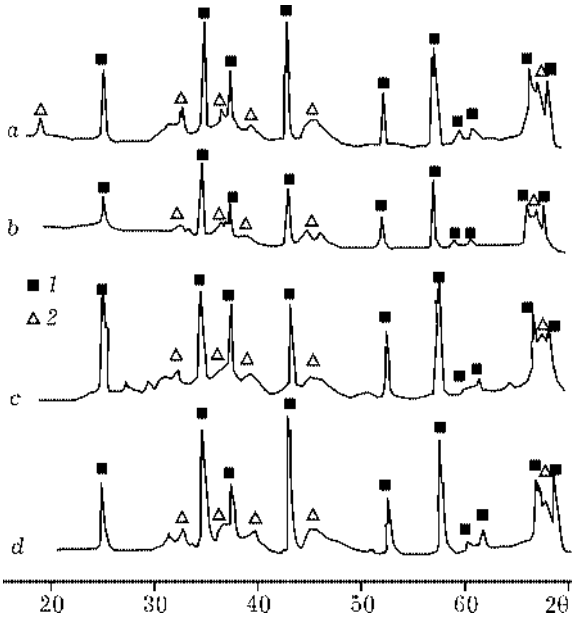

Fig. 6. Phase composition: *a* – Al_2O_3, no MA; *b* – composition with Al_2O_3, no MA, after "ageing" for 7 days; *c* – Al_2O_3, MA in air for 30 min; *d* – Al_2O_3, MA in water for 30 min; *1* – α-Al_2O_3; *2* – γ-Al_2O_3.

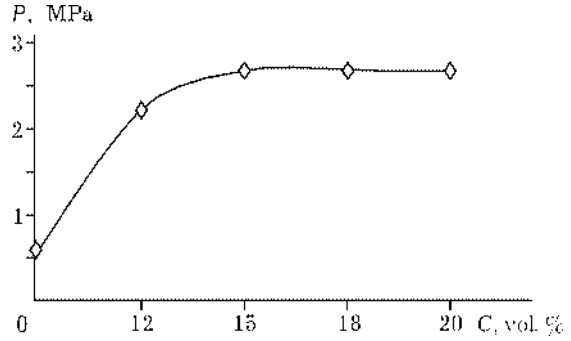

Fig. 7. Dependence of adhesion on the content of mechanically activated oxide (*C*) in the nonactivated powder.

TABLE 1
Design matrix

No.	Content of carbamide X_1, %	Content of boric acid X_2, %	Adhesion, mm	Fireproof efficiency, s
1	1.5	3	56	107
2	3.5	3	80	100
3	1.5	5	8	58
4	3.5	5	36	70
5	2.5	4	68	78

wooden plates protected by the composition were heated on thermoscales starting from 200 °C with a cooling rate of 9 °C/min. The time during which the sample loses 9 % of its mass (1st group of fireproof efficiency, GOST 16363) was measured. The design matrix with levels of design is given in Table 1.

The response functions were calculated using regression analysis for the adhesion parameter Y_1 and fireproof efficiency parameter Y_2:

$$Y_1 = 119.1 + 9.0X_1 - 25.5X_2 + X_1X_2 \quad (1)$$

$$Y_2 = 206.0 - 17.8X_1 - 31.6X_2 + 4.8X_1X_2 \quad (2)$$

The standard statistical check of these equations showed that the models are adequate and that the regression factors play a significant role. Analysis of the equations suggests that the optimum values of the functions (Y_1 and Y_2) in the chosen range of parameters (X_1 and X_2) are achieved for the matrix row corresponding to run No. 2. The negative values of coefficients in the fireproof efficiency eq. (2) are indicative of the closeness of the chosen range of parameters to their optimum values. The positive value of the coefficient at the parameter in the adhesion eq. (1) indicates that carbamide plays a special role during crystallization.

Certification tests of a fireproof composition of optimum formulation (3.5 mass % carbamide and 3.0 mass % boric acid) were performed at a specialized laboratory of the Emergency Agency of Kazakhstan. The tests revealed the high fireproof efficiency of the composition, which enables the conversion of wood into fire-resistant materials qualified as 1B group of fireproof efficiency (mass loss of the construction 7 %, the maximum temperature of flue gases up to 230 °C).

To obtain a fireproof composition, the following flow chart (Fig. 8) has been developed. The starting alumina is mechanically activated in a high-stress grinding machine. Mechanically activated oxide *3* in amounts of up to 12 % is used as an additive to filler *4*. Binder *5* is made by mixing the functional additives: carbamide *6* and boric acid *7* with liquid glass *8* in a mechanical paddle stirrer *9*. Fireproof composition *12* is produced by mixing the binder, the mechanically activated oxide, and the filler in the vibrating mill *11*.

The properties of the fireproof composition are presented in Table 2.

The composition exhibits increased stability and operation life compared to the analogs [8, 9]. Pilot-line production of the composition has been put into service by the Korund Company (Kazakhstan).

CONCLUSIONS

Based on the experimental data it has been established that the wetting of particles in the composition based on LG and Al_2O_3 occurs by the chemical adsorption mechanism. Chemisorption bonds are formed between the silicate ions and the atoms of the plane with $d = 4.56$ Å of γ-Al_2O_3. Mechanical activation of G-00 type alumina, as well as annealing of $Al(OH)_3$, accelerates the process and increases adhesion by shifting the plane atoms from their equilibrium positions. It has been found that a high level of adhesion is possible through addition of 12 vol. % mechanically activated

TABLE 2

Performance specifications of the composition

Parameter	Characteristics	Measuring procedure in accordance with GOST
Visual appearance	Homogeneous mixture	
Drying time at +20 °C and relative humidity of air 75 %, h, no more than	21	19007
Viscosity according to VZ-4 viscosimeter at +20 °C, s, no more than	90	8420
Adhesion at (+20 ± 0.5) °C, MPa, no less than	3	15140
Fireproof properties:		
combustibility group	1B	16363
independent burning, s	0	30244
Characteristics of fire and explosion hazard:		
combustibility group	Noncombustible material	12.1.044
flash point	Not available	
self-ignition point	»	
Operation conditions:		
temperature, °C	From −50 to +80	
relative humidity, %	Up to 95	
Consumption per 1 m^2 for combustibility group 1B, kg	0.6	16363
Service life of coating, yrs	8	
Shelf-life in a tightly closed tare from date manufactured, yrs	2	
Fire protection barrier for metal with coating thickness, mm:		
0.5	REI*30	30247.0
1.5	REI 75	
2.0	REI 120	
Consumption per 1 m^2 for the fire protection barrier of metal, kg, at coating thickness, mm:		
0.5	0.6	
1.5	1.2	
2.0	1.8	

*REI − basic kinds of the limiting states of building constructions by fire-retarding quality (R − loss of load-carrying capacity; E − loss of integrity; I − loss of heat insulating capacity).

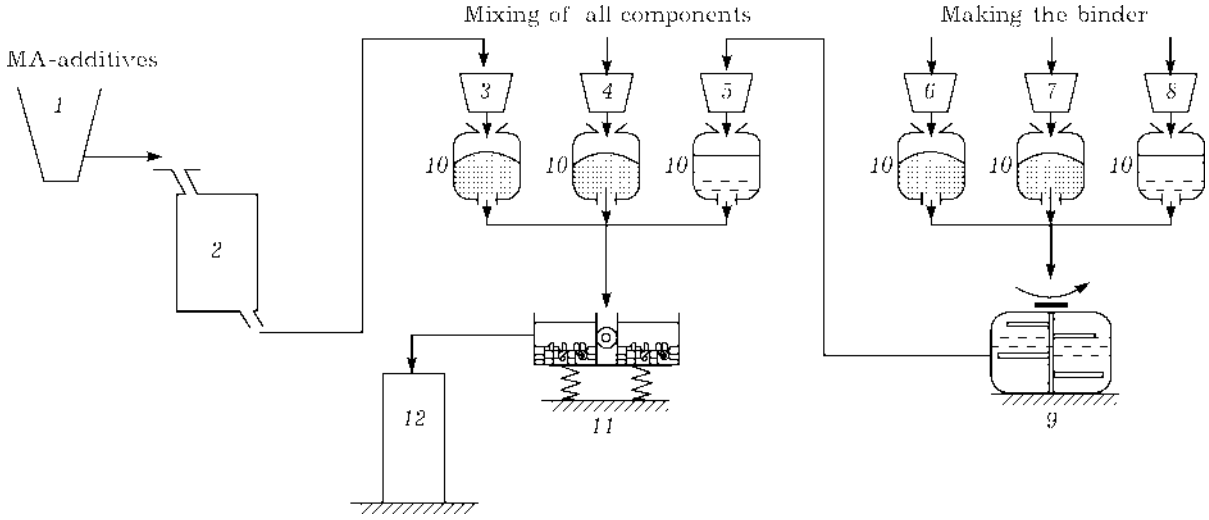

Fig. 8. Recommended flow chart: *1* − container with Al_2O_3 (G-00); *2* − continuous-action planetary mill; *3* − mechanically activated oxide additive; *4* − Al_2O_3 (G-00), no preset dispersity of MA; *5* − finished binder; *6* − container with carbamide; *7* − container with boric acid; *8* − container with LG; *9* − mechanical paddle stirrer; *10* − batcher; *11* − VM; *12* − container with finished composition.

alumina with respect to the total amount of the filler. The optimum filler content of 52 vol. % strengthens the composition by altering the cohesive type of film destruction at small filler concentrations through rupture of mechanically fragile solid phase of LG to the adhesion type of destruction in the contact zone between LG and the particle surface. To ensure functionality of the composition, optimum fractions were determined by the CFE method for the fire retardant additive (boric acid) and the bloating agent (carbamide) (3.0 and 3.5 %, respectively). The developed flow chart for the composition production includes the processes of binder preparation and mixture with functional additives, MA of alumina as filler additive, dosing, and stirring of components. The obtained composition shows high performance characteristics and is environmentally sound.

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