Influence of Additives on Masonry and Protective Paints’ Quality

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Abstract. The environment is one of main factors influencing the living conditions of urban population in Russia nowadays. One of the main drawbacks restraining the aesthetic improvement process of modern Russian cities is unsatisfactory protection of buildings from atmospheric phenomena. Moreover, industrial waste in modern industrial cities of Russia prevents a long-lasting decoration of urban buildings. The article presents an overview of the composition and physical properties of masonry paints applied in the Chelyabinsk region. The traditional technology of coatings obtaining is studied, the drawbacks of this technology are examined, the new materials and applications are offered. The influence of additives on the basic properties of masonry paints, viz. weather resistance, viscosity, hardness, cost, is considered. The application of new technologies utilizing industrial waste can solve the above-stated problem, which also, along with improving basic physical and chemical properties, will result in the cost reduction and the increase of the masonry paints hardness.

1. Introduction

Urban standards of living in any city are influenced by natural environment [1-5], good ecology [6-8], healthcare [9,10], level of housing maintenance [11,12], water supply [13-15], energy supply [16,17], transportation and city infrastructure [18-21], etc. It is obvious that a very important factor influencing the psychological condition of urban population is the aesthetical appearance of buildings and constructions. A well-known fact is that, unlike cities in many developed countries, average Russian industrial cities like Chelyabinsk have their own features in architecture and planning, which promote the problem of unsatisfactory aesthetical appearance of the modern architecture. It is noticeable that, contrary to Moscow, St Petersburg and several other cities where aesthetical appearance has been maintained for a long period, average cities, especially industrial ones, lack such opportunity: only the aesthetical conditions of buildings in city downtowns could match modern urban planning requirements, while buildings in other parts of a city, especially in the suburbs, require restoration of their both front and rear sides.

The main reason for such unsatisfactory conditions is the insufficient protection from atmospheric precipitation caused by the significantly short lifetime (not exceeding three years) of lime mortars applied in whitewashing of buildings and other constructions. In developed countries, special high-
quality phosphate paints with lifetime of over 10 years are applied to protect buildings and constructions from atmospheric phenomena.

2. The composition and properties of applied masonry paints

Front paints of buildings and constructions in use in modern Russian conditions are covered with liquid-glass based masonry paints with additives of zinc whitewash and calcium borate. Such masonry paints are produced in accordance with Russian standards and have the following properties: covering capacity –120 to 520 g/m2, silicification period – 8 hrs, viscosity – 14.5 to 16 s, atmospheric hardness – 8 to 9 points. This implies that such paints are applicable only in areas with relatively small precipitation, viz. in arid or semi-arid territories. The maturing period of coatings in such paints does not exceed 10 days under outdoor application temperature of 20 to 25°C and, as a consequence, such coatings are easily washed off under high humidity, e.g. during rain or snow. [1].

To protect metal surfaces, three-packing paint “Silicazinc-2” containing high-modulus sodium liquid glass as a binder (18%), zinc powder as a reinforcing agent (72%), also water solution of diethylene glycol (9,5%) and monosubstituted calcium phosphate or monobasic calcium phosphate as a curing agent (0,5%), is applied. Such paints are obtained by blending liquid glass (with density of 1.18 to 1.19 g/sm3, and silica modulus of 4.0 to 4.5) with zinc powder. Such paints are applied to metal surfaces of products, then are dried up for 24 hrs, and, finally, are hardened by plunging the product in water solution of the curing agent.

The basic properties of coatings produced from such paints are as follows: pot life – no less than 6 hrs, viscosity immediately after application – no more than 30 s, after 6 hrs – no more than 36 s; impact coating resistance – 40 conditional units (c.u.); coating bend – no more than 5 mm; adhesion – no more than 2 points, pendulum hardness – no less than 0.6 c.u.

Silicate paints based on potassium (or sodium) liquid-glass, with various structures are also applied. For example, one of such paints is silicate paint based on sodium liquid-glass (with percentage of sodium liquid-glass of 30 to 50), specific gravity (sp.gr.) of 1.39 to 1.36, modulus of 2.5 to 3.5; also containing 50…70% floured pearlite sifted through a sieve having density of 10000 holes per cm2; also 1 to 5% of painting pigment. The above-mentioned paints, however, are inapplicable to the fronts of buildings and constructions due to their low atmospheric hardness.

The improvement of sodium liquid-glass based silicate paints can be obtained by means of adding various binders (film-forming agents) as polysilicates, silica sols, quaternary ammonium silicates. Quaternary ammonium silicate-based paint-and-lacquer materials outperform potassium liquid glass in such characteristics as pot life, water resistance and stress-strain properties.

Emulsion silicate paints can be produced by means of applying polymer dispersions such as acrylate, styrene acrylate, styrene-butadiene latexes. The function of emulsion silicate paints is to protect cement concrete, cement plaster and cement-lime plaster, lime-and-sand and ceramic brick. Coatings produced from such paints have good adhesion, improved hardness and atmospheric hardness. The drawback of the use of such paints is complex production and application process, and also high consumption of scarce organic film-forming agents.

The table 1 below enlists the quality parameters of two different types of glass compared with the standardized requirements.

Complex-micelle structured liquid glass containing soda glass, soda-and-sulphate glass, is obtained by heat treatment of white sand with soda (K2CO3 or Na2CO3) in furnaces at 1600ºC; with subsequent mould casting of melts, thus obtaining silicate blocks on cooling; with further dissolution of the blocks in water autoclaves at temperatures of 110 to 120°C; and, as a result, with obtaining liquid glass. complex-micelle structured liquid glass is applied in masonry paint production.

Such liquid glass solidifies while micelles are formed by coagulation of silicic acid gel and its transition into (SO2)n. As the mass of silicon acid within liquid glass increases, the solidification of silicon acid is hastened, thus improving the product resistance, but this process is very slow. To hasten the solidification of liquid glass, a curing agent, e.g. sodium silicofluorid, is applied, which accelerates
the process via the formation of colloid silicic acid which due to syneresis thickens, thus forming gel which cements filling material grains.

Table 1. Quality parameters of liquid glass obtained by chemical technology compared with standardized data in accordance with GOST (Russian Standard) 13078-81.

| Parameter name                               | Soda glass       | Soda-and-sulphate glass | GOST (Russian Standard) 13078-81 requirements |
|----------------------------------------------|------------------|-------------------------|---------------------------------------------|
| Mass fraction of SiO$_2$, %                  | 71.5…76.6        | 71.5…73.5               | 71.0…73.0                                   |
| Mass fraction of Fe$_2$O$_3$ or Al$_2$O$_3$, no more than, % | 0.6              | 1.0                     | 0.4…0.8                                     |
| Mass fraction of CaO, no more than, %        | 0.1              | 0.2                     | 0.2                                         |
| Mass fraction of K$_2$O or Na$_2$O, %        | 22.5…27.6        | 25.3…27.3               | 24.8…26.7                                   |
| Silica modulus, %                            | 2.7…3.5          | 2.7…3.0                 | 2.7…3.3                                     |
| Density, g/cm$^3$                            | 1.36…1.50        | 1.36…1.50               | 1.30…1.50                                   |

Such liquid glass solidifies while micelles are the formation of micelles by means of coagulation of silicic acid gel and, hence, its transition into (SO$_2$)$_n$. Assuming that the mass of silicon acid is hastened, thus improving the product resistance, although the solidification process is very slow. To hasten the solidification of liquid glass, it is required to apply a curing agent, e.g. sodium silicofluoride, which accelerates the process via the formation of colloid silicic acid which due to syneresis thickens, thus forming gel which cements filling material grains [2].

The traditional technology of obtaining liquid glass, however, has the following disadvantages:
1. High power expenses during sand fusion and silicate blocks dissolution;
2. Three-staged process consisting of raw materials fusion, melt casting, silicate-block dissolution;
3. Insufficient water resistance and hardness of products based on liquid glass.

In this connection, obtaining liquid glass by traditional methods is economically inefficient.

3. The features of the production of aluminosilicate masonry and protective paints

3.1. The influence of the quantity of sodium aluminate on the strength of the product

Aluminosilicate binders are obtained by mixing solutions of sodium aluminates and sodium silicates with Na$_2$O/Al$_2$O$_3$ ratio of 1.60 to 1.80 in aluminate. The mixture of such solutions forms sodium aluminosilicate gels [3]. aluminate solution with Na$_2$O/Al$_2$O$_3$ ratio of 5.95 is mixed with tri-modal liquid glass at all volume ratios, whereas with the ratio Na$_2$O/Al$_2$O$_3$<1.98 there forms gel which precipitates if more than 60 % aluminium oxide is introduced into the binder [4]. The maximum mass rate of Al$_2$O$_3$, which does not violate the stability of the binder, is 10% (in terms of dry oxides).

The composition of aluminium oxide in binders also influences the strength of heat-insulating materials and products obtained by application of various quantities of aluminosilicate binders, which is confirmed by the results of a research [3]. Table 2 given below contains the influence of 2 different filling agents in the mixed bond onto the compression strength of the tested samples at 5 various volume ratios of aluminate solution in liquid glass [3].

The above given data show that the strongest samples are produced of mixed binder at the ratio of Al(OH)$_3$/NaOH=0.2 and the volume ratio of sodium aluminate to liquid glass, equal to 20:80. The maximum mass fraction Al2O3 in binders not violating their stability is 10% (in terms of dry oxides). Along with the increase of aluminium ratio, the binder thickens thus transforming into jelly-like compound. As a result, the influence of the Al2O3 content on the viscosity of binders at the following ratios of sodium aluminate to liquid glass 10/90, 20/80, 30/70, 40/60 was researched. It was shown that the 10/90 ratio requires maximum proportion of Al2O3 equal to 1.5%, the 20/80 ratio requires 4.5%, the 50/50 ratio requires 6.5%.
The influence of the reactivity of filling agents on the astringency of mixed binders.

| The ratio of aluminium hydroxide and alkali, sodium aluminate and liquid glass in the binder | Compressive strength of samples, MPa, after the period of 1 to 28 days |
|---|---|
| | 1 day | 3 days | 7 days | 14 days | 28 days |
| Filling agent — nepheline slag L:S=0.3 ml/g | | | | | |
| 0.2/20:80 | 45.0 | 52.0 | 50.0 | 50.0 | 49.0 |
| 0.2/30:70 | 16.0 | 30.0 | 45.0 | 45.0 | 45.0 |
| 0.2/40:60 | 17.5 | 30.0 | 36.0 | 35.0 | 34.0 |
| 0.3/20:80 | 41.0 | 60.0 | 60.0 | 52.0 | 50.0 |
| 0.3/30:70 | 13.0 | 22.5 | 41.0 | 50.0 | 40.0 |
| Filling agent — acid slag L:S = 0.2 mg/g | | | | | |
| 0.2/20:80 | 15.0 | 26.0 | 37.5 | 39.0 | 45.0 |
| 0.2/40:60 | 11.0 | 22.5 | 30.0 | 30.0 | 30.0 |
| 0.3/20:80 | 15.0 | 24.0 | 30.0 | 34.0 | 41.0 |
| 0.3/40:60 | 11.0 | 20.0 | 30.0 | 30.0 | 31.5 |
| 0.3/20:80 | 15.0 | 26.0 | 30.0 | 35.0 | 25.0 |

3.2. The influence of modifying agents on the properties of aluminosilicate binders

The properties of aluminosilicate binders are substantially influenced by modification process. Metastable aluminosilicate solutions as well as liquid glass are sensitive not only to processing conditions like temperature or pH, but also to agent additives. Various agents influence the polymerization degree of aluminosilicates and, in consequence, their structure and other properties [3].

Two procedures of modifying aluminosilicates can be applied. In accordance with the first procedure, substances forming polymeric compounds are introduced into the solution. For instance, binders with improved astringency are obtained by mixing liquid glass (L.g.) with sodium zincate (S.z.) which, for its turn, is obtained by the dissolution of zinc hydroxide in 40 %-diluted alkali. An analysis of astringency of the samples obtained with the application of liquid glass possessing molar ratio SiO₂/Na₂O=3, density $\rho = 1.47$ g/cm³ and sodium zincate solution possessing molar ratio Na₂O/ZnO=1.4 density $\rho = 1.42$ g/cm³, are given the following results (see Table 3) [3].

Table 3. The influence of reactivity of the modified silicate binders on strength of the samples.

| The ratio of aluminium hydroxide and alkali, sodium aluminate and liquid glass in the binder | Volume ratio in the binder | Compressive strength of samples, MPa, after the period of 1 to 90 days |
|---|---|---|
| | | 3 days | 7 days | 38 days | 3 months |
| L.g./S.z. | 50/50 | 13.0 | 27.0 | 30.0 | 40.0 |
| L.g./S.z. | 25/75 | 15.0 | 30.0 | 36.0 | 53.0 |
| L.g./S.z. | 75/25 | 15.0 | 22.5 | 22.5 | 36.0 |

Although strongly alkaline environment does not allow complexing, the strength properties of samples containing mixed binders are higher than of those containing liquid glass, due to the influence of additives reducing the viscosity of liquid glass thus improving its astringent properties.
In accordance with the second procedure, substances either altering pH, or having an influence both on structuring process in the system and also on polymerizing process, are introduced into the binder. In this case, the stability of binders remains unchanged with insignificant increasing or decreasing, if additives with percentage up to 2 are introduced. Coatings and products manufactured with the application of such binders not only have heightened strength, but also have high water resistance which is very important for masonry and protective paints.

3.3. Mineral raw materials used for the production of aluminosilicate binders
The above analysis of technological processes shows that the main raw materials applied for obtaining aluminosilicate binders are liquid sodium glass (GOST-Russian standard 13078-81), sodium hydroxide (GOST-Russian standard 4328-77) commercial alumina and aluminium hydroxide, zinc oxide (GOST-Russian standard 202-84) with chemical compositions given in table 4 [4,5].

| Parameter name                  | Liquid glass | NaOH   | Al(OH)₃ | Zn(OH)₂ |
|--------------------------------|--------------|--------|---------|---------|
| Mass fraction of SiO₂, %        | 71.0…73.0    | 0.02   | –       | –       |
| Mass fraction of ZnO, %         | –            | –      | 91…96   | –       |
| Mass fraction of Fe₂O₃, no more than, % | 0.2…0.4  | –      | 0.3     | 0.2…0.8 |
| Mass fraction of Al₂O₃, no more than, % | 0.2…0.4 | –      | 97.0    | 0.2…0.4 |
| Mass fraction of Na₂O, %        | 24.8…26.7    | > 97.0 | –       | –       |
| Silica modulus, %               | 2.7…3.3      | –      | –       | –       |
| Density, g/cm³                  | 1.30…1.50    | –      | 3.1…3.5 | 5.1…5.5 |

3.4. Obtaining aluminosilicate binders from waste products
Aluminum hydroxides and zinc hydroxides are economically inefficient for production of aluminosilicate binders, especially in the presence of considerable volumes of etching wastes obtained from metal alloys. Such wastes containing small amounts of zinc, cupric and magnesium impurities, improve their astringent properties and, consequently, the strength of the manufactured products. The etching of such products with 40%-diluted alkali obtain considerable volumes of spent etching solution (SES) with chemical compositions given in table 5 [5].

| Component name                  | Aluminum-base alloys | Zinc-base alloys |
|--------------------------------|----------------------|-----------------|
|                                | Duralumin | Silumin | Magnalium | TsAM-10-2 | TsAM -10-5 | TsA -15 |
| NaOH                           | 2.8…3.8   | 2.9…3.4 | 3.6…4.0  | 3.2…3.4  | 3.4…3.6  | 3.4…3.8  |
| Na₂SiO₃                        | –         | 9.6…10.1 | –        | –         | –         | –         |
| Na₂ZnO₂                        | –         | –       | –        | 47…50    | 46…49    | 34…37    |
| CuO                            | 0.2…0.4   | –       | –        | 0.1…0.2  | 0.3…0.4  | –         |
| AlNaO₂                         | 48…52     | 46…49  | 52…57   | 6.7…7.4  | 6.6…7.2  | 9.4…10.2 |
| Water                          | 42…46     | 39…42  | 38…44   | 43…46    | 44…47    | 49…52    |

Spent etching solutions of products on the base of such alloys, despite a significant proportion of valuable substances, are applied in industry only partially, which results in their accumulation at enterprises and consequent environmental pollution. At the same time, many foreign and Russian
companies re-use such waste solutions after regeneration for pickling non-ferrous metal products or utilize after processing for further manufacturing of various materials and products. In addition, many foreign and Russian companies subject such spent solutions either to reprocessing and further application in etching non-ferrous metal products, or to special processing and further obtaining various materials and products.

4. Conclusions

Thus, the current study of synthesis technologies of obtaining liquid glass, phosphate and aluminosilicate binders, and, using them as a base, weather resistant masonry paints, has affirmed that to obtain them in the most efficient way, the following procedures should be applied.

To produce masonry paints depending on waste availability, there are recommended either sodium liquid glass, obtained by means of ash dust wastes remained after ferrosilicon and ferrochrome silicon production or sodium liquid glass produced by traditional technologies with the addition of 10% micro-dust wastes of ferrosilicon production; monosubstituted zinc, cupric, ferrous phosphates as curing agents in masonry paints, monosubstituted aluminium or chromia-alumina phosphates as coatings for metallurgical kiln linings.

To produce phosphate masonry paints, such components as wastes of hard zinc, ash dust remained after non-ferrous metal remelting, copper- and nickel-smelting production are recommended.

To produce aluminosilicate binders, there are recommended liquid glass of the above composition; etching wastes of aluminium using sodium aluminosilicate alkali; sodium zincate or spent etching solution of zinc-base alloy are recommended to produce modifying agents for sodium aluminosilicates.

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