Influence of crystallized glyoxal on properties of gypsum construction mixes

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Abstract. The article presents the results of research of crystallized glyoxal influence on properties of gypsum binding and dry construction mixes. The article describes construction mixes with crystallized glyoxal formulation, processing technology of equal distribution of crystallized glyoxal in construction mixes, structure formation of construction mix with varied proportions of glyoxal and technical and performance characteristics of hardened construction mixes. It is discovered that maximum strength of construction mortar made of dry construction mixes is achieved by 0,1% of glyoxal content in construction gypsum.

1. Introduction
Various modifying additives are used in modern production of dry construction mixes. Process of structure formation of construction mortar made of dry construction mixes is accomplished within “mineral binder – filler material – water” system. It is possible to modulate properties of mixes and make construction mortars with specified qualities for various operating conditions by means of introduction of different organic and mineral modifying additives.

Introduction of modifying additives in dry construction mixes facilitates management of technological and mechanical properties of mixes and mortars, reduction of power consumption, which allows utilizing modern technology and increases competitive advantage of produces in terms of its quality and applicability. Development and production of liquid and powdered multi-purpose modifying additives for construction mixes is essential today [1, 2, 3]. Surface active substances, water-soluble polymers, water dispersions of polymers and electrolyte additives are utilized as modifying additives in construction mixes nowadays[4, 5, 6].

Crystallized glyoxal can be named among new additives widely used in various branches of industry [7]. In production of construction materials this new additive is still rarely used due to lack of research on structure formation processes, lack of scientifically approved formulation and production techniques, reliable data on objective technical and performance characteristics of final construction product and specification documents.

2. Materials and methods
2.1. Characteristic of initial materials
As initial materials in the research of gypsum mixes and dry construction mixes we used gypsum plaster, crystallized glyoxal, methylcelluloseof Bermocoll type, sand, tartaric acid and hydrated lime. The enumerated substances have the following characteristics:
- gypsum plaster, G5 type, standard consistency 55%, beginning and end of solidification process is in 6 and 30 minutes accordingly. Gypsum plaster complies with requirements of All Union State Standard (GOST) 125-79;
- mortar river sand, size modulus 1.96, real and apparent density is 2500 and 1430 kg/m³ accordingly, concentration of pulverous and argillaceous admixtures is 1.5%. Sand complies with requirements of All Union State Standard (GOST) 8736-93;
- hydrated lime, concentration of CaO + MgO is 69%, water content is 3%, 0.08 mm sieve residue percentage is 12%. Hydrated lime complies with requirements of All Union State Standard (GOST) 9179-77;
- crystallized glyoxal is water-soluble large grain powder. Structural formula of crystallized glyoxal is given below (Figure 1).

![Figure 1. Structural formula of crystallized glyoxal.](image)

- Concentration of crystallized glyoxal in additive is 84.4%, type A. Crystallized glyoxal is manufactured by Tomsk LLC “Novochem” and complies with requirements of TOR2633-004-67017122-2011 [7]. Crystallized glyoxal with market-grade particle size is badly combined with dry construction mixes and is not dissolved in water under traditional methods of production of mortar mixes. On solidifying of gypsum block non-dissolved particles of glyoxal can be found throughout the whole body that is why in the research we used glyoxal powdered to 200 m²/kg specific surface.

Technical characteristics of methylcellulose and tartaric acid are given below (Tables 1, 2).

### Table 1. Technical characteristics methylcellulose of Bermocoll type.

| Parameter                      | Standard          |
|-------------------------------|-------------------|
| Apparent density, kg/m³       | 400…600          |
| Product density, gr/cm³       | 1,33              |
| Water content (in package), % | about 4           |
| Salt content (NaCl), %        | about 4           |
| Water solution reaction       | Neutral / faintly acid |
| Coating properties under 20 C and relative humidity under stretching, MPa, % | 45…55, 25…35 |

### Table 2. Physical and chemical parameters of tartaric acid.

| Parameter                                      | Standard          |
|-----------------------------------------------|-------------------|
| 1. Weight percentage of tartaric acid (C₄H₆O₆), %, not less than | 99,5              |
| 2. Weight percentage of water-insoluble substances, %, not more than | 0,010             |
| 3. Weight percentage of residue on ignition (in form of sulphates), %, not less than | 0,03              |
| 4. Weight percentage of sulphates (SO₄), %, not more than | 0,010             |
| 5. Weight percentage of phosphates (PO₄), %, not more than | 0,0020            |
| 6. Weight percentage of chlorides (Cl), %, not more than | 0,0020            |
| 7. Weight percentage of iron (Fe), %, not more than | 0,0010            |
| 8. Weight percentage of calcium (Ca), %, not more than | 0,002             |
2.2. Research procedure

For research of gypsum binding mixes a standard procedure described in All Union State Standard 125-79 was used; for research of gypsum dry mixes standard procedures described in All Union State Standard 31386-2008 and 31387-2008 were used.

Ready components were thoroughly mixed in blending tank for 5 minutes. Then the dry mix was poured into water and was mixed in forced mixer for 5 – 7 minutes. From final blend sample 70x70x70 cubes were molded. Technological tests on watered mix were performed immediately after its preparation and physical and mechanical tests were performed on naturally hardened 7 days old sample cubes. In tests amount of glyoxal was 0,1; 0,5 and 1,0% upon 0,4 water-gypsum ratio.

3. Results and analysis

Water requirement (standard consistency with given plasticity) and kinetics of structure formation (period of hardening and strength of samples at different times) were chosen as main criteria of building gypsum mixes with glyoxal additive quality evaluation.

Gypsum mixes standard consistency research results are given in Figure 2. Standard consistency of gypsum paste under introduction of crystallized glyoxal modifying additive insignificantly rises from 55% (control sample) to 60% (1% of glyoxal).

![Figure 2. Influence of crystallized glyoxal on standard consistency of gypsum paste.](image)

In gypsum mixes with crystallized glyoxal acceleration of initial structure formation is observed. In addition, introduction of 1% of glyoxal leads to drastic reduction of gypsum paste hardening period: beginning of hardening process is reduced from 20 (without glyoxal adding) to 10 minutes and termination of hardening process is reduced from 15 to 5 minutes accordingly (Figure 3). In gypsum mixes introduction of 1% of glyoxal leads to sufficient raise in heat emission under hydration.

![Figure 3. Influence of crystallized glyoxal on period of hardening of gypsum paste.](image)
Research results of crystallized glyoxal impact on strength parameters of 7 days old hardened gypsum mixes are presented in Figure 4. It is proved that introduction of 0,1% of glyoxal leads to significant improvement of compressive strength from 8 to 16 MPa (100%). In case amount of glyoxal is raised over 0,5% strength characteristics of hardened gypsum mixes do not change.

![Figure 4. Influence of crystallized glyoxal on strength of gypsum mixes.](image)

In the research of influence of glyoxal on characteristics of dry construction mixes, the content of dry construction mix produced in Tomsk by LLC “Bogatyr” was accepted as a basic one. Maximum strength gain of solutions made of dry construction mixes (80%) was achieved with introduction of 0,1% of glyoxal. Research results are given in Figure 5. Increase in glyoxal amount over 0,1% leads to decrease in strength characteristics of solutions.

![Figure 5. Influence of crystallized glyoxal on strength of dry gypsum construction mixes.](image)

Optimized composition of dry construction mixes with crystallized glyoxal additive recommended for industrial utilization is given in Table 3.
Table 3. Compositions of dry construction mixes with crystallized glyoxal.

| No | Type | Material consumption, kg, per 1 ton of mix |
|----|------|--------------------------------------------|
|    |      | construction gypsum | sand | methylcellulose | hydrated lime | tartaric acid | glyoxal |
| 1  | 25   | 766              | 200  | 1,9           | 30,0          | 1,0           | 0,8     |

Comparative physical and mechanical characteristics of control and developed mixes with crystallized glyoxal are given in Table 4. In solutions made of 0,1% crystallized glyoxal-added mixes adhesion (bond strength) of solution increases by 50%. It is suggested that strength and adhesion increase becomes possible due to formation of cross-linking polymeric structures of glyoxal with other additives of construction mixes. This hypothesis is being further physically and chemically tested.

Table 4. Physical and mechanical characteristics of dry construction mixes.

| Parameter                      | Physical and mechanical characteristics of mixes with standard additives in accordance with TOR 5745-002-61212785-2012 | Physical and mechanical characteristics of mixes with crystallized glyoxal additive |
|-------------------------------|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| Dry mix                       | 0,3                                                                                                             | 0,3                                                                              |
| Water content, %, not more than | 1,25 sieve residue percentage, %, not more than                                                                 | 5                                                                               |
| Binding mix                   | 8-12                                                                | 12-14                                                                            |
| Cone slump, cm                | 95                                                                  | 95                                                                               |
| Water holding capacity, %, not less than | 45                                                                  | 50                                                                               |
| Retaining of initial mobility, min, not less than | 2.5                                                                                                           | 4,5                                                                              |
| Solution                      | 2.5                                                                                                             | 4,5                                                                              |
| Compressive strength at 7 days old, MPa | 1200                                                             | 1200                                                                             |
| Average density, kg/m3, not more than | 0,4                                                                | 0,6                                                                              |

3. Technology of production of crystallized glyoxal-based dry construction mixes

Utilization of glyoxal in the form of fine powder (surface area=200 m²/kg) into production of mixes does not add complexity to existing technology of dry construction mixes production. Introduction of glyoxal in recommended quantities along with other polymer additives is performed by measuring device directly into concrete mixing drum. Glyoxal is added after all other additives after which dry construction mix is stirred for 2 – 3 minutes more. Production technology manual on production of dry gypsum mixes by LLC “Bogatyr” in Tomsk, Russia was developed.

4. Conclusion

The research allowed discovering peculiarities of influence of crystallized glyoxal with surface area=200 m²/kg on properties of gypsum and dry construction mixes, developing composition of dry construction mixes and technology of their preparation, working out production technology manaulon production of dry mixes in construction. The reported study was supported by RFBR, research project No. 14-03-31922/14 _mol_a. (“My first grant”) and by LLC “Novochem” (Tomsk, Russia).
Acknowledgement
The research performed with the financial support of Russian Foundation for Basic Research, Competition of research projects performed by young scientists (My First Grant) No. 14-03-31922 “Studying composite acid fluoride-based binders of enhanced water resistance to obtain dry building mixes”.

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