Study on properties of conducting contacts made of aluminophosphate compositions for low-e glasses with electric heating

K O Savenko¹, S V Chuppina²

¹JSC «RGC», vil. Pargolovo, Vyborg highway 503, St. Petersburg, Russia
²LLC «NMP Group», Marshal Blucher ave., 78 litas N, St. Petersburg, Russia

E-mail: ¹savenkostia@mail.ru, ²tchoup@mail.ru

Abstracts. This paper presents the results of a study of aluminophosphate compositions with different contents of PMS-N copper powder and SHS-carbon obtained from lignin for the formation of current-conducting contacts on the surface of low-emission glass with electric heating. The specific volumetric resistance of coatings made of aluminophosphate composition before and after their curing was determined. It is shown that the holding temperature of 100 °C and the holding time of 5 hours can be considered the optimal mode of curing aluminophosphate compositions on low-emission glass. It is shown that the wear resistance of aluminophosphate compositions containing PMS-N copper and SHS-carbon is primarily affected by the thickness of the formed layer. The pull-off strength was determined for the resulting coating of the aluminophosphate composition containing PMS-N copper and SHS-carbon, the value of which was 8.2 MPa.

Key words: electric heated glass, Low-E glass, conductive contact, aluminophosphate composition, copper powder brand PMS-N, SHS-carbon.

1. Introduction

At present, metallized tapes, silver-containing pastes with and without glass frit, and metal powders are most often used as a conductive contact on low-emission glasses with electric heating [1, 2]. These technologies for the formation of conductive contacts on the surface of low-emission glasses have their pros and cons. Metallized tapes are less reliable conductive contacts, and one of the main disadvantages of silver-containing pastes and powders is the high cost of either the material itself or the equipment for forming a conductive contact from these materials.

In science and technology, aluminophosphate binders (APhB) are widely used as adhesive compositions [3 - 5]. However, there is no information in the literature on their use as a conductive contact for low-emission glass with electric heating.

The aim of this work is to study the properties of conductive contacts made of aluminophosphate compositions on low-emission glasses with electric heating, namely, to study the effect of temperature and time on the curing process of aluminophosphate compositions on the surface of low-emission glass, their wear resistance and adhesion by normal pull-off method.

The object of the study is APhB with different mass ratios of such fillers as: copper powder Cu grade PMS-N (corresponds to national standard GOST 4960-2017 "Electrolytic copper powder. Technical conditions"), SHS-carbon (obtained from LLC "EcoGrafen", St. Petersburg, using an original method of carbonization of natural biopolymers in the process of self-propagating high-temperature synthesis [6, 7], the starting material is lignin).

The resulting filled compositions were applied using a SERILOR® universal squeegee on the conductive surface of low-emission glass, and then subjected to heat treatment in air (at various parameters of temperature and holding time). In the course of the study, the electrical resistance of the adhesive compositions applied to the conductive surface of the low-emission glass was measured using a Mastech MAS830 multimeter. Specific volumetric electrical resistance was calculated by the formula:

\[ \rho_v = \frac{R \cdot S}{l} \]
where, $\rho_v$ - specific volumetric electrical resistance [Ohm • m], R - electrical resistance of the sample [Ohm], S - cross-sectional area of the sample [m²]; l - sample length [m].

Wear (abrasion) tests were carried out using a SET-AT 360 abrasion instrument used to determine the service life of the coatings.

The adhesion strength of conductive coatings was determined by the normal pull-off method on the testing machine RMU-005-01 (on copper samples with an area of about 3 cm², at a speed of 10 mm / min) equipped with a special device that ensures the perpendicularity of the breakout force to the gluing plane.

2. Samples preparation for compositions based on APhB

To obtain the APhB, the following components were used (wt%):
- 85% solution of $\text{H}_3\text{PO}_4$ - 65.4;
- $\text{Al(OH)}_3$ - 22.6;
- $\text{H}_2\text{O}$ - 12.

The mixture of components was placed in a WB-12 water bath, heated to 100 °C with a heating rate of 1.3 °C/min and kept at this temperature for 30 min, with periodic stirring and control of the pH level, the value of which was kept at 1.5 ± 1.8.

The finished APhB, cooled to 40 °C, was added with stirring copper powder Cu grade PMS-N and SHS-carbon in various percentages of the weight of the APhB.

Copper powder of grade PMS-N consists of large crystals of complex dendritic branched asymmetric shape [8], its granulometric composition is not standardized; to obtain the composition, additional processing of the powder particles was not carried out. The mass fraction of Cu in the powder is 99.5%, the particle size is not more than 224 microns, the bulk density of the powder is from 2.5 to 3.5 g/cm³.

The obtained SHS carbon is a black powder, the average number of graphene layers of powder particles is from 2 to 5. The particles are volumetric-plane particles. Graphene structures represent a complex hierarchical system. Native 2D particles (with a side of ≈ 25 nm) form 2D macroparticles, which, in turn, self-organize into stacks (from 2 to 5 layers). The specific surface area of the powder particles is 570 m²/g, the true density is 1.910 g/cm³ [9, 10].

To conduct a study on the choice of the optimal temperature and time of curing of conductive aluminophosphate compositions, groups of samples No. 1 and No. 2 (10 samples in each group) were obtained with the content of components, according to Table 1.

3. The definition of the optimal curing temperature and time for the formation of conductive composition samples

A LOIP LF-25/350-GG1 drying oven was used to determine the optimal heat treatment time for conductive aluminophosphate compositions containing Cu. For the study, we used samples of coatings from aluminophosphate compositions of groups No. 1 and No. 2.

In the process of testing coatings from aluminophosphate compositions formed on the surface of low-emission glass, the samples were subjected to heat treatment at 100 and 150 °C, respectively. The initial
heat treatment (curing) time was 1 hour, the heating rate was 1 °C/min; after this time elapsed, the test groups of samples were cooled to room temperature (20 °C) at a rate of 1 °C/min. Cooled groups of samples were taken out of the drying oven to measure electrical resistance using a Mastech MAS830 portable multimeter. Then the specific volumetric electrical resistance of the sample $\rho_v$ of the aluminophosphate layer was calculated according to the formula 1. Then the samples were again placed in a drying oven for 1 hour at a heat treatment temperature corresponding to the group.

The layer thickness of the formed groups of samples was 0.43 and 0.25 mm, for groups No. 1 and No. 2, respectively. The geometric dimensions and thickness of the formed layer did not change during the heat treatment, which indicates the absence of shrinkage.

The end of the test was taken as the achievement of constant specific volumetric electrical resistance by the samples. The results of measurements of the average specific volumetric electrical resistance of samples of groups 1 and 2 during their heat treatment are presented in Table 2. The effect of temperature and time of curing on the specific volumetric electrical resistance of groups of samples and No. 2 is shown in Figure 1.

### Table 2. Influence of the heat treatment time on the average specific volumetric electrical resistance of the groups of coating samples No. 1 and No. 2

| Heat treatment time, h | Average specific volumetric electrical resistance, Ohm $\cdot$ m |
|------------------------|---------------------------------------------------------------|
|                        | for samples of group № 1 (curing temperature 100 °C) | for samples of group № 2 (curing temperature 150 °C) |
| 0                      | $6,44 \cdot 10^{-5}$ | $5,09 \cdot 10^{-5}$ |
| 1                      | $4,65 \cdot 10^{-5}$ | $2,71 \cdot 10^{-5}$ |
| 2                      | $3,96 \cdot 10^{-5}$ | $2,35 \cdot 10^{-5}$ |
| 3                      | $2,80 \cdot 10^{-5}$ | $1,78 \cdot 10^{-5}$ |
| 4                      | $2,62 \cdot 10^{-5}$ | $1,60 \cdot 10^{-5}$ |
| 5                      | $2,34 \cdot 10^{-5}$ | $1,52 \cdot 10^{-5}$ |
| 6                      | $2,34 \cdot 10^{-5}$ | $1,52 \cdot 10^{-5}$ |

According to the data in Table 2 and Figure 1, it can be concluded that samples of coatings from aluminophosphate compositions formed on the surface of low-emission glass reach constant values of specific volume electrical resistance after five hours of heat treatment (group of samples No. 1 was cured at a temperature of 100 °C, group of samples No. 2 - at 150 °C). However, in Figure 1, one can notice a sharper jump in the change in the specific volumetric electrical resistance of the group of samples No. 2 at a heat treatment temperature of 150 °C. Taking into account the obtained data, the optimal curing mode can be considered: holding temperature 100 °C, holding time 5 hours. It is also worth noting that, according to the literature data [8], in this temperature range, no sintering of copper particles occurs.
Figure 1. Influence of curing temperature and time on specific volumetric electrical resistance of groups of samples No. 1 and No. 2

Following this optimal mode of heat treatment, the remaining samples of coatings from aluminophosphate compositions containing copper powder and SHS-carbon were cured (sample groups 3-7). The results of calculating the specific volumetric electrical resistance of the formed samples of coatings from aluminophosphate compositions before and after heat treatment are presented in Table 3.

Table 3. Specific volumetric electrical resistance of coatings formed from aluminophosphate compositions (APhB + Cu + SHS-carbon; formation conditions: temperature 100 °C, holding time 5 h)

| Group of samples, № | APhB content, mas.% | Cu powder content, mas.% | SHS-carbon powder content, mas.% | Average specific volumetric electrical resistance, Ohm • m |
|---------------------|---------------------|--------------------------|---------------------------------|---------------------------------------------|
|                     |                     |                          |                                 | before curing after curing                   |
| 1                   | 57,99               | 42,01                    | 0                               | 6,44·10^{-5} 2,34·10^{-5}                  |
| 2                   | 57,92               | 42,08                    | 0                               | 5,09·10^{-5} 1,52·10^{-5}                  |
| 3                   | 58,29               | 41,41                    | 0,3                             | 3,02·10^{-5} 1,30·10^{-5}                  |
| 4                   | 60,02               | 39,48                    | 0,5                             | 3,99·10^{-4} 1,83·10^{-4}                  |
| 5                   | 58,04               | 41,06                    | 0,9                             | 5,02·10^{-5} 2,51·10^{-5}                  |
| 6                   | 60                  | 38,47                    | 1,53                            | 4,2·10^{-4} 1,94·10^{-4}                   |
| 7                   | 60                  | 37,53                    | 2,47                            | 4,36·10^{-4} 2,95·10^{-4}                  |

Table 3 shows that samples with a Cu powder content of at least 41 wt% have the lowest specific volumetric electrical resistance. In this case, the addition of SHS-carbon of more than 0.5 wt% to the composition of the APhB with Cu powder leads to an increase in the resistivity of the sample in comparison with the samples close in Cu powder mass content. The addition of SHS-carbon (in an amount less than 0.5 wt%) to the aluminophosphate composition (with a Cu powder content of at least 41 wt%) leads to a decrease in the resistivity of the formed conductive layer, which is possibly caused by an increase in the contact area between conductive particles and the creation of a more efficient electrically conductive network inside the composite layer, which is characterized by a loose packing of particles, as schematically shown in model A in Figure 2. And the increase in the resistivity of a composition with a copper content with the addition of SHS-carbon of more than 0.5 wt% is possibly due to agglomeration of SHS-carbon particles and their deposition on the surface of copper particles, which negatively affects the conductivity of the coating layer, as schematically shown in model B in Figure 2. It can also be caused by an "excessive" increase in the...
density of the conductive mesh, which was observed in the work on study of the dependence of the electrical conductivity of polymer composite materials with carbon black [11].

![Figure 2. Schematic models of the distribution of particles of PMS-N grade Cu powder and SHS-carbon inside the composite (dendritic copper particles in the diagram are presented as ellipses outlining them)](image_url)

In this study, a group of samples of an aluminophosphate composition with a content of copper powder and SHS-carbon in a ratio of 41.4 and 0.3 wt.%, respectively, has the lowest specific electrical resistance of $1.30 \times 10^{-5}$ Ohm $\cdot$ m (sample group No. 3).

### 4. Investigation of the wear resistance of cured samples of the composition based on APhB

To study the wear resistance of the formed conductive contact based on APhB with a content of copper powder and SHS-carbon in a ratio of 41.4 and 0.3 wt.%, respectively (group of samples No. 3), we used a SET-AT 360 abrasive wear device, which is usually used for determination of the service life of polymer matrix coatings.

The device is equipped with an electric motor that regulates its speed. This motor converts circular movements into linear ones and, before the number of movements (cycles) set on the counter, swings 10 cm to the right - to the left. Each cycle on the counter indicates a 20 cm abrasive path. The abrasive material is a 158 × 224 mm Scotch-Brite abrasive sponge.

The test sample of a low-emission glass, on the surface of which a layer of the composition is formed, is fixed in the installation with the low-emission coating upward. During the test, the abrasive sponge moves at a speed of 9 m/min over the surface of the test specimen. The initial number of cycles was set at 100; after hundreds of cycles were completed, the test sample was examined for signs of abrasion of the formed layer. If there were no such signs, then the test was continued for another 100 cycles. The end of the test was considered the manifestation of the first signs of abrasion of the sample (formed layers) to the substrate, which is the low-emission glass coating.

For the collection of statistical data, samples of coatings made of aluminophosphate compositions containing SHS-carbon (group of samples No. 3-7) were also tested for wear resistance.

A visual examination of the surface of APhB-based conductive contacts using a Levenhuk DTX 500 Mobi digital microscope (at 20x magnification) did not reveal any defects (pores, microcracks, foreign inclusions) or any mechanical damage. The results of the wear tests are presented in Table 4.

#### Table 4. Results of tests for wear resistance of coating samples made of aluminophosphate compositions containing copper and SHS-carbon

| Group of samples, Ne | Cu powder content, mas.% | SHS-carbon powder content, mas.% | Thickness of the formed layer, mm | Number of abrasion cycles |
|---------------------|-------------------------|---------------------------------|----------------------------------|--------------------------|
| 3                   | 41,41                   | 0,3                             | 0,25                             | 1000                     |
| 4                   | 39,48                   | 0,5                             | 1,23                             | 1400                     |
| 5                   | 41,06                   | 0,9                             | 0,45                             | 1200                     |
| 6                   | 38,47                   | 1,53                            | 1,23                             | 1400                     |
| 7                   | 37,53                   | 2,47                            | 1,23                             | 1400                     |
Based on the data obtained, it can be concluded that the wear resistance of aluminophosphate compositions containing copper and SHS carbon is primarily affected by the thickness of the formed layer. The mass content of SHS-carbon (from 0.3 to 2.5 wt.%) in the composition does not have a significant effect on the wear resistance of the coating formed from it. Moreover, the number of withstood cycles for abrasion of the tested samples corresponds to the wear resistance of a conductive coating made of a silver-containing paste FERRO GSSP SP 1892 (1100-1200 cycles with a layer thickness of 0.2 mm), baked into the surface of low-emission glass due to the content of glass frit in the composition [1].

5. Study of the adhesion strength of coatings samples from a filled aluminophosphate composition

The adhesive ability of the conductive layer made of the filled aluminophosphate composition was judged by the values of the ultimate strength of the coating upon detachment of the sample. A test piece was obtained by gluing two cylindrical bases made of contact metal (copper) with an applied and cured test conductive layer based on APhB with a content of copper powder and CBC carbon in a ratio of 41.4 and 0.3 wt%, respectively. (group of samples No. 3), 0.3 mm thick. Gluing was carried out in special casings, cylinders, into which the samples were inserted along a sliding fit (to maintain alignment), the holding time was 7 days. For gluing, an epoxy composition was used: epoxy resin ED-20 according to GOST 10587-84 (50 wt.%) and a hardener - polyethylene polyamine according to TU 6-02-594-85 (10-12 wt.%), filler - kaolin according to GOST 19607 -74 (50 wt%); the pull-off strength of the adhesive joint at separation was 20 MPa.

Using the method of processing the results in accordance with section 5 of GOST 27890-88, the adhesion strength of the coating at separation was calculated, the value of which was 8.2 MPa. In all cases, a mixed type of separation was observed (adhesive-cohesive: at the interface between the conductive coating and the substrate and along the conductive coating). 10 parallel measurements were carried out. The relative measurement error did not exceed 15%.

This value of pull-off strength (8.2 MPa) is consistent with the literature data on the study of the adhesive strength of conductive phosphate cements containing powders of copper grade PM-2 and CuO (analytical grade) [12].

6. Conclusion

The study of the effect of temperature and time of curing on the specific volumetric electrical resistance of coatings (dependences for layers of aluminophosphate compositions containing PMS-N grade copper powder dried at temperatures of 100 and 150 °C) was carried out. It is shown that samples of coatings made of aluminophosphate compositions formed on the surface of low-emission glass reach constant specific volumetric electrical resistance after five hours of heat treatment.

From the results of tests for wear resistance of coatings made of aluminophosphate compositions with SHS-carbon, we can conclude:
- the wear resistance of coatings made from these compositions is influenced, first of all, by the thickness of the formed layer;
- the mass content of SHS-carbon (from 0.3 to 2.5 wt.%) in the composition does not have a significant effect on the wear resistance;
- the number of successful abrasion cycles of the tested samples corresponds to the wear resistance of silver-containing pastes with glass frit used in practice for the formation of conductive contacts.

A test for the adhesion strength of conductive coatings samples made of an aluminophosphate composition with a content of copper powder and SHS-carbon in a ratio of 41.4 and 0.3 wt%, respectively, was carried out. It is shown that the pull-off strength of the joint at separation is 8.2 MPa, while in all cases a mixed type of separation was observed. The obtained value is not inferior to the values of the pull-off strength for conductive phosphate cements containing powders of Cu grade PM-2 and CuO.

References

[1] Savenko K O and Chuppina S V 2018 Types of conductive contacts on low-emission glasses with electric heating Repair. Recovery. Modernization 4 pp 32-35
[2] Savenko K O and Chuppina S V 2018 Types of conductive pastes on low-emission glass with electric heating Fourth Interdisciplinary Scientific Forum with international participation «New materials and Advanced Technologies» 4 pp 609-612
[3] Bakunov V S, Khalikov R M, Shayakhmetov A U et al. 2016 Hardening of the aluminum phosphate composition by heating Refractories and technical ceramics 3 pp 24-27

[4] Khaydarshin E A, Shayakhmetov U Sh, Khalikov R M et al. 2016 Physico-chemical features of hardening of aluminophosphate composition Eng. Phys. Bulletin of the Bashkir University 21(1) pp 27-31

[5] Savenko K O and Chuppina S V 2020 Use of alumophosphate compounds as conductive contact on low-emission glasses with electric heating Repair. Recovery. Modernization 10 pp 32-37

[6] Voznyakovskii A P, Neverovskaya A Yu, Otvalko Ja A et al. 2018 Facile synthesis of 2D carbon structures as a filler for polymer composites Nanosystems: Physics, Chemistry, Mathematics 9(1) pp 32-37

[7] Sytschev A E and Merzhanov A G 2004 T Self-propagating high-temperature synthesis of nanomaterials Russian chemical reviews 73(2) pp 147–159

[8] Ovechkina T A, Gryzunova N N, Vikarchuk A A, et al. 2017 Specific behavior of electrolytic copper powders of different morphological forms in temperature fields Letters on materials 7(2) pp 120-124

[9] Voznyakovskii A P, Shugaley I V, Novikova I I et al. 2019 Comparative studies of the effectiveness of usage of 2D graphene structures of various prehistory in biopreparations Rock-breaking and metal-working tools-technique and technology of its production and application 22 pp 342–347

[10] Levashov E A, Rogachev A S, Yukhvid V I et al. 1999 Physico-chemical and technological bases of self-propagating high-temperature synthesis Binom p 176

[11] Abdulin M I, Basyrov A A, Khaltaev N V, et al. 2014 Study of the dependence of the electrical conductivity of polymer composite materials on the degree of plasticization of the copolymer and the type of polymer matrix Actual problems of Humanities and natural Sciences 11(1) pp 24-27

[12] Fedorov N F, Kozhevnikova L V and Lunina M N 1973 conductive phosphate cements Proceedings of the 6th All-Union Conference on Heat-resistant Coatings 6 pp 390–392