УДК 666.21:666.112.43

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# DEVELOPMENT AND INDUSTRIAL TESTING OF CASED GLASS COMPOSITIONS FOR CRYSTAL PRODUCTS

On the basis of fusibility coefficient calculation, study of temperature coefficient of linear expansion and crystallization ability optimized compositions for synthesis of cased glass with completely removed PbO, what lowers material costs, improves working conditions and reduces emissions of lead compounds in the production of overhead crystal products were developed. Simultaneously, the problem of waste products utilization was solved.

**Introduction.** The preparation of overhead crystal products with the combination of coloured and colourless glass zones was run in by glass industry of the Republic. Combined with the properties characteristic of crystal glass, casing improves the aesthetic value of the goods which are in popular demand despite their rather high prices. Traditionally glass compositions with high PbO content (34–38%) are used for the purpose. However, they do possess a number of both technological and ecological limitations. Technological ones include high volatility of PbO as well as its tendency to deposition in the melt. Increased aggressiveness of glass melts with high PbO content results in rapid refractory lining corrosion and frequent repairs of melting furnaces. PbO is introduced into the batch in the form of red lead which is a substance of Class 1 hazards. It affects the environment and makes work at the industrial enterprise more difficult.

The aim of the present research has been to prepare coloured cased glass which does not contain lead oxide but still possesses the main characteristics typical of the composition used in industry, and to develop crystal goods production technology using it as casing.

Analysis of literature on the problem [1–3] has made it possible to formulate the requirements for glass compositions used in the production of overhead crystal products:

– to make casing flow by forming a thin layer on the surface of crystal glass goods its fusibility is to be much higher;

– casing is to conform with crystal glass in a number of characteristics, among them temperature coefficient of linear expansion, solidification temperature range and mechanical properties.

An important task has been to find oxides that could replace PbO in cased crystal glass compositions without worsening their main characteristics (transparency, luster, lack of tints). The combination of certain oxides (BaO and CaO) has been chosen as a replacement. Our opinion is that the role of calcium oxide in domestic glass compositions has been underestimated. This oxide having relatively high partial coefficient of refraction and being a very strong flux contributes to lowering the consumption of energy in melting. Besides, there is a large amount of relatively cheap and rather pure CaO, its source being technogenic $CaCO_3$, the waste in nitrophoska production.

**Results and their discussion.** Experimental compositions of cased glass were designed in the $Na_2O–K_2O–CaO–BaO–B_2O_3–SiO_2$ system. To cut down the number of experiments, methods of experimental design such as «composition-property» diagrams were applied, optimality criteria being fusibility coefficient proposed by A.N. Dauvalter and temperature coefficient of linear expansion (TCLE). Fig. 1 deals with calculated values of the fusibility coefficient and the range of compositions of the system involved in which the content of CaO, BaO and $SiO_2$ varied within the following limits, wt. %: $SiO_2$ – 47.0–54.5; CaO – 5.0–12.5; BaO – 20.5–28.0. The content of $K_2O$, $Na_2O$ and $B_2O_3$ remained unchanged. 0.3% of $Sb_2O_3$ was used as a refining agent.

Analysis of the fusibility coefficient values allowed to reveal the following regularities in the dependence of fusibility upon the composition of experimental glasses:

– desired level of fusibility is observed in glasses with more than 22 wt. % content of BaO;

– replacement of BaO with CaO greatly improves the fusibility of glasses; – increase in the $SiO_2$ content reduces the fusibility coefficient of glasses.

Based on the results of the fusibility coefficient calculation, crystallization resistance and TCLE of cased glasses it has been established that glasses of 3–8 compositions are the best to meet the requirements imposed on casing, their crystallization ability and properties being given in Fig. 2 and Table 1 respectively. According to the results of studying their crystallization ability in the temperature range of 600–1000 °C, glasses of 3–8 compositions are characterized with high stability of glassiness.

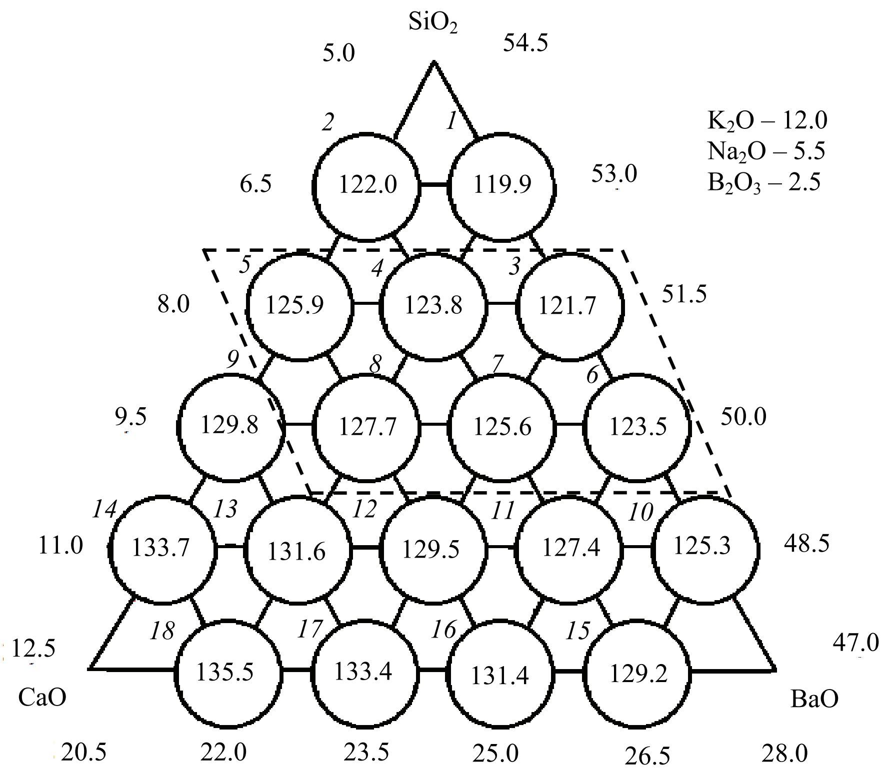


Fig. 1. Glass compositions (their numbers are italicized) of $Na_2O$–$K_2O$–CaO–BaO–$B_2O_3$–$SiO_2$ system section with constant content, wt. %: of $Na_2O$ – 5.5; $K_2O$ – 12.0; $B_2O_3$ – 2.5 and their fusibility coefficients *C* (given in circles on the diagram)

It provides wide safe interval of overhead products moulding, excluding the possible crystallization of liquid glass melt in the furnace and during glass working.

According to the data given in Table 1 the glasses studied show high values of refraction index, density, TCLE. Special attention should be paid to their hardness (by Vickers) and resistance to grinding as these are very important parameters as far as labour intensity of overhead products decoration (cutting and polishing) is concerned.

It has been established that the values of both the parameters decrease when the content of BaO and CaO in glass composition increases. However, cased glass composition used in industry possesses lower values of the above mentioned characteristics and that is why requires less labour effort, when mechanically worked.

Experiments have shown that coherence of TCLE values of the sealed glasses does not play an important part as it does while combining ceramic materials with vitrous glass (ceramics glazing), perhaps, because the materials combined are close in their chemical nature as well as due to small thickness of the casing layer and its elasticity.

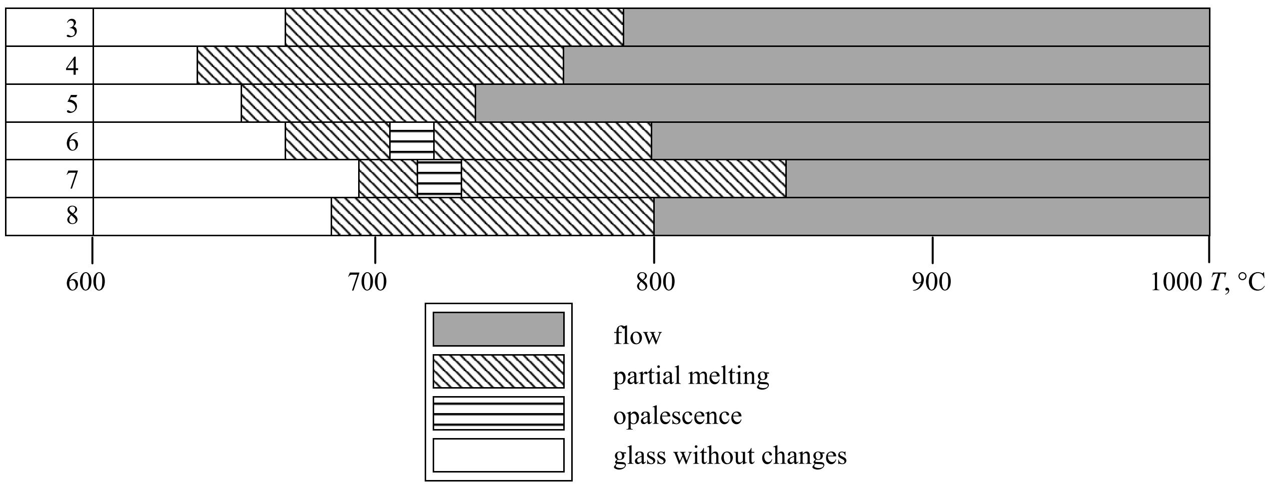


Fig. 2. Crystallization ability of glass compositions (N 3–8)

**Properties of glass samples**

| Number of glass composition (q. v. Fig. 1) | Refraction index, *n* | Density ρ, kg/m$^3$ | Microhardness *H*, MPa | TCLE, $\alpha \cdot 10^7$ K$^{-1}$ | Resistance to grinding, conv. un. |
|---|---|---|---|---|---|
| 3 | 1.5629 | 2806 | 3399 | 121.0 | 722 |
| 4 | 1.5619 | 2875 | 3389 | 121.6 | 716 |
| 5 | 1.5606 | 2945 | 3379 | 122.3 | 711 |
| 6 | 1.5668 | 2889 | 3367 | 123.1 | 708 |
| 7 | 1.5658 | 2959 | 3357 | 123.7 | 702 |
| 8 | 1.5649 | 3032 | 3347 | 124.4 | 697 |

In any case the difference in the TCLE values of basic and cased glasses being $20 \cdot 10^{-7}$ K$^{-1}$ does not cause substantial stress in the samples and articles after their annealing. Special attention should be paid to the difference in vitrification temperature $T_g$ of the glasses under consideration. It is not to exceed 20–25°C. Casing glass composition № 3 meets this requirement and it has been chosen for industrial testing at the PRUE "Borisov Crystal Glassworks".

In the batch room of this unitary enterprise glass mixture was compounded in accordance with the batch formula developed, such colorants as CoO, $MnO_2$ and $TiO_2$ being introduced.

Melting of optimum composition glass was conducted in the batch furnace during 16 hours at the maximum temperature (1480 ± 10)°C, glass melt blocking before worked.

Blue glass prepared was centrifuged to produce funnel which after being annealed in a furnace annealing were forwarded to the furnace for lead crystal glass melting. The preheated funnel was placed onto a semifinished future vase. Then blowing to produce the crystal glass vessel covered with a thin overhead layer of coloured glass was performed in the mould. Final products were covered with diamond thread in the cutting shop, after which they were chemically polished, i.e. they went through the complete cycle of industrial treatment.

While preparing overhead crystal products of small sizes the use of the glass composition involved caused the decrease of melting temperature and increased the number of good articles. There were certain difficulties while working with large size products due to smaller "length" of glass in comparison with the composition used at the industrial enterprise concerned.

According to the results obtained during the industrial melting the following changes have been made in the chemical composition of glass № 3 when used for crystal products casing:

– $SiO_2$ content has been lowered to 50.5 wt. % for decreasing refractoriness;

– $K_2O$ content has been lowered from 11.0 to 9.5 wt. % at the expense of corresponding increase of $Na_2O$, that permits to reduce the cost of the batch;

– CaO content has been lowered to 4.0 wt. %.

It is well known that an important component of glass batch is cullet. According to the data received at the PRUE "Borisov Crystal Glassworks" the percentage of cullet of the products concerned is 40–70% (for the articles of intricate shape). That's why introduction of cullet of the articles concerned into the batch is obligatory.

Introduction of return cullet into the composition is usually aimed at:

– environmental protection;

– melting process intensification (as cullet melting requires less heat than batch melting, it is possible to increase the furnace output);

– saving energy (It is estimated that the introduction of 10 % of cullet allows to save 2.0–3.5 per cent of fuel, depending on glass composition);

– saving raw materials.

The latter is especially significant in the preparation of cased glasses for crystal products since in this case scarce, expensive raw materials such as barium carbonate, boric acid, potash, soda ash, colorants and others are used.

The study of the condition of stored glass culet at the "Borisov Crystal Glassworks" unitary enterprise has shown that the barrier to using overhead crystal products cullet is lack of information on the thickness of casing layer as well as that of the wall characteristic of different types of articles, which does not permit to take into account the quantity of colorants introduced with the cullet.

Data on the article wall thickness were obtained after the study of samples of cullet of different types of overhead crystal products by using Lioto optical microscope.

It is established that casing layer thickness hardly depends on the type of the article, but its wall thickness changes drastically while passing from producing small to large ones. After studying 178 samples the weighed mean value ratio of casing layer thickness to that of the base glass $\delta_{casing}/\delta_{cryst}$ has been found to be 0.106, the latter used while developing transition glass compositions. The ratio involved has made it possible to determine the amount of coloring oxides as well as that of PbO introduced into glass composition with glass cullet.

Under the agreement with the "Borisov Crystal Glassworks" unitary enterprise administration it was decided to introduce 30% of industrial cullet into the batch used for the preparation of cased glass, chemical composition of the former being $SiO_2$ – 50.7; PbO – 32.0; $K_2O$ – 9.3; $Na_2O$ – 5.4; $B_2O_3$ – 0.6 (wt. %).

In industrial melting of cased glass the batch/cullet relation in per cent by mass was 70/30. Cased glass funnel were prepared and used for the production of trial consignment of goods.

**Conclusion.** The feasibility of replacing cased glass composition used in modern industry with the developed one is shown to be determined by the following factors:

– reduction of inputs on raw materials due to removal of expensive red lead from the batch (1.6 times);

– improvement of working conditions in the batch room, cased glass melting department, edge cutting and polishing departments due to the absence of PbO (a substance of Class 1 hazards) which usually accumulates in living organisms;

– reduction of lead compounds emission into the environment, it being a most important problem of domestic glass production today;

– lowering glass melt tendency to form cords and bubbles, which increases good products output.

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*Received 14.03.2014*