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LOW-MELTING GLASSES BASED ON LEAD-BORATE SYSTEMS (REVIEW)

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The development status of low-melting glasses, which are used, specifically, as fluxes for obtaining silicate paints, is analyzed. The results of development work and patent data obtained in this field over the last 30 years are presented.

Key words: low-melting glass, borate systems, fluxes, silicate paints.

Low-melting noncrystallizing glasses are used as solders, marking enamels, various kinds of glass-to-glass, glass-to-metal, and metal-to-metal seals, as well as low-melting fluxes for depositing various figures and inscriptions on glass articles [1].

Work is now being performed to increase the production of articles decorated with paints, expand the color range of paints, and improve the processes used to prepare and deposit paints on glass. Application of paint to glass articles makes it possible to obtain long-lasting, high-quality, artistic figures; this expands and improves the selection of commercial forms of such articles [2].

Most low-melting noncrystallizing glasses are synthesized in the systems $ZnO – PbO – B_2O_3$, $PbO – B_2O_3 – SiO_2$, and $ZnO – PbO – B_2O_3 – SiO_2$, which contain substantial quantities of PbO. The formulations of the fluxes used to decorate glass based on the proposed systems are diverse, since the flux compositions depend on the purpose and color of the silicate paints. The content of PbO in the low-melting flux compositions which have been developed ranges from 52 to 78 wt.%. An especially large amount of PbO (80 – 90 wt.%) is present in borate glasses [3].

Lead-containing glasses have a special place in the theory of glass formation. In silicate glasses with O : Si = 4 the ratio of the oxygen ions participating in the bonds between the tetrahedra is practically zero, and according to Stevels it is impossible to obtain glass because the silicon – oxygen tetrahedra are isolated and an extended structural network does not exist. However, lead orthosilicate $2PbO \cdot SiO_2$ exists in the glassy state. This shows that a substantial fraction of PbO acts as a glass-former, forming the structural groups $[PbO_4]$.

Petsold has studied the three-component phase diagram for $ZnO – PbO – B_2O_3$ quite thoroughly. He determined the phases that crystallize at 600°C from fused glasses. Three ternary compounds were obtained: $2PbO \cdot ZnO \cdot B_2O_3$ (melts incongruently at 575°C), $PbO \cdot 2ZnO \cdot B_2O_3$ (melts incongruently at 730°C), and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ (melts incongruently at 680°C). A fourth, B_2O_3-rich, ternary compound melting incongruently below 600°C could exist [4]. Since all compounds in the system melt at relatively low temperatures, the glass-forming melts in the system are also low-melting but all eutectics are polylead compositions.

The two-component system $PbO – B_2O_3$ is of interest for the production of ceramic glazes and certain types of glass. Geller and Bunting have studied this system [5]. Four chemical compounds have been discovered in the system: $4PbO \cdot B_2O_3$, $2PbO \cdot B_2O_3$, $5PbO \cdot 4B_2O_3$, and $PbO \cdot 2B_2O_3$. The lowest-melting eutectic in the system with temperature 500°C contains 93.7%[2] PbO and 6.3% B_2O_3, i.e., it also is distinguished by a high PbO content.

Data on glass formation in the system $ZnO – PbO – B_2O_3$ are presented in [6]. The glass-formation region lies in the following range (molar content %): PbO — 20 – 80, B_2O_3 — 20 – 80, and ZnO — 45 – 65. This shows that glass with a lower PbO content can be obtained. Together with noncrystallizing low-melting glasses, glass cements based on the system $ZnO – PbO – B_2O_3$ are also widely used [7]. All the most common compositions of glass crystal cements produced domestically and abroad include (molar content, %) 40 – 70 PbO, 10 – 45 ZnO, and 10 – 25 B_2O_3 and contain $2PbO \cdot ZnO \cdot B_2O_3$, $PbO \cdot 2ZnO \cdot B_2O_3$, and $4PbO \cdot 2ZnO \cdot 5B_2O_3$ as the main crystalline phases. The introduction of 1.4% SiO_2, 1.4% BaO or 1.2% Al_2O_3 as addi-

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[2] Here and below, unless otherwise stated, the content by weight.

TABLE 1.

Flux	Content, wt.%			
	SiO_2	B_2O_3	PbO	Na_2O
1	25.40	–	74.60	–
2	22.46	7.47	66.40	3.40
3	16.93	15.83	67.34	–
4	15.98	36.06	47.96	–
5	5.69	17.59	76.22	–
6	10.00	10.00	70.00	10.00

tives into glass with the compositions (%) 71.5 – 79.1 PbO, 5.3 – 18.0 B_2O_3, and 10.1 – 12.1 ZnO did not result in the appearance of new crystalline phases but it did make it possible to regulate the proneness to cracking and the crystallization rate, sometimes intensifying the latter process considerably.

Thus, practically all low-melting glasses are distinguished by a substantial PbO content — 40 – 80%.

In connection with the ecological problems due to the synthesis of fluxes using highly toxic PbO, it is necessary to obtain low-melting glasses based on system with low lead content. For this reason, it is important to develop flux compositions with lower PbO content, which can be regarded as class 1 hazards, and lower synthesis temperatures while maintaining the required physical – chemical properties.

Fluxes used for decorating articles made of high-quality glass are distinguished by the lowest melting temperatures, since the paint deposition temperature must not exceed 560 – 580°C (20 – 30°C lower than the softening temperature). Such fluxes are obtained primarily on the basis of glasses in the zinc-borate systems with high PbO content — 50 – 80%.

The CLTE of flux must not deviate from that of the base by more than 5%. For larger deviations, hairline cracks appear on the surface of the paint; but, the appearance of such cracks is not always cause for rejection because they impart a unique decorative aspect to the articles.

An important property of fluxes is their chemical resistance to various reagents — water and weak solutions of alkali and acids. The introduction of PbO into fluxes imparts to them not only positive properties (luster, good flowability at temperatures below the softening temperature of the glass) but also negative properties. All polylead fluxes possess low chemical resistance (aside from the high toxicity of the PbO itself).

The chemical properties of low-melting glasses used as fluxes (Table 1) are presented in [1], and the compositions of paints from the Dulevo Paint Works are presented in Table 2. Evidently, the PbO content is mainly 66 – 76 wt.%.

High PbO content was also observed in a number of subsequent works concerning low-melting glass. The low-melting glasses proposed in USSR Inventor's Certificate No. 1130542 contain (%): 43.7 – 68.8 PbO, 9.4 – 29.1 B_2O_3, 1.8 – 19.6 ZnO, 1.9 – 14.8 SiO_2, 3.6 – 4.9 CuO, and 1.9 – 8.7 Al_2O_3. According to USSR Inventor's Certificate No. 1323540 the glasses contain (%): 66.2 – 67.9 PbO, 5.5 – 5.6 ZnO, 7.3 – 7.5 SiO_2, 9.4 – 10.6 B_2O_3, 1.6 – 1.7 ZrO_2, and 8.2 – 8.5 PbF_2. The softening temperatures of the glasses are 363 – 367°C, and the CLTEs are 99.3 – 102.8. Patent No. 37899 in the People's Republic of Bulgaria proposes low-melting glass compositions (%): 4 – 25 SiO_2, 50 – 80 PbO, 3 – 21 B_2O_3, 0.2 – 1.5 Al_2O_3, 0.2 – 7 Na_2O with coloring oxides in amounts up to (%) 0.4 CuO, 4.5 NiO, and 2.5 Co_2O_3.

Further research in the field of low-melting glass has led to the introduction of additional oxides, which together with decreasing the melting point made them corrosive and much more expensive.

For example, USSR Inventor's Certificate No. 1114635 proposes a low-melting glass, containing CdO and fluorides, with the composition (%): 34 – 43 B_2O_3, 9 – 22 ZnO, 1019 CdO, 1 – 10 PbO, 14 – 22 PbF_2, 2 – 8 AlF_3, 0.5 – 3 Al_2O_3, 6 – 15 BaO, and 0.1 – 5 TiO_2. The CLTE of the glasses falls in the range $(82 – 97) \times 10^{-7}$ K^{-1}. Cadmium oxide also is present in low-melting glass (USSR Inventor's Certificate No. 1183470) together with PbO (%): 6.5 – 9.5 SiO_2, 2.4 – 4.5 Al_2O_3, 14.5 – 18.5 B_2O_3, 68.5 – 71.5 PbO, and 1.0 – 3.0 CdO.

Low-melting glasses in the system PbO – B_2O_3 – TeO_2 – SiO_2 with PbO molar content ranging from 5 to 65% but with expensive TeO_2 present were synthesized in [8]. The Japa-

TABLE 2.

Paint	Content, wt.%							Flow temperature, °C	CLTE, 10^{-7} K^{-1}
	PbO	SiO_2	B_2O_3	Na_2O	Li_2O	CdO	TiO_2		
Ultrasoft	78.0	10.0	12.0	–	–	–	–	500 – 520	95 – 100
Soft	64.0	14.5	18.0	–	–	3.5	–	550 – 580	85 – 90
Soft, acid-resistant	56.0	30.0	4.0	2.0	2.0	3.5	2.5	570 – 580	85 – 95
For glassware	52.0	33.0	2.5	2.5	1.5	3.5	5.0	580 – 585	85 – 95
For bottles*	50.0	25.0	7.0	3.0	–	3.5	2.5	585 – 610	90

* Bottle paint also contains 7.0% ZrO_2 and 1.5% NaF.

nese claim No. 62-36040 proposes glass containing a substantial amount (up to 80%) of TeO_2 (%): 10 – 80 TeO_2, 8 – 50 PbO, 3 – 40 B_2O_3, 3 – 30 ZnO, 0.25 (WO_3 + MoO_3), 0 – 10 (Al_2O_3 + La_2O_3), 0 – 25 RO with softening temperature 285 – 367°C and CLTE (112 – 155) × 10^{-7} K^{-1}; USSR Inventor's Certificate No. 1303568 proposes the following (%): 30 – 70 TeO_2, 6 – 14 V_2O_5, 0.1 – 8 Bi_2O_3, 12 – 40 PbO; the CLTE of the glasses is (180 – 220) × 10^{-7} K^{-1}.

The Japanese claim No. 60-57620 describes the development of a low-melting solder with the following composition (%): 75 – 84 PbO, 3 – 10 Bi_2O_3, 7 – 12 B_2O_3, 0 – 5 ZnO, 1 – 10 V_2O_5, 0 – 10 SnO_2, 0 – 5 Tl_2O (the sum PbO + Bi_2O_3 + Tl_2O is 8.3 – 8.8%), as well as the expensive components Bi_2O_3, Tl_2O, and V_2O_5. Bismuth oxide was also present in the glass (Japanese claim No. 62-52141).

There are comparatively few works on low-melting glasses with low or zero PbO content. Low-melting glass with a low lead content is described in the USSR Inventor's Certificate No. 1375588 (%): 15 – 17 V_2O_5, 25 – 32 B_2O_3, 7 – 22 ZnO, 19 – 21 PbO, and 14 – 27 BaO. The drawback of this glass is that it contains V_2O_5, which is easily reduced to lower degrees of oxidation.

Quite exotic compositions of low-melting glasses are presented in the Japanese claim No. 62-128945 (%): 10 – 90 La_2O_3, 20 – 85 Dy_2O_3, 2 – 60 Y_2O_3, 5 – 60 Al_2O_3, 5 – 45 BeO, and 3 – 35 B_2O_3.

Work on decreasing the content of PbO in low-melting glasses and fluxes for decorating articles has led to the development of lead-free compositions (%): 49.0 P_2O_5, 8 – 10 B_2O_3, 14 – 15 Na_2O, 17.0 ZnO, 6 – 9 CaO (Socialist Republic of Rumania Patent No. 82942), and 11 – 16 P_2O_5, 20 – 24 B_2O_3, 0.1 – 8 Na_2O, 34 – 49 ZnO, 0.1 – 6 K_2O, 0.1 – 8 Na_2O, 2 – 16 Al_2O_3, 0.1 – 5 CdO, 1 – 16 SiO_2 (USSR Inventor's Certificate No. 1330095). However, the glass compositions are very unstable, just as their properties are, because of the volatility of P_2O_5.

A number of investigations on obtaining low-melting fluxes were performed at the Belarus State Technological University. Low-lead and low-melting glasses based on the system ZnO – SrO – B_2O_3 with small additions of PbO, SiO_2, and Al_2O_3 (the total molar content of the additions is 20%), ZnO – PbO – B_2O_3 – LiO, and ZnO – B_2O_3 – PbO – BaO – SiO_2 (Republic of Belarus Patents Nos. 7406, 7923, and 9738) [9 – 11].

The glasses with the lowest melting point were found to be glasses with molar content 15 – 20% PbO (or up to 35%). Thus, according to Republic of Belarus Patent No. 7406, the low-melting glasses contain the following (%): 13.0 – 25.5 PbO, 20.0 – 27.5 B_2O_3, 18.5 – 40.0 ZnO, 2.0 – 4.0 SiO_2, 3.0 – 6.0 Al_2O_3, 10.0 – 26.0 SrO, 1.5 – 3.0 Li_2O. Compositions with somewhat higher PbO content are proposed in Republic of Belarus Patent No. 7923 (%): 35 – 45 PbO, 15 – 25 B_2O_3, 18 – 25 ZnO, 3 – 8 SiO_2, and 7 – 19 BaO.

Standard methods were used to study the physical – chemical properties of these glasses: CLTE, softening onset temperature $t_{s.o}$, microhardness, and chemical resistance to water.

The composition dependences of the properties ($t_{s.o}$ and CLTE) in the experimental glass systems were studied. It was established that $t_{s.o}$ of the experimental glasses ranges from 440 to 560°C and the CLTE lies in the range (63 – 80) × 10^{-7} K^{-1}. The glasses with the lowest value of $t_{s.o}$ (450 – 460°C) have higher PbO content. An increase of the PbO content in the experimental systems has a considerable effect on the change of this parameter.

The largest change of the properties is observed with PbO molar content 10 – 20%. A substantial slowing of the decrease of $t_{s.o}$ and growth of the CLTE is seen at PbO molar content 20%. Therefore, the most acceptable compositions are those containing not more than 20% PbO. They are characterized by $t_{s.o}$ in the range 450 – 480°C, which makes it possible to use them as fluxes in the manufacturing of silicate paints. The microhardness of the experimental glasses is 3100 – 6500 MPa.

Investigations of the chemical resistance to water showed that the experimental glasses are resistant to water. The mass losses on boiling (powder method) for 1 h are 0.02 – 0.09%. It follows from here that the chemical resistance to water is 99.98 – 99.91%.

Physical – Chemical Properties of Glasses in the System ZnO – PbO – B_2O_3 – (+ R_mO_n) Containing up to 20% (Molar Content) PbO

$t_{s.o}$, °C	450 – 490
CLTE^{-7} K^{-1}	68 – 71
Microhardness, MPa	6000 – 6500
Chemical resistance to water, %	99.98 – 99.91

The results show that the optimal glasses are found in the composition range with PbO molar content up to 20% and low B_2O_3 content. As a result, the optimal glasses were recommended for use as protective coatings, low-melting fluxes for paints, solders, and seals.

Polyzinc glasses exhibit the highest flowability. However, prototype tests showed that the deposition temperature of the paints based on the flux compositions developed on glass articles was 580 – 600°C, which is somewhat higher than the recommended temperature limits — 550 – 580°C. In addition, the values of the CLTE for the glass compositions developed were lower than for high-quality glass.

Borate-based glasses as a base for synthesis of low-melting and low-lead glazes, fluxes, and solders were investigated in [12].

The investigations were performed in the following systems:

1) B_2O_3 – Al_2O_3 – K_2O with constant content of Li_2O, PbO, ZnO, and CaO;

2) B_2O_3 – ZnO – SrO with constant content of Li_2O, PbO, SiO_2, and Al_2O_3;

3) B_2O_3 – ZnO – PbO with constant content of SiO_2 and BaO; and,

4) B_2O_3 – Al_2O_3 – CaO with constant content of MgO, SrO, and BaO.

The content of the main glass former, B_2O_3, varied in the range 20 – 60%.

The glasses were made in corundum crucibles in an electric furnace and in chamotte crucibles in a gas furnace. The lowest-melting glasses were found to belong to the systems 2 and 3. A temperature of 900°C is sufficient to synthesize them. The glasses in the systems 1 and 4 are also low-melting and can be synthesized at temperatures 1000 – 1100°C. Consequently, practically all glasses can be classified as ultralow-melting.

Characteristically, the glassy state is highly stable in all of the experimental glasses. Almost none of the glasses show any indications of crystallization in the temperature interval 600 – 900°C with soaking time 1 h. There are no crystallization exopeaks on the DTA curves of the glasses. Only system-2 glasses exhibit weak exothermal effects in the temperature range 700 – 730°C.

Measurements of $t_{s.o}$ (by pressing a metal rod under load 98×10^{-2} N into the glass) and the CLTE (on a DKV-5A vertical dilatometer) are performed for all glasses.

In practically all systems, B_2O_3 has the most active effect on $t_{s.o}$, but the effect is to increase the values. In system 1, the glasses with the lowest value of $t_{s.o}$ occur in the part of the system with lower boron and higher potassium content. In system 2, the glasses with low values of $t_{s.o}$ lie in the high-zinc (and low-boron) region. In system 3, lead oxide most actively decreases $t_{s.o}$, which, in general, is logical. Finally, the highest values of $t_{s.o}$ are observed in the system 4, though the B_2O_3 content in these glasses is high.

Considering that the founding temperatures are very low (900 – 1100°C) for all glasses, it can be concluded that all glasses are very “short” and the temperature intervals between the melting and softening onset temperatures in all boron glasses (from 900 – 1000 to 440 – 600°C) are substantially smaller than in ordinary silicate glasses (from 1500 to 560 – 600°C). It should be noted especially that, as established in determining $t_{s.o}$, high-zinc compositions are subject to liquation, though it is known that a wide region of liquation exists in the system B_2O_3 – ZnO.

Glasses in the system 1 characterized by the highest CLTEs, which range from 80×10^{-7} to 93×10^{-7} K^{-1}. Since the values of $t_{s.o}$ are low, these glasses can be recommended as a basis for obtaining low-lead solder glasses, which are used, for example, in picture tubes where the CLTE of the glass about 90×10^{-7} K^{-1}, while the screen with the cone is sealed at temperature 440 – 450°C. The glasses in system 2 have comparatively high CLTEs. But, the range of values of the CLTE in them is much wider than in system 1. Close values of the CLTE are observed in the systems 3 and 4 — $(60 – 70) \times 10^{-7}$ K^{-1}.

TABLE 3.

Glass system	$t_{s.o}$, °C	CLTE, 10^{-7} K^{-1}
1	440 – 515	80.6 – 93.3
2	440 – 490	60.3 – 80.3
3	430 – 530	53.7 – 67.0
4	530 – 640	62.7 – 73.7

The variation limits of the thermal properties of the glasses in the experimental systems are presented in Table 3.

However, all glass compositions developed with PbO content decreased to 20% required additional treatment either to increase the CLTE (systems 2 – 4) or decrease the fusing temperatures (system 4).

In summary, the problem of developing compositions of low-melting, noncrystallizing glasses with low PbO content is still topical.

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