

The title of the invention is:

Glass frits containing zinc, free from lead and cadmium,
process for their manufacture and their use.

Remarks:

The application was transferred from the original applicants
Degussa Aktiengesellschaft, to the above applicant on 02.12.95.



Glass frits containing zinc, free from lead and cadmium, process for their manufacture and their use.

Description

The invention concerns glass frits containing zinc, free from lead and cadmium, a process for their manufacture and their use. The glass frits of the invention have a softening point of less than 510°C and are suitable for the manufacture of decorative coatings for glass, vitroceramics and other non-porous materials.

The conventional process for the manufacture of decorative coatings that can be fired, namely glazes, decorative colours and enamels, intended for the decoration of glass and other ceramic and non-ceramic materials, for which firing temperatures of less than 750°C are required, necessitates the use of glass frits with a low melting point, the composition of which mostly has a high lead content. By reason of the toxicity of the said glass frits containing lead to potential users and workers in the manufacture and processing of these products, and with concern for the environment, there is currently a rapidly increasing demand for glass frits free from lead and cadmium.

Many glass frits free from lead and cadmium have been proposed in the literature. It was however established that these products do not always answer the requirements for one or other of the technical properties.

A lead-free glass frit composition is thus known from US-A 4,446,241 which substantially contains Li_2O , B_2O_3 , SiO_2 and 2-33 wt.% of $\text{SnO}_2 + \text{CaO}$ and 2-33 wt.% of $\text{ZrO}_2 + \text{La}_2\text{O}_3$;



optional constituents are Al_2O_3 , SrO , BaO , Na_2O and F . The glass softening temperature (fibre softening point) of these glass frits is between 535°C and 609°C . The softening temperature greater than 535°C and the Li_2O content, which has a harmful influence on the mechanical properties, limit the possibilities for use. Li^+ migrates into the decorated glass during firing and reduces the mechanical strength of the decorated object.

Non-toxic glass frits with a softening point less than 535°C but which also have a high Li_2O content (9-13 wt.%) are also known from EP-B 0 294 502.

Glass frits which were known from US-A 4,537,862 have softening points in the same region as the frits indicated above. Their composition is based substantially on B_2O_3 , SiO_2 , 10-18 wt.% of ZrO_2 and 10-18 wt.% of rare earth metal oxides, the weight ratio between ZrO_2 and the rare earth metal oxides being critical and being 1 to 1 up to 1.4 to 1. This type of glass frit is, by virtue of its rare earth oxide content, very expensive.

Glass frits according to EP-A 0 347 379 with a firing temperature around 600°C contain in addition to SiO_2 , B_2O_3 , alkali metal oxides and $\text{ZrO}_2 + \text{TiO}_2$, 38-43 wt.% of Bi_2O_3 . In view of the toxicological properties, specialists view the very high level of Bi_2O_3 as a disadvantage.

A route that is often taken to obtain glass frits free from lead and cadmium with a low softening point consists of adding zinc oxide to the composition of the glass frit:

The composition of the glass frit of US 4,315,778 substantially contains for example 30-45% SiO_2 , 13-18% B_2O_3 , 12-15% alkali metal oxides, 4-10% ZrO_2 , 18-23% ZnO and



4-10% F (indicated in wt.%). The composition of the glass frit absorbing UV radiation according to EP-A 0 321 297 contains 19-45% SiO_2 , 20-33% B_2O_3 , 8-15% alkali metal oxides, 2-25% of one or more oxides of the series Ce, Mn, Fe, Co, Cu, V and Mo, and may contain in addition among others 0-35% ZnO, preferably 8-21% ZnO (indicated in wt.%). Other glass frit compositions containing zinc, free from lead and cadmium, have been described in GB-B 1 013 597 (12-13 wt.% of ZnO), GB-B 768 925 (4-15 wt.% of ZnO), JP-A 155040/81 (1-15 wt.% ZnO), JP-A 186438/85 (20-25 wt.% of ZnO) and EP-B 0 267 154.

The essential ingredients of glass frits of EP-B 0 267 154, having a softening point between 450°C and 600°C, are 5-14 mol% of Na_2O , 8-25 mol% of ZnO, 6-13 mol% of B_2O_3 and 45-60 mol% of SiO_2 and the optional constituents are K_2O , Li_2O , CaO, SiO, BaO, Bi_2O_3 , Al_2O_3 , ZrO_2 , TiO_2 and WO_3 .

The object of the invention is to provide other glass frits and/or compositions on which they are based, the softening point of which is less than 510°C, and which contain zinc but are free from lead and cadmium. Another object lies in the possibility of using the glass frits as base frits for decorative coatings such as glazes and enamels which may be fired at the lowest temperatures possible so as to be sure of avoiding distortions of the object to be decorated, such as glass in particular.

We have discovered glass frits containing zinc, free from lead and cadmium, the softening point of which (the glass transition temperature) is less than 510°C, which are characterized in that they are composed substantially of :



31 to 50 mol% ZnO
10 to 44 mol% SiO₂
11 to 35 mol% B₂O₃
11 to 25 mol% Na₂O
0 to 4 mol% Li₂O
0 to 10 mol% TiO₂
0 to 25 mol% ZrO₂
0 to 12 mol% CaO
0 to 12 mol% SrO
0 to 12 mol% BaO
0 to 8 mol% F,

wherein the sum of CaO, SrO and BaO is less than or equal to 12 mol%.

Essential constituents of these glass frits of the invention are thus ZnO, B₂O₃, SiO₂ and Na₂O, the ZnO content being greater than with glass frits known hitherto. This high ZnO content is responsible for the remarkable properties of these glass frits.

"Substantially" means that the glass frits may contain, in addition to the compounds indicated, a total of less than 2 mol%, preferably less than 1 mol%, of other metal oxides, for example Al₂O₃, SnO₂, CeO₂, La₂O₃, MgO and P₂O₅. The content of colouring metal oxides such as Fe₂O₃, MnO, CaO and Cr₂O₃ is as a general rule as low as possible, the total thus being less than 0.5 mol%.

Preferred glass frits are composed as follows :



33 to 45 mol% ZnO
10 to 40 mol% SiO₂
11 to 31 mol% B₂O₃
11 to 20 mol% Na₂O
0 to 4 mol% K₂O
0 to 4 mol% Li₂O
0 to 10 mol% TiO₂
0 to 10 mol% ZrO₂
0 to 10 mol% CaO
0 to 10 mol% SrO
0 to 10 mol% BaO
0 to 8 mol% F,

wherein the sum of CaO, SrO and BaO is less than or equal to 10 mol%.

The glass frits which are particularly preferred consist of 33-45 mol% of ZnO, 11-35 mol% of SiO₂, 11-31 mol% of B₂O₃, 11-20 mol% of Na₂O and 0-4 mol% of F.

The presence of the quantities quoted of B₂O₃ and Na₂O is required in combination with ZnO and SiO₂ for obtaining glass frits with a softening point less than 510°C, preferably between 450°C and 485°C. By increasing the boric oxide (B₂O₃) content it is also possible to reduce the coefficient of thermal expansion; on the other hand the B₂O₃ content should be limited in order to preserve the chemical resistance. An increasing Na₂O content enables on the one hand the softening point to be decreased, and on the other hand increases the coefficient of expansion, so that its content must also be limited. The presence of TiO₂ as a constituent in the composition of the frit increases resistance to acid materials. An addition of ZrO₂ increases the resistance of frits to alkaline materials.



The presence of the alkaline earth oxides BaO, SrO and CaO brings about an increase in the softening point and a simultaneous improvement in chemical resistance. For toxicological reasons, the BaO and SrO contents will generally be kept low.

The manufacture of glass frits is known to specialists. A mixture of powdered glass raw materials, oxidized or forming oxides during fusion and, if necessary, of fluorinated glass raw materials, is melted between 1100°C and 1300°C, in particular between 1150°C and 1200°C; the molten product is then chilled suddenly by letting the melt flow for example into water, and it is ground, if necessary, into a powder by employing the conventional methods. Raw materials that are suitable as the principal constituents of the glass frit are silica sand, zinc oxide, boric acid or borax and sodium carbonate. The optional constituents are suitably used in the oxidized form - TiO_2 , ZrO_2 , CaO, SrO, BaO and/or in the form of carbonates - K_2CO_3 , Li_2CO_3 . Fluorine is preferably introduced into the formula of the frit in the form of NaF, AlF_3 or Na_2SiF_6 ; as the frit melts, part of the fluorine is generally removed in the form of gas, the remaining part being retained in the frit in the form of fluoride. The ratio of the quantities of raw materials used in the manufacture of the glass frit corresponds to that of the glass frit of the invention.

Glass frits having the composition according to the claims are suitable as a base frit for the manufacture of decorative coatings that can be fired at a temperature of less than 750°C, in particular however lower than 630°C and preferably between approx. 530°C and less than 600°C. Decorative coatings are to be understood to mean glazes and enamels and decorative colours. Glazes may contain, other than the base frit, coloured transparent glass frits.



Enamels contain, other than the base frit, inorganic pigments. The base frit and the pigments are ground together in known manner. The ratio by weight between the base frit and the pigment or pigments of an enamel conventionally lies in the range of 95 to 5 to 80 to 20. For the manufacture of so-called decorative colours, the glass frit/pigment mixture is subjected to a sintering process with subsequent grinding.

On account of their low firing temperature, decorative coatings containing the glass frits of the invention are suitable for the decoration of glass, vitroceraamics and other non-porous ceramic and non-ceramic, possibly metallic, materials. The use of this type of coating for the decoration of glass should be particularly emphasised since it enables the prevention of any distortion of the object to be decorated. For decoration, the glass frit is ground with an addition of mineral pigment to an average fineness of 5-10 μm in most cases; the ground frit-pigment mixture is dispersed in a conventional organic printing medium and the paste obtained is applied by the conventional methods, for example silk screen printing, spray gun application or stamping, to the object to be decorated; the decoration is then fired. The decorative coatings obtained by using the glass frits according to the invention are particularly suitable for the decoration of perfumery or cosmetics bottles, drinking glasses and bottles.

The glass frits of the invention have, as has been disclosed, a higher ZnO content than glass frits free from lead and cadmium known in the past. It could not be foreseen that glass frits having a ZnO content clearly greater than that of frits known up to now would melt at less than 510°C while having excellent technical properties, good chemical resistance being among them.



Examples

The following examples present in tabular form (tables 1 to 3) the composition of glass frits of the invention as well as their coefficient of thermal expansion α between 0°C and 300°C and their softening point (= glass transition temperature T_g , determined by dilatometry). The manufacture of the glass frits was carried out, as described above, using silica sand, soda, boric oxide, zinc oxide, and/or in addition ZrO_2 , NaF and/or Na_2SiF_6 , CaO, SrO and BaO at a fusion temperature of between 1150°C and 1200°C. The frits of table 2 gave particularly good results in the decoration of glass.

Table 1

Example

No.	1	2	3	4	5
Na_2O (mol%)	13.9	16.9	19.8	17.4	19.3
ZnO (mol%)	39.7	37.7	44.7	39.8	34.2
B_2O_3 (mol%)	16.5	15.1	11.7	30.9	11.3
SiO_2 (mol%)	29.9	30.3	23.8	11.9	35.2
α_o^{300} ($\cdot 10^{-7} \cdot K^{-1}$)	79.0	94.3	85.3	87.0	101
T_g (°C)	502	467	465	465	486

Table 2

Example

No.	6	7	8	9	10
Na ₂ O (mol%)	16.4	15.9	17.9	15.9	15.7
ZnO (mol%)	35.8	34.7	38.5	40.5	37.6
B ₂ O ₃ (mol%)	19.4	24.0	26.0	28.2	28.0
SiO ₂ (mol%)	24.8	21.9	13.9	11.7	15.0
F (mol%)	3.6	3.5	3.7	3.7	3.7
α_o^{300} ($\cdot 10^{-7} \cdot K^{-1}$)	87.8	86.3	93.7	83.7	81.6
Tg (°C)	475	485	450	465	475

Table 3

Example

No.	11	12	13
Na ₂ O (mol%)	16.5	11.1	15.3
ZnO (mol%)	33.5	35.5	37.7
B ₂ O ₃ (mol%)	14.7	17.8	20.0
SiO ₂ (mol%)	22.6	22.8	17.0
F (mol%)	7.2	7.2	
ZrO ₂ (mol%)	5.5	5.6	
CaO (mol%)			5.2
SrO (mol%)			2.9
BaO (mol%)			1.9
α_o^{300} ($\cdot 10^{-7} \cdot K^{-1}$)	89.6	72.7	87.4
Tg (°C)	475	505	510



Glass frits containing zinc, free from lead and cadmium,
process for their manufacture and their use.

Claims

- 1) Glass frits containing zinc, free from lead and cadmium, with a softening point (glass transition temperature) less than 510°C , characterized in that they are composed substantially of

31 to 50 mol% ZnO
10 to 44 mol% SiO_2
11 to 35 mol% B_2O_3
11 to 25 mol% Na_2O
0 to 4 mol% Li_2O
0 to 10 mol% TiO_2
0 to 25 mol% ZrO_2
0 to 12 mol% CaO
0 to 12 mol% SrO
0 to 12 mol% BaO
0 to 8 mol% F ,

wherein the sum of CaO , SrO and BaO is equal to or less than 12 mol%.

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- 2) Glass frits according to claim 1,
characterized in that
they are composed substantially of

33 to 45 mol% ZnO
10 to 40 mol% SiO₂
11 to 31 mol% B₂O₃
11 to 20 mol% Na₂O
0 to 4 mol% K₂O
0 to 4 mol% Li₂O
0 to 10 mol% TiO₂
0 to 10 mol% ZrO₂
0 to 10 mol% CaO
0 to 10 mol% SrO
0 to 10 mol% BaO
0 to 8 mol% F,

wherein the sum of CaO, SrO and BaO is equal to or
less than 10 mol%.

- 3) Glass frits according to claim 1,
characterized in that
they are composed substantially of

33 to 45 mol% ZnO
11 to 35 mol% SiO₂
11 to 31 mol% B₂O₃
11 to 20 mol% Na₂O
0 to 4 mol% F.

- 4) Process for the manufacture of glass frits according
to one of claims 1 to 3 by fusion between 1150°C and
1200°C of a mixture of powdered glass raw materials,
oxidised or forming oxides, and if necessary
fluorinated glass raw materials, and sudden chilling
of the melt,





characterized in that
the glass raw materials are used in such quantities
that the mixture is composed substantially of

31 to 50 mol% ZnO
10 to 44 mol% SiO₂
11 to 35 mol% B₂O₃
11 to 25 mol% Na₂O
0 to 4 mol% Li₂O
0 to 10 mol% TiO₂
0 to 25 mol% ZrO₂
0 to 12 mol% CaO
0 to 12 mol% SrO
0 to 12 mol% BaO
0 to 8 mol% F,

wherein the sum of CaO, SrO and BaO is equal to or
less than 12 mol%.

- 5) Use of the glass frits according to one of claims 1 to
3 as a base frit for the manufacture of decorative
coatings which can be fired at a temperature of less
than 630°C preferably ones intended for the decoration
of glass.

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