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(54) Titre : PROCEDE POUR EMPECHER LA REMONTEE D'ION D'ARGENT DANS DES EMAILS
(54) Title: PREVENTING SILVER ION MIGRATION IN ENAMELS

(57) Abrégé/Abstract:
Disclosed is a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^{+} ion migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

ABSTRACT OF THE DISCLOSURE

Disclosed is a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ ion migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

Preventing Silver Ion Migration In Enamels

This invention relates to glass frits which, screen-printed on their own, in an overlayer or in an enamel, are capable of stopping the heat-activated migration of Ag^+ ions between a support of float glass and a silver-based resistive layer.

Enamel compositions for glass are well known among experts:

They are generally formed after firing by a vitreous phase supplied by the frit(s) used and a coloring and opacifying crystalline pigment phase to which other compounds may be added to obtain various effects. They are suitable for various applications and may be used inter alia for forming borders at the periphery of sheets of flat float glass which are thermoformed and then tempered for use as glazing in motor vehicles.

Originally used with the sole object of protecting the adhesive used to fix the sheets of glass (windscreens, rear windows, side windows) to bodywork against the ultraviolet radiation in sunlight, these strips of black or grey enamel were subsequently the subject of aesthetic research, attempts having been made in particular to use these enamels to conceal the lateral silver collectors of heated rear windows and the welding spots of the connecting terminals of the current supply wires. Now, it has been found that, after the heat treatment required for curving and tempering, none of the enamels of conventional composition are capable of completely concealing the silver collectors applied in superposed form and heated with the enamel or the above-mentioned weld spots.

Various studies have demonstrated the existence of heat-activated transport of the Ag^+ cations from the resistive layer through the enamel to the enamel/glass interface, thus revealing the presence of collectors behind the enamel by an interse colorimetric contrast.

It is known from US-PS 4,837,383 that it is desirable to prevent the migration of silver when using an enamel consisting of a glass flux based on a glass frit, pigments, elemental aluminium and/or lithium oxide and a vehicle for paste formation. Published European patent application EP-A 0 377 062 claims improvements in the silver-based opacity of enamels by the addition before paste formation of silicon, boron, carbon, lead and/or silver in their elemental forms.

For obvious reasons of cost (silver), special operating conditions necessitated by the introduction of highly reducing elements, such as silicon or boron, stability to acids (lithium) or toxicity (lead), additions of the type mentioned have not proved entirely satisfactory. The enamels developed with additions such as these in conjunction with the present state-of-the-art in this field show that, despite the aesthetic interest there is in completely concealing the silver collectors by enamel, such solutions limit the range of colours currently useable by the automotive industry to a few blacks and to a few greys.

In addition, the quality of the masking effect obtained is largely influenced by the firing cycle as a whole.

Accordingly, the present invention provides an enamel barrier layer for stopping the migration of silver cations from the collectors to the glass during the firing of a combination of flat glass with an enamel barrier layer and,

above this enamel layer, a resistive layer of silver which would have the disadvantages of the systems mentioned above.

Thus, by eliminating the need to form a paste of the additives mentioned above, the present invention offers a general solution to the problems discussed in the foregoing.

More particularly, the invention provides a glass frit, comprising 0.05 to 15.0 mol% of sulphur, a sulfide or a mixture thereof.

More specifically, the present invention provides a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ ion migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

The present invention also provides a glass surface having deposited thereon an enamel barrier-layer capable of preventing the migration of Ag^+ ions, the layer being formed from a glass frit, and optionally one or more colorants and/or opacifiers, the glass frit being essentially free of lead and comprising 15 to 70% by weight

zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

The present invention also provides a method of preventing silver migration into glass, the method comprising the steps of placing an enamel barrier-layer formed from a glass frit, and optionally one or more colorants and/or opacifiers, between sheet glass and a resistive-layer containing silver, wherein the enamel barrier-layer is capable of preventing Ag^+ ion migration, and firing at a temperature of from 450°C to 800°C, wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

The present invention also provides a composite glass product comprising sheet glass, an enamel barrier-layer, and a silver resistive-layer, the composite glass product made by a method comprising the steps of placing an enamel barrier-layer formed from a glass frit, and optionally one or more colorants and/or opacifiers, between sheet glass and a resistive-layer containing silver, wherein the enamel barrier-layer is capable of preventing Ag^+ ion migration,

and firing at a temperature of from 450°C to 800°C, wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

The present invention also provides a composite glass article comprising a glass support-layer, an enamel barrier-layer deposited on the glass support layer, and a silver resistive-layer deposited on the barrier-layer, the enamel barrier-layer being capable of preventing Ag^+ ion migration, and being formed from a glass frit, and optionally one or more colorants and/or opacifiers, wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

The present invention also provides a process for the production of a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass,

0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, the process comprising the steps of melting a mixture comprising (a) glass-forming oxide compounds, or non-oxide compounds which form glass-forming oxides, corresponding to 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and (b) 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, at a temperature of 1,000° to 1,300°C, to dissolve the sulfur or the sulfides in the glass, cooling suddenly to form granules, and grinding the granules to form a frit.

The present invention also provides a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, the glass frit being produced by a process comprising the steps of melting a mixture comprising (a) glass-forming oxide compounds, or non-oxide compounds which form glass-forming oxides, corresponding to 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and (b) 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, at a temperature of 1,000° to 1,300°C, to dissolve the sulfur or the sulfides in the glass, cooling

suddenly to form granules; and grinding the granules to form a frit.

Preferably, the frits contain zinc sulfide.

In another embodiment of the invention, the frits contain zinc oxide, preferably in a quantity of 30 to 65% by weight.

In another embodiment of the invention, the frits contain coloring metal oxides.

In another embodiment, the invention relates to a glass frit obtained by fusion of a mixture of oxides and/or non-oxide compounds (fluorides, carbonates) at temperatures of 1,000 to 1,300°C, followed by sudden cooling, characterized in that it contains from 0.05 to 15 mol% sulfur, zinc sulfide or other sulfides.

In another embodiment, the invention relates to the use of the glass frits to form enamel barrier layers for stopping the migration of silver from a resistive silver layer to the

glass during the firing of a combination of sheet glass with one or more enamel layers, including the enamel barrier layer, and - above this layer - a resistive silver layer.

It has been found that the addition of 0.05 to 15.0 mol - % sulfur or sulfides (preferably zinc sulfide) to a mixture of oxides and/or non-oxide compounds for the production of a glass frit provides the frit with the property of stopping the heat-activated diffusion within the frit of the Ag^+ cations from the collectors of the resistive network based on silver.

In addition to sulfur and/or sulfides, the frits consist of a suitable association of oxides in a vitrifiable composition. The expert knows many different associations of oxides which, after fusion, give glass frits, see for example US 4,892,847, EP-A-0 377 062 and EP-A-0 294 502.

The choice of the oxides determines the properties of the glass frits, for example their softening point, their thermal expansion coefficient and their stability to bases and acids. In general, the colorless glass frits contain oxides selected from:

SiO_2,	Al_2O_3,	TiO_2,	ZnO,	MgO,	Li_2O,
B_2O_3	Bi_2O_3	SnO_2	PbO	CaO	Na_2O
	La_2O_3	ZrO_2	MnO	BaO	K_2O
	V_2O_5	MoO_3			

although other oxides, for example P_2O_5, Cr_2O_3, Fe_2O_3, CuO, NiO, CoO, WO_3, CeO_2, etc. may also be present. According to

the invention, frits based on borosilicates, particularly zinc borosilicates, are preferred. It is for this reason that they contain silicon dioxide in a quantity of 15 to 40% by weight and boron trioxide in a quantity of 5 to 25% by weight and preferably 15 to 70% by weight and, above all, 30 to 65% by weight zinc oxide.

The introduction of sulfur during dry-mixing of the composition before melting may be carried out either in the form of flowers of sulfur or in the form of sulfides, although dissolution and retention in the structure of the glass vary according to the method of introduction selected. The advantage of ZnS over elemental sulfur and the other sulfides is that it remains stable up to the fusion of the eutectics of the oxides of the mixture and it is only within this molten mixture that ZnS is progressively dissolved. Accordingly, the elimination of SO_2 and the loss of elemental sulfur are avoided with ZnS. In addition, it has been found that zinc is an element which promotes stabilization of the sulfur in the vitreous atomic structure.

In principle, other sulfides than ZnS, for example sulfides of alkali metals, alkaline earth metals or of Mn, Fe, Co, Ni, Cu, Cd, Sn, Pb, Sb, Bi, may be introduced into the mixture to be melted. However, it should be pointed out that some of these sulfides, such as for example MnS, FeS, Cu_2S, CdS, PbS, color the vitreous mass. In addition, the introduction of these sulfides in large quantities can cause liquid-phase separation within the molten mass. It is pointed out that the presence of elemental sulfur in the frits according to the invention is necessary for the interaction with the Ag^+ cations and that, introduced in the form of sulfides, these sulfides are at least partly dissociated (ZnS begins to dissociate at around 900°C) during

melting of the fusible mixture so that, thereafter, it is only the sulfur which reacts with the Ag^+ cations in an enamel barrier layer containing the vitreous structure of such frits.

The principle of the process for producing the glass frits is known to the expert. To make the glass frits according to the invention, a mixture consisting of (a) oxides and/or compounds which form oxides by melting into a vitrifiable composition corresponding to the composition of the frit and (b) one or more compounds selected from sulfur, zinc sulfide and other sulfides in a quantity of 0.05 to 15 mol-% of the mixture is melted at temperatures of 1,000 to 1,300°C, after which the molten glass is suddenly cooled in water.

Subsequent grinding of the granules obtained provides the ready-to-use frit powder.

The mixture mentioned above is preferably composed of oxides, although alkali metal and alkaline earth metal oxides are often introduced in the form of carbonates. Melting is carried out conventionally in a refractory ceramic crucible or in a furnace having a suitable lining. The fragments of the frits are ground after cracking (preferably 90% smaller than $20 \cdot 10^{-6}$m) by known grinding techniques for glass frits.

By virtue of their ability to stop the migration of silver, the glass frits according to the invention may be used to form enamel barrier layers. These enamels may be colorless or colored, transparent or opaque. The enamel barrier layers may contain other frits as the vitrifiable compound although the essential constituent is always a frit

containing sulfur. The enamel barrier layers according to the invention stop the migration of silver during firing of the combinations of sheet glass with one or more enamel layers, including the barrier layer, and - above the last enamel layer - a resistive silver layer. The function which the vitreous structures of the enamel barrier layer perform in stopping the migration of silver is also effective at the temperatures required for curving and tempering the sheets of glass. The enamel barrier layer may be situated between the glass, for example a sheet of flat glass, and a resistive network based on silver and conceals the silver collectors if the enamel is colored and preferably opaque. Now, the barrier layer may be situated between an opaque colored enamel applied to the glass and a resistive silver layer.

The enamel of the unfired barrier layer is formed by one or more frits according to the invention, colorants and/or opacifiers where a decorative effect is required and a vehicle for paste formation, for example a screen-printing oil based on solvents, natural resins and/or thermoplastics. The vehicle for paste formation is selected according to the final application envisaged. It must provide for effective suspension of the particles and must be completely consumed during firing and tempering. The enamel of the barrier layer and/or a subjacent enamel of conventional composition have to meet certain requirements and, in the case of decorative enamels, must have above all a sufficient pigment content to satisfy the color and opacity requirements.

The enamels of the barrier layers according to the invention are applied by screen printing either directly or by way of a transfer or another intermediate support. The average thickness per layer after firing is between $5 \cdot 10^{-6}$m and $50 \cdot 10^{-6}$m.

In cases where a barrier layer which is colorless or colored in the mass is interposed between a crude and dry enamel which itself is applied by screen printing and the resistive silver layer, disorientation of the meshes of the screen printing cloths used for one or other of the applications will be favorable. In this way, firing of the combination of glass (with all the enamel layers) and the resistive silver layer (for example 60 to 80% by weight silver) is carried out in a single operation.

The heat treatment, i.e. firing followed by tempering, of the combinations of glass/enamel barrier layer/resistive silver layer or glass/conventional enamel layer/enamel barrier layer/resistive silver layer is carried out in various types of furnace, according to the intended application of the enamelled glass. The firing temperature is also determined by the composition of the frit(s) used in the enamels. In general, the firing temperature varies from 450°C to 800°C and preferably from 550°C to 750°C.

In tests (see Example 10) it was found that, in the enamels described in DE-OS 38 32 937 and DE-OS 38 38 196 which are formed by a conventional frit, a vehicle and, in addition, a sulfide of copper, zinc, iron, tin or aluminium, there was no favorable action in stopping the Ag^+ cations, i.e. there was no effective interaction between sulfide and Ag^+.

The S - Ag^+ interaction and the resulting arrest of the Ag^+ cations is thus a quality unique to enamels of which the frits contain elemental sulfur and/or a sulfide dissolved in the vitreous mass. Frits which do not contain dissolved sulfur and which are applied on their own or in association

cations during their heat-activated migration towards the interface with the glass. In addition, the direct intrcduction of sulfides into the enamel, as in the documents cited above, i.e. as an associated pigment charge, causes a significant colorimetric drift whereas the use of a frit according to the invention (containing sulfur) causes no such drift.

The invention is illustrated by the following Examples in conjunction with the accompanying drawing, in which:

Figure 1 shows the X ray diffraction spectrum obtained with the frit of Example 3.

Examples 1 to 4

Frits having the following composition were prepared for colorless barrier layers:

Composition of the frit	1	2	3	4
	mol-%			
ZnS	1.98	3.99	4.82	5.00
SiO_2	21.86	34.99	19.76	29.00
B_2O_3	12.64	20.08	11.42	18.00
ZnO	63.52	30.09	64.00	35.45
Na_2O		6.30		6.00
BaO		4.55		4.65
ZrO_2				1.90

Dry mixing of the oxides except for Na_2O and BaO, which were added with Na_2CO_3 and $BaCO_3$, melting at 1,150 to 1,200°C, quenching in water, grinding, stoving. To obtain the enamel barrier layer, the frits were made into a paste with a vehicle and the enamel was applied by screen printing.

Examples 5 and 6

Introduction of the sulfur in the form of flowers of sulfur or cadmium sulfide.

Composition of the mixture for melting	5	6
	mol-%	
S	15.00	-
CdS	-	6.04
SiO_2	18.95	20.95
B_2O_3	10.97	12.11
ZnO	55.08	60.89

The frits were produced in the same manner as in Examples 1 to 4.

Example 7

The frit may be pigmented as such without affecting its barrier properties. In Example 7, the dissolution of a black colored inorganic pigment of the copper chromite spinel type enables a brown frit to be obtained with its barrier properties intact. Dry mixing of the frit of Example 2 (85.36% by weight) with a black spinel pigment (14.64% by

weight), melting, quenching, grinding and stoving to obtain an intermediate frit.

The brown frit consists of 70% by weight of the frit of Example 1 and 30% by weight of the intermediate frit mentioned above. To obtain the enamel for a barrier layer: disintegration of the two frits in alcohol to form a homogeneous mixture, stoving, paste formation.

Examples 8 and 9

Black and grey opaque enamels masking the silver collectors.

Composition of the enamel	8	9
	by weight	
Frit of Example 4	75	77.5
Black pigment, copper chromite spinel type	25	12.5
Titanium dioxide		10.0
Color of the enamel	Black	Grey

Disintegration of the compounds in alcohol, stoving and paste formation for application as a barrier layer.

Example 10

(for comparison with DE-OSS 38 32 937 and 38 38 196)

Tests for introduction of sulfides into the enamel (composition in parts by weight):

	a	b	b	d	e	f
Vitreous enamel powder VA 641 (DPC LIMOGES)	7.2	7.2	7.2	7.2	7.2	7.2
ZnS (ALDRICH)	1.6					
ZnS (PROLABO)		1.6				
Cu_2S			1.6			
FeS				1.6		
CdS					1.6	
MnS						1.6
VEHICLE MX 54 (DPC LIMOGES)	2.8	2.8	2.8	2.8	2.8	2.8
COLOUR OF ENAMEL	BLUISH GREY	BLUISH GREY	DEEP GREY-RED	BROWN-ISH GREY	GREEN GREY	GREEN GREY
COLORIMETRIC DIFFERENCES ΔE IN RELATION TO THE ENAMEL VA 641 AS REFERENCE	13.40	10.11	6.15	14.80	5.30	11.40

Application of the enamels to glass (4 mm); superposition of the enamelled glass with the silver paste SP 1230 (Degussa AG); vertical firing and tempering for 3.5 minutes at 680°C. None of the enamels of Example 10 is effective in stopping the migration of the silver.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ ion migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

2. The glass frit according to claim 1, wherein said sulfide is zinc sulfide.

3. The glass frit according to claim 1, wherein said sulfide is at least one member of the group consisting of sulfides of alkali metals, alkaline earth metals, Mn, Fe, Co, Ni, Cu, Cd, Sn, Sb, and Bi.

4. The glass frit according to claim 1, 2 or 3, wherein 30 to 65% by weight of said zinc oxide is present.

5. The glass frit according to any one of claims 1 to 4, further comprising colored metal oxides.

6. The glass frit according to any one of claims 1 to 4, which is colorless.

7. A glass surface having deposited thereon an enamel barrier-layer capable of preventing the migration of Ag^+ ions, the layer being formed from a glass frit, and optionally one or more colorants and/or opacifiers, the glass frit being essentially free of lead and comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

8. The enamel barrier-layer according to claim 7, wherein said sulfide is zinc sulfide.

9. The enamel barrier-layer according to claim 7, wherein said sulfide is at least one member of the group consisting of sulfides of alkali metals, alkaline earth metals, Mn, Fe, Co, Ni, Cu, Cd, Sn, Sb, and Bi.

10. The enamel barrier-layer according to claim 7, 8 or 9, further comprising colored metal oxides.

11. A method of preventing Ag^+ ion migration into glass, the method comprising the steps of:

placing an enamel barrier-layer formed from a glass frit, and optionally one or more colorants and/or opacifiers, between sheet glass and a resistive-layer containing silver, wherein the enamel barrier-layer is capable of preventing Ag^+ ion migration; and

firing at a temperature of from 450°C to 800°C;

wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

12. The method according to claim 11, wherein said temperature is from 550°C to 750°C.

13. A composite glass product comprising sheet glass, an enamel barrier-layer and a silver resistive-layer, the composite glass product made by a method comprising the steps of:

placing an enamel barrier-layer formed from a glass frit, and optionally one or more colorants and/or opacifiers, between sheet glass and a resistive-layer containing silver, wherein the enamel barrier-layer is capable of preventing Ag^+ ion migration; and

firing at a temperature of from 450°C to 800°C;

wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

14. A composite glass article comprising a glass support-layer, an enamel barrier-layer deposited on said glass support layer, and a silver resistive-layer deposited on said barrier-layer, said enamel barrier-layer being capable of preventing Ag^+ ion migration, and being formed from a glass frit, and optionally one or more colorants and/or opacifiers, wherein the glass frit is essentially free of lead and comprises 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprises, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides.

15. The composite glass article according to claim 14, which is glass for an automobile.

16. A process for the production of a glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, the process comprising the steps of:

melting a mixture comprising (a) glass-forming oxide compounds, or non-oxide compounds which form glass-forming oxides, corresponding to 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and (b) 0.05 to 15 mol% of at least one

member of the group consisting of sulfur and sulfides, at a temperature of 1,000° to 1,300°C, to dissolve said sulfur or said sulfides in said glass;

cooling suddenly to form granules; and

grinding said granules to form a frit.

17. A glass frit, essentially free of lead, for forming an enamel capable of preventing Ag^+ migration, the glass frit comprising 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and further comprising, dissolved in the glass, 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, the glass frit being produced by a process comprising the steps of:

melting a mixture comprising (a) glass-forming oxide compounds, or non-oxide compounds which form glass-forming oxides, corresponding to 15 to 70% by weight zinc oxide, 15 to 40% by weight silicon dioxide and 5 to 25% by weight boron trioxide, and (b) 0.05 to 15 mol% of at least one member of the group consisting of sulfur and sulfides, at a temperature of 1,000° to 1,300°C, to dissolve said sulfur or said sulfides in said glass;

cooling suddenly to form granules; and

grinding said granules to form a frit.

Figure 1

