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(54) **Title:** LOW TEMPERATURE FSREABLE THICK FILM SILVER PASTE

(57) **Abstract:** The present invention is directed to an electroconductive thick film paste composition comprising Ag and a Pb-free Bi-based glass frit both dispersed in an organic medium, wherein the paste is fireable at temperatures below 420°C. The paste is especially useful for forming electrodes on substrates such as glass or films, particularly electrochromic glass or films, that would be damaged by higher firing temperatures. The present invention is further directed to a device comprising an electrode formed from the paste composition and, in particular, to an electrochromic device comprising such an electrode.



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TITLE

LOW TEMPERATURE FIREABLE THICK FILM SILVER PASTE

FIELD OF THE INVENTION

5 The present invention is directed primarily to a thick film paste composition that is fireable at low temperatures and electrodes formed from the composition.

TECHNICAL BACKGROUND OF THE INVENTION

10 Light transmission properties of electrochromic films or glasses change with the application of a voltage. The electrochromic material changes from a transparent state to a colored opaque or translucent state. Electrochromic devices are used in a variety of applications. One example of such electrochromic devices are electrochromic smart windows that are used to control the amount of light and heat allowed to pass through.

15 Smart windows can save costs of heating and air-conditioning and provide adjustable lighting. Electrochromic smart windows can be used between rooms to provide walls with different states of light transmission. Electrochromic materials have also been used to tint rear-view mirrors in automobiles and to protect displays under glass in museum cases and

20 picture frames from the damaging effects of ultra-violet and visible light.

Electrodes for applying a voltage are a necessary aspect of electrochromic devices. Current electrochromic materials suffer damage at temperatures above about 420°C. The electrodes must therefore be formed at temperatures below 420°C. There is an on-going need to

25 provide thick film paste compositions that can be fired at temperatures below 420°C while maintaining electrical performance and other relevant properties of the resulting electrodes and devices. Preferably, the paste is Pb-free. The present invention provides a silver thick film paste composition that simultaneously provides a Pb-free system with lower

30 firing temperatures while maintaining electrical and mechanical performance.

SUMMARY OF THE INVENTION

The present invention provides a thick film paste composition

35 comprising:

- (a) 65-85 wt% Ag;
- (b) 1-8 wt% Pb-free bismuth-based glass frit; and

(c) organic medium;

wherein the Ag and the bismuth-based glass frit are dispersed in the organic medium, wherein the wt% are based on the total weight of the paste composition and wherein the paste composition is fireable at temperatures below 420°C, the bismuth-based glass frit comprising 65-78 wt% Bi₂O₃, 7-12 wt% B₂O₃, 11-15 wt% ZnO and 0.5-8 wt% SiO₂, based on the total weight of the bismuth-based glass frit.

The invention also provides a device, and in particular an electrochromic device, comprising an electrode formed from the instant paste composition, wherein the paste composition has been fired at temperatures below 420°C to remove the organic medium and form the electrode.

DETAILED DESCRIPTION OF THE INVENTION

The conductive thick film paste composition of the instant invention contains a Pb-free Bi-based glass frit that enables paste firing temperatures below 420°C and provides an electrode that has good electrical and adhesion properties. In one embodiment the Bi-based glass frit enables paste firing temperatures not exceeding 405°C. The paste is especially useful for forming electrodes on substrates such as glass or films, particularly electrochromic glass or films, that would be damaged by higher firing temperatures.

The conductive thick film paste composition comprises silver, the Bi-based glass frit that is Pb-free, and an organic vehicle. It can be used to form screen printed electrodes on devices such as electrochromic devices but is also useful in defoggers, refrigerator or freezer windows and any other applications that require low firing thick film paste. The paste composition comprises 65-85 wt% silver, 1-8 wt% Bi-based glass frit and an organic medium, wherein the Ag and the Bi-based glass frit are both dispersed in the organic medium and wherein the weight percentages are based on the total weight of the paste composition.

Each component of the thick film paste composition of the present invention is explained in detail below.

Silver

In the present invention, the conductive phase of the paste is silver (Ag). The silver can be in the form of silver metal, alloys of silver, or

mixtures thereof. Typically, the silver particles are in a flake form, a spherical form, a granular form, a crystalline form, a powder, or other irregular forms and mixtures thereof. The silver can be provided in a colloidal suspension. The silver can also be in the form of silver oxide (Ag₂O), silver salts such as AgCl, AgNO₃, AgOOCCH₃ (silver acetate), AgOOCF₃ (silver trifluoroacetate), silver orthophosphate (Ag₃PO₄), or mixtures thereof. Other forms of silver compatible with the other thick-film paste components can also be used.

In one embodiment, the thick-film paste composition comprises coated silver particles that are electrically conductive. Suitable coatings include phosphorous and surfactants. Suitable surfactants include polyethyleneoxide, polyethyleneglycol, benzotriazole, poly(ethyleneglycol)acetic acid, lauric acid, oleic acid, capric acid, myristic acid, linolic acid, stearic acid, palmitic acid, stearate salts, palmitate salts, and mixtures thereof. The salt counter-ions can be ammonium, sodium, potassium, and mixtures thereof.

The particle size of the silver is not subject to any particular limitation. In one embodiment, an average particle size is less than 10 microns; in another embodiment, the average particle size is less than 5 microns.

The instant thick film paste composition comprises 65-85 wt% silver, based on the total weight of the paste composition. In one embodiment the thick film paste composition comprises 70-80 wt% silver.

25 Bi-Based Glass Frit

A component of the paste composition is a Bi-based glass frit. In one embodiment, the Bi-based glass frit may include more than one glass composition. In an embodiment, the Bi-based glass frit may include a glass composition and an additional composition, such as a crystalline composition.

The Bi-based glass frit may be prepared by mixing Bi₂O₃, B₂O₃, ZnO, SiO₂ and other oxides to be incorporated therein (or other materials that decompose into the desired oxides when heated) using techniques

understood by one of ordinary skill in the art. Such preparation techniques may involve heating the mixture in air or an oxygen-containing atmosphere to form a melt, quenching the melt, and grinding, milling, and/or screening the quenched material to provide a powder with the desired particle size.

- 5 Melting the mixture of bismuth, boron, zinc, silicon and other oxides to be incorporated therein is typically conducted to a peak temperature of 800 to 900°C. The molten mixture can be quenched, for example, on a stainless steel platen or between counter-rotating stainless steel rollers to form a platelet. The resulting platelet can be milled to form a powder. Typically,
10 the milled powder has a d_{50} of 0.1 to 3.0 microns. One skilled in the art of producing glass frit may employ alternative synthesis techniques such as but not limited to water quenching, sol-gel, spray pyrolysis, or others appropriate for making powder forms of glass.

The starting mixture used to make the Bi-based glass frit includes,
15 based on the total weight of the starting mixture of the Bi-based glass frit, 65-78 wt% Bi_2O_3 , 7-12 wt% B_2O_3 , 11-15 wt% ZnO and 0.5-8 wt% SiO_2 .

In a further embodiment, in addition to the Bi_2O_3 , B_2O_3 , ZnO and SiO_2 , the starting mixture used to make the based glass frit includes one or more oxides and their amounts selected from the group consisting of
20 0.1 to 5 wt% of CaO , 0.1 to 5 wt% of BaO , 0.1 to 2 wt% of Al_2O_3 , 0.1 to 2 wt% of Na_2O and 0.1 to 2 wt% of Li_2O , based on the total weight of the starting mixture of the Bi-based glass frit.

In one embodiment, the, the starting mixture includes 2 to 4 wt% BaO and 0.1 to 2 wt% Al_2O_3 , again based on the total weight of the
25 starting mixture of the Bi-based glass frit.

In one embodiment, the Bi-based glass frit may be a homogenous powder. In a further embodiment, the Bi-based glass frit may be a combination of more than one powder, wherein each powder may separately be a homogenous population. The composition of the overall
30 combination of the 2 powders is within the ranges described above. For example, the Bi-based glass frit may include a combination of 2 or more different powders; separately, these powders may have different compositions, and may or may not be within the ranges described above;

however, the combination of these powders is within the ranges described above.

In an embodiment, the Bi-based glass frit composition may include one powder which includes a homogenous powder including some but not all of the desired elements of the Bi-based glass frit composition, and a second powder, which includes one or more of the other desired elements. For example, a composition may include a first powder including Bi, B and Zn and O, and a second powder including TiO_2 . In an aspect of this embodiment, the powders may be melted together to form a uniform composition. In a further aspect of this embodiment, the powders may be added separately to a thick film composition.

Glass compositions, also termed glass frits, are described herein as including percentages of certain components. Specifically, the percentages are the percentages of the components used in the starting material that was subsequently processed as described herein to form a glass composition. Such nomenclature is conventional to one of skill in the art. In other words, the composition contains certain components, and the percentages of those components are expressed as a percentage of the corresponding oxide form. As recognized by one of ordinary skill in the art in glass chemistry, a certain portion of volatile species may be released during the process of making the glass. An example of a volatile species is oxygen. It should also be recognized that while the glass behaves as an amorphous material it will likely contain minor portions of a crystalline material.

If starting with a fired glass, one of ordinary skill in the art may calculate the percentages of starting components described herein using methods known to one of skill in the art including, but not limited to: Inductively Coupled Plasma-Emission Spectroscopy (ICPES), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), and the like. In addition, the following exemplary techniques may be used: X-Ray Fluorescence spectroscopy (XRF); Nuclear Magnetic Resonance spectroscopy (NMR); Electron Paramagnetic Resonance spectroscopy (EPR); Mössbauer spectroscopy; electron microprobe Energy Dispersive

Spectroscopy (EDS); electron microprobe Wavelength Dispersive Spectroscopy (WDS); Cathodo-Luminescence (CL).

One of ordinary skill in the art would recognize that the choice of raw materials could unintentionally include impurities that may be incorporated into the glass during processing. For example, the impurities may be present in the range of hundreds to thousands ppm. The presence of the impurities would not alter the properties of the glass, the thick film composition, or the fired device.

The content of the Bi-based glass frit in the instant thick film paste composition is typically 1-8 wt%, based on the total weight of the thick film paste composition. In one embodiment, the content is 2-7 wt %. The Bi-based glass frit is a necessary component of the instant low temperature fireable paste composition but also can play an important role as a component in other such thick film paste formulations.

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Organic Medium

The inorganic components of the thick-film paste composition are mixed with an organic medium to form viscous pastes having suitable consistency and rheology for printing. A wide variety of inert viscous materials can be used as the organic medium. The organic medium can be one in which the inorganic components are dispersible with an adequate degree of stability during manufacturing, shipping and storage of the pastes, as well as on the printing screen during the screen-printing process.

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Suitable organic media have rheological properties that provide stable dispersion of solids, appropriate viscosity and thixotropy for screen printing, appropriate wettability of the substrate and the paste solids, a good drying rate, and good firing properties. The organic medium can contain thickeners, stabilizers, surfactants, and/or other common additives. One such thixotropic thickener is thixatrol. The organic medium can be a solution of polymer(s) in solvent(s). Suitable polymers include ethyl cellulose, ethylhydroxyethyl cellulose, wood rosin, mixtures of ethyl cellulose and phenolic resins, polymethacrylates of lower alcohols, and the monobutyl ether of ethylene glycol monoacetate. Suitable solvents include terpenes such as alpha- or beta-terpineol or mixtures thereof with other solvents such as kerosene, dibutylphthalate, butyl carbitol, butyl

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carbitol acetate, hexylene glycol and alcohols with boiling points above 150°C, and alcohol esters. Other suitable organic medium components include: bis(2-(2-butoxyethoxy)ethyl adipate, dibasic esters such as DBE, DBE-2, DBE-3, DBE-4, DBE-5, DBE-6, DBE-9, and DBE 1B, octyl epoxy
5 tallate, isotetradecanol, and pentaerythritol ester of hydrogenated rosin. The organic medium can also comprise volatile liquids to promote rapid hardening after application of the thick-film paste composition on a substrate.

The optimal amount of organic medium in the thick-film paste
10 composition is dependent on the method of applying the paste and the specific organic medium used. The instant thick-film paste composition contains 10 to 30 wt% of organic medium, based on the total weight of the paste composition.

If the organic medium comprises a polymer, the polymer typically
15 comprises 8 to 15 wt% of the organic composition.

Preparation of the Thick Film Paste Composition

In one embodiment, the thick film paste composition can be prepared by mixing Ag powder, the Bi-based glass frit powder, the organic
20 medium and any other component, e.g., additional glass frit or other inorganic additives, in any order. In some embodiments, the inorganic materials are mixed first, and they are then added to the organic medium. In other embodiments, the Ag powder which is the major portion of the inorganics is slowly added to the organic medium. The viscosity is
25 typically in the range of 60 to 75 Pas. The viscosity can be adjusted, if needed, by the addition of solvents. Mixing methods that provide high shear are useful.

Electrode-Forming Process

30 The thick film paste composition can be deposited by screen-printing, plating, extrusion, inkjet, shaped or multiple printing, or ribbons.

In the electrode-forming process, the thick film paste composition is deposited, e.g., by screen printing, and dried. It is then heated at temperatures below 420°C to remove the organic medium and sinter the

inorganic materials, thereby forming the desired electrode. The heating can be carried out in air or an oxygen-containing atmosphere. This step is commonly referred to as "firing." The firing temperature profile is typically set so as to enable the burnout of organic binder materials from the dried thick film paste composition, as well as any other organic materials present. In one embodiment, the firing temperature is below 420°C. In another embodiment, the firing temperature does not exceed 405°C. The firing can be conducted in a belt furnace. Multiple temperature zones, for example 3 to 11 zones, can be used to control the desired thermal profile.

The electrodes formed using the thick film paste composition of the invention have resistivities in the range of 2-5 mOhm/sq/25 µm.

EXAMPLE

Bismuth-Based Glass Frit Preparation

A bismuth-based glass frit composition was prepared by mixing and blending Bi₂O₃, B₂O₃, ZnO, SiO₂, BaO and Al₂O₃ powders to result in a bismuth-based glass frit comprising 73.0 wt% Bi₂O₃, 9.5 wt% B₂O₃, 13.0 wt% ZnO, 1.0 wt% SiO₂, 3.0 wt% BaO and 0.5 wt% Al₂O₃. The blended powder batch materials were loaded to a platinum alloy crucible then inserted into a furnace and heated at 900°C in air or O₂ for one hour to melt the mixture. The liquid melt was quenched from 900°C by removing the platinum crucible from the furnace and pouring the melt through counter rotating a stainless steel rollers gapped to 0.010 -0.020". The resulting material was coarsely crushed in a stainless steel container. The crushed material was then ball-milled in an alumina-silicate ceramic ball mill with zirconia media and water until the D₅₀ was 0.5-0.7 microns. The ball-milled material was then separated from the milling balls, wet screened and dried by hot air oven. The dried powder was run through a 200 mesh screen to provide the bismuth-based glass frit used in the thick film paste preparations described below.

Thick Film Paste Composition Preparation

The thick film paste was prepared by mixing Ag, the bismuth-based glass frit powder as described above in Example 1 and the organic medium. The Ag used was a coated silver flake powder with a d_{50} of 0.4-0.8 μm . The proportions of ingredients used in this Example were 70.3 parts by weight Ag, 5.2 parts by weight bismuth-based glass frit and an organic medium with 14.5 parts by weight of ethyl cellulose resin dissolved in a beta terpineol solvent and 3 parts by weight beta terpineol for a total of 93 parts by weight.

The bismuth-based glass frit was added to the organic medium with continued stirring followed by the addition of the Ag. Since the silver was the major portion of the solids it was added slowly to insure better wetting. The paste was then passed through a three-roll mill at a 1 mil gap several times. The degree of dispersion was measured by fine of grind (FOG) to insure that the FOG was less than or equal to 20/10. The FOG was 11/5 and the viscosity was 65 Pas.

Test Electrode

The paste composition was screen printed onto a glass slide in a serpentine pattern. The paste was dried and then fired in air in a 11-zone belt furnace at temperatures not exceeding 405°C. The firing temperature profile extended over about 30 minutes. The sample was at temperatures above 400°C for 3.17 minutes. The temperature never exceeded 405°C. The fired sample had a thickness of 14.9 μm and the average value of resistivity measurements was 2.9331 mOhm/sq/25 μm .

Adhesion was measured by a cross hatch test based on ASTM D-3359-78. On a scale of 1 to 5 with 5 representing no material removal, i.e., excellent adhesion, the adhesion was rated at 5.

Claims

What is claimed is:

- 5
1. A thick film paste composition comprising:
thick film paste composition comprising:
 (a) 65-85 wt% Ag;
 (b) 1-8 wt% Pb-free bismuth-based glass frit; and
10 (c) organic medium;
wherein said Ag and said bismuth-based glass frit are dispersed in
said organic medium, wherein the wt% are based on the total
weight of said paste composition and wherein said paste
composition is fireable at temperatures below 420°C, said bismuth-
15 based glass frit comprising 65-78 wt% Bi₂O₃, 7-12 wt% B₂O₃, 11-15
wt% ZnO and 0.5-8 wt% SiO₂ based on the total weight of said
bismuth-based glass frit.
 - 20 2. The paste composition of claim 1 comprising 70-80 wt% Ag and 2-7
wt% bismuth-based glass frit, wherein said wt% are based on the
total weight of said paste composition.
 - 25 3. The paste composition of claim 1, said bismuth-based glass frit
further comprising one or more oxides and their amounts selected
from the group consisting of 0.1 to 5 wt% of CaO, 0.1 to 5 wt% of
BaO, 0.1 to 2 wt% of Al₂O₃, 0.1 to 2 wt% of Na₂O and 0.1 to 2 wt%
of Li₂O, based on the total weight of said bismuth-based glass frit.
 - 30 4. The paste composition of claim 1, said bismuth-based glass frit
further comprising 2 to 4 wt% BaO and 0.1 to 2 wt% Al₂O₃, based
on the total weight of said bismuth-based glass frit.
 - 35 5. A device comprising an electrode formed from the paste
composition of any of claims 1-4, wherein said paste composition
has been fired at temperatures below 420°C to remove the organic
medium and form said electrode.

6. The device of claim 5, wherein said device is an electrochromic device.
- 5 7. The device of claim 5, wherein said paste composition has been fired at temperatures not exceeding 405°C to remove the organic medium and form said electrode.
8. The device of claim 6, wherein said paste composition has been fired at temperatures not exceeding 405°C to remove the organic
10 medium and form said electrode.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/041067

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01B1/22 H01B1/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/189126 A1 (PRUNCHAK ROBERT [US]) 30 July 2009 (2009-07-30) paragraphs [0019], [0021], [0022]; claims 1-24 -----	1-8
A	EP 0 463 826 A1 (JOHNSON MATTHEY INC [US]) 2 January 1992 (1992-01-02) claims 1,7; table 2 -----	1-8
A	US 2009/188555 A1 (CASTILLO IMELDA [US] ET AL) 30 July 2009 (2009-07-30) the whole document -----	1-8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/041067

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009189126 A1	30-07-2009	CA 2712348 A1	06-08-2009
		CN 101932535 A	29-12-2010
		EP 2247547 A1	10-11-2010
		JP 2011510897 A	07-04-2011
		KR 20100125273 A	30-11-2010
		RU 2010135771 A	10-03-2012
		US 2009189126 A1	30-07-2009
		US 2010244205 A1	30-09-2010
		WO 2009097264 A1	06-08-2009

EP 0463826 A1	02-01-1992	CN 1060280 A	15-04-1992
		EP 0463826 A1	02-01-1992
		JP 4270140 A	25-09-1992

US 2009188555 A1	30-07-2009	CA 2712552 A1	06-08-2009
		CN 101932662 A	29-12-2010
		EP 2238209 A1	13-10-2010
		EP 2275503 A2	19-01-2011
		JP 2011512426 A	21-04-2011
		KR 20100125274 A	30-11-2010
		RU 2010135770 A	10-03-2012
		US 2009188555 A1	30-07-2009
		WO 2009097266 A1	06-08-2009
