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SEALING GLASS PASTE

The present invention relates to a sealing glass paste and, in particular, to a sealing glass paste for
5 sealing the glass face plate to the glass funnel of a cathode ray tube (CRT). The sealing glass paste is applied to the edges of one part (either the face plate or the funnel) in the form of a ribbon. The remaining part is then placed in contact with the
10 paste and the assembly is heated to evaporate the solvent, burn out the binder and fuse the sealing glass.

Wet coating techniques for sealing glass or ceramic parts have been proposed and generally have
15 involved pastes having a sealing glass distributed throughout a binder/solvent system in which the solvent is an organic solvent. When the assembly has been formed it is then heated to evaporate the solvent, burn out the binder and fuse the glass. For
20 example, US-A-4014845 discloses a binder/solvent system which comprises a polymeric material which is a polymer containing oxygen and a monomer of an alkyl methacrylate and a solvent for the polymeric material.

For sealing glasses which contain PbO and which
25 melt and flow at low temperatures, preferably at below 475°C, such as PbO-B₂O₃-ZnO, the binder/solvent system which has been used commercially comprises nitro-cellulose/amyl acetate or similar esters. Nitro-cellulose has many disadvantages for use in such
30 systems, but it has been tolerated because it does not cause the dielectric breakdown of the sealing glasses caused by reduction of PbO to Pb.

US-A-4099979 discloses that the use of, for example, Pb₃O₄ in the sealing glasses containing PbO

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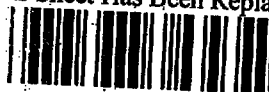
and the pastes made therewith, prevents the reduction of PbO to Pb. The specification discloses that small amounts of a hydroxypropyl cellulose binder can be added to the nitrocellulose/amyl acetate binder/
5 solvent system. This system still, however, involves the use of organic solvents.

WO-A-9500583 discloses a dry coating technique designed to overcome some of the difficulties inherent in applying a sealant to substrates via a binder/
10 solvent system. This technique relies on using an unsaturated polyester prepolymer which is subsequently postcured via a free radical crosslinking step. This dry coating technique is generally useful for bonding metals, ceramics and plastics. However it cannot be
15 used for TV glass sealing pastes because the polymer, by virtue of its chemical nature, would leave too much carbonaceous residue after burn out.

We have now developed a sealing glass paste which overcomes the problems of the prior art and which
20 comprises an aqueous binder system thus overcoming, in particular, the problems which are encountered with volatile organic solvent systems.

Accordingly, the present invention provides a sealing glass paste which comprises at least one
25 sealing glass frit powder and an aqueous binder which comprises an aqueous solution of at least one cellulosic material which does not contain nitrogen, the aqueous binder burning out or decomposing at a temperature of below 475°C to leave less than 2% by
30 weight of residues based on the total weight of the solids content of the binder.

Examples of cellulosic materials for use in the present invention are methyl cellulose, hydroxypropyl



cellulose, hydroxypropyl methylcellulose, or a mixture thereof.

Wetting agents may also be incorporated into the vehicle in an amount of up to about 5% by weight in order to improve the wetting of the frit glass powder after mixing. Suitable wetting agents include poly(ethylene glycol) alkyl ethers and silicone additives.

Dispersants may also be added to the vehicle formulation in order to improve the shelf life of the resultant glass frit paste. One type of dispersant is a surfactant, such as a polyphosphate, phosphate ester, metal silicate or metal carbonate which may be included in an amount of up to about 2% by weight. The surfactant adsorbs onto adjacent ceramic particles and inhibits coalescence via electronic stabilisation. Another class of dispersant is a water soluble polymeric dispersant such as polyoxyethylene, poly(vinyl alcohol), poly(acrylic acid) or poly(vinylpyrrolidone) which may be included in an amount of up to about 5% by weight.

The vehicle may also contain antifoam agents in an amount of up to about 1% by weight in order to minimise foaming during mixing and/or dispensing, which could potentially lead to bubble formation. Defoamers based on polyoxyethylene or silicones are appropriate additives.

The aqueous binder may additionally contain a biocide in an amount of up to 1% by weight, for example glutaraldehyde, or a thickening agent, for example Viscalex HV30 (Allied Colloids).

The sealing glass paste generally comprises from 65 to 95 percent by weight of the sealing glass frit powder and from 5 to 35 percent by weight of the

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aqueous vehicle, more preferably from 80 to 95 percent by weight of the sealing glass and from 20 to 5 percent by weight of the aqueous vehicle.

5 The sealing glass frit powder preferably has a particle size in the range of from 1 to 150 μ m more preferably 10 to 50 μ m. The aqueous vehicle of the present invention may be used to formulate sealing glass pastes with any suitable sealing glass, including those which contain PbO. Preferred sealing
10 glasses for use in the present invention typically contain lead oxide, silicon dioxide, boron oxide, zinc oxide and barium oxide. Additional glass forming oxides include zirconium oxide and manganese dioxide.

15 The aqueous vehicle which is used in the sealing glass pastes of the present invention generally comprises from 0.1 to 15% by weight, preferably from 0.5 to 2% by weight, more preferably from 1.0 to 1.5% by weight, of the cellulosic material such as methyl-cellulose, hydroxypropyl cellulose, hydroxypropyl-
20 methyl cellulose, or a mixture thereof dissolved in water. The cellulosic material used in the present invention will generally have a molecular weight in the range of from 500 to 2,000,000, preferably in the range of from 10,000 to 100,000. The aqueous vehicle
25 which is obtained by dissolving the cellulose derivatives in water preferably is a free flowing colourless liquid generally having a viscosity of from 10 to 4000 cPs, preferably from 25 to 500 cPs.

30 The aqueous binder burns out at a temperature of below 475° to leave less than 2% by weight of residues, preferably less than 1.5% by weight of organic residues, more preferably less than 1% by weight of residues as measured by thermogravimetric analysis.

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The sealing glass paste of the present invention is prepared by admixing the aqueous vehicle with the sealing glass frit powder for a sufficient period of time to ensure that a uniform frit paste is obtained.

5 The sealing glass paste of the present invention may be applied to the surfaces to be joined by any suitable means, for example by dispersion via a gravity feed or pressure feed device. Thus beads or a ribbon of the paste may be applied to one or both of
10 the surfaces to be joined. The surfaces which are to be joined are then formed into an assemblage which is heated to a temperature at which the sealing glass will soften and fuse and at which the cellulose
15 derivative binder will be burnt out. In the assembly of cathode ray tubes, the assemblage is subjected to the heating conditions of the Lehr cycle.

 The present invention also includes within its scope an assembly which comprises at least two portions which are joined by a sealing glass paste as
20 detailed above, and, in particular where the assembly is a cathode ray tube.

 The aqueous binder system which is used in the present invention possesses the following advantages:

- 25 i) the carbonaceous residue levels are very low, less than 2% by weight, after the frit is subjected to the appropriate heating cycle;
- ii) contamination from water which is known to give rise to rheological instability in the
30 case of conventional nitrocellulose/ester systems is not an issue with the present invention;

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iii) the sealing glass pastes do not contain volatile organic solvents and thus there are no problems with VOC emissions.

The present invention will be further described with reference to the following non-limiting Examples.
In the Examples the following definition is used:

Lehr Cycle

The Lehr cycle used in the following Examples was as follows: heat from room temperature to 450°C at 10°C/min, hold at 450°C for 45 minutes and then cool to room temperature.

In the Examples the residue content of the various binders used was measured by thermogravimetric analysis (Perkin Elmer TGA7) run in air using a program simulating the Lehr cycle. The following results were obtained.

		<u>% residues</u>
20	Methylcellulose(Benecel M042 Hercules)	<0.1%
	Methylcellulose(Methocel A4C Dow Chemical Company)	<0.1%
	Hydroxypropylcellulose (Klucel G Hercules)	.0.5%
25	Hydroxypropylmethycellulose (Aldrich)	1.0%
	Hydroxypropylmethycellulose (Methocel E4M Dow Chemical Company)	0.4%
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EXAMPLE 1

Methyl cellulose (1.25g) (Benecel M042 Hercules) was dissolved in water (98.75g). 1.5g of this solution was added to 12.5g of TV sealing glass having a major proportion of particles of particle size in the range of from 10 to 100 μ m. (Corning glass 7590 frit powder). Glutaraldehyde (50 mg) was then added. The frit paste was then thoroughly mixed by hand for a period of seven minutes. This frit paste was dispensed onto a glass substrate as a bead and this was fired under the Lehr cycle conditions.

A grey/green coloured frit was obtained after firing.

EXAMPLE 2

Hydroxypropylmethyl cellulose (0.75g) (Aldrich), and hydroxypropyl cellulose (0.5g) (Klucel G Hercules) were dissolved in deionised water (98.75g). 1.5g of this solution was added to and mixed by hand with 12.5g of a TV sealing glass (Corning glass 7590 frit powder) for a period of six minutes. This frit paste was dispensed onto a glass substrate as a bead and this was fired under the Lehr cycle conditions.

A grey coloured frit was obtained after firing.

EXAMPLE 3

Hydroxypropylmethyl cellulose (0.75g) (Aldrich), hydroxypropyl cellulose (0.25g) (Klucel G Hercules) and methylcellulose (0.25g) (Benecel M042 Hercules) were dissolved in deionised water (98.75g). 1.5g of this solution was added to and mixed by hand with 12.5g of

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a TV sealing glass (Corning glass 7590 frit powder) for a period of six minutes. This frit paste was dispensed onto a glass substrate as a bead and this was fired under the Lehr cycle conditions.

5 A grey coloured frit was obtained after firing.

EXAMPLE 4

10 An aqueous frit vehicle was prepared by dissolving methylcellulose (0.65g) (Methocel A4C Dow Chemical Company), hydroxypropylmethylcellulose (0.65g) (Methocel E4M Dow Chemical Company) and glutaraldehyde (0.1g) in water (98.6g). TV sealing glass (Techneglas CV685, 17.77g) was mixed with the aqueous frit vehicle
15 (2.23g) until the paste was homogeneous. A bead of the paste approximately 2.5cm long and 2cm wide was dispensed onto a square glass panel (7.5cm wide, thickness 2mm). This paste was dried in an oven at
20 80°C for 10 minutes in order to volatilise the water.

Finally, the dried bead was fired under the Lehr cycle conditions. After cooling, a fused frit bead was obtained which was green/grey in appearance.

EXAMPLE 5

25 An aqueous frit vehicle was prepared by dissolving methylcellulose (0.65g) (Methocel A4C Dow Chemical Company), hydroxypropylmethyl cellulose (0.65g) (Methocel E4M Dow Chemical Company) and glutaraldehyde
30 (0.1g) in water (98.6g). TV sealing glass (Techneglas CV685, 17.77g) was mixed with the aqueous frit vehicle (2.23g) until the paste was homogeneous. A bead of the paste was dispensed onto the edge of a square pre-cut piece of TV screen (7.5cm wide, thickness 1.5cm).

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5 A second piece of TV screen was then clamped against the paste under slight pressure, thereby forming a composite arrangement. This assembly was dried in an oven at 80°C for 10 minutes in order to volatilise the water.

10 Finally, the dried assembly was heated under the Lehr cycle conditions. After cooling, the assembly was found to be sealed, with the frit seal being green/grey in appearance.

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REPLACED**CLAIMS:**

1. A sealing glass paste which comprises at least one sealing glass frit powder and an aqueous binder
5 which comprises an aqueous solution of at least one cellulosic material which does not contain nitrogen, the aqueous binder burning out at a temperature of below 475°C to leave less than 2% by weight of
10 residues based on the total weight of the solids content of the binder.
2. A sealing glass paste as claimed in claim 1 wherein the aqueous binder comprises an aqueous
15 solution of methyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, or a mixture thereof.
3. A sealing glass paste as claimed in claim 1 or claim 2 which comprises 65 to 95 percent by weight of
20 the sealing glass frit powder and 5 to 35 percent by weight of the aqueous vehicle.
4. A sealing glass paste as claimed in any one of the preceding claims which comprises up to 5% by
25 weight based on the total weight of the composition of a wetting agent.
5. A sealing glass paste as claimed in any one of the preceding claims which comprises up to 1% by
30 weight based on the total weight of the composition of a antifoam agent.
6. A sealing glass paste as claimed in any one of the preceding claims which comprises up to 2% by



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weight based on the total weight of the composition of a surfactant.

5 7. A sealing glass paste as claimed in any one of the preceding claims which comprises up to 2% by weight based on the total weight of the composition of a polymeric dispersant.

10 8. A sealing glass paste as claimed in any one of the preceding claims which comprises up to 1% by weight based on the total weight of the composition of a biocide.

15 9. A sealing glass paste as claimed in any one of the preceding claims wherein the sealing glass frit powder has a particle size in the range of from 10 to 50 μ m.

20 10. A sealing glass paste as claimed in any one of the preceding claims wherein the sealing glass contains PbO.

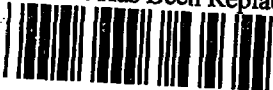
25 11. A sealing glass paste as claimed in any one of the preceding claims wherein the aqueous vehicle comprises from 0.5 to 2% by weight of the cellulosic material dissolved in water.

30 12. An assembly which comprises at least two portions which are joined together by a sealing glass paste as claimed in any one of the preceding claims.

13. An assembly as claimed in claim 12 wherein the portions which are joined together are formed from glass.



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14. An assembly as claimed in claim 13 which is a cathode ray tube.

5 15. A method for joining two surfaces together
which comprises applying to at least one surface a
sealing glass paste as claimed in any one of claims 1
to 11, forming an assembly of the surfaces to be
joined and subjecting the assembly so formed to
10 heating in order to soften and fuse the sealing glass
frit in the sealing glass paste.

15 16. A method as claimed in claim 15 wherein the
assembly is heated to a temperature of below about
475°C.

