

The present invention relates to pastes for the production of strip conductors, resistors, capacitors and solders from pulverulent materials present in liquid dispersion from the group comprising metals, metal compounds and/or metal alloys and/or boron and/or carbon, processes for their production and their use.

Pastes for the production of strip conductors, resistors, capacitors or solders based on organic solvents are sufficiently well known. Also known are such pastes for the production of optical coatings and for shielding from magnetic, electromagnetic or neutron radiation.

The coating of substrates with such pastes, which are dispersions of pulverulent materials in organic binders and/or solvents, has likewise been common practice for many years. Thus pastes are known from the patents US-A 4 024 629 and US-A 4 546 065, in which mixtures of cyclohexanol, ethanol and toluene are mentioned as typical dispersants and solvents. These mixtures of known polar, non-polar and aromatic solvents are ecologically unacceptable in various respects. They are odour-intensive, flammable, hazardous to effluents and in some cases toxic. When using these pastes the industrial safety measures and the devices to prevent emissions have to be of a correspondingly complicated nature.

In general it can be stated that all currently known pastes are produced on the basis of conventional organic solvents, optionally in combination with binders. If such pastes contain binders, the latter are used for film formation.

Water varnishes contain pigments in combination with one or more water-dilutable binders. Thus DE-A 4133487 describes the use of metal pigments in combination with water-dilutable binders based on polyesters, polyacrylates or



polyurethanes. The function of the binders is the formation of a coherent film which encloses the pigment to be applied and thereby fixes and protects it.

Similarly US 5171631 describes the incorporation of the pigment titanium dioxide used as a dyestuff into a system consisting of organic binders - in this case based on vinyl acetate/butyl acrylate copolymers with the use of alumina trihydrate as a non-ionic rheological additive, introduced into the solvent propylene glycol. In this case the applied layer also only functions in the presence of the binder or binders.

DE-A 4202705 describes the coating of substrates with noble metals consisting of a water-based system in which the metal component is present as a solution. Here as well a polymeric organic film or matrix former is required. The noble metal to be deposited is in this case precipitated from a solution by in situ reduction directly on the surface, wherein the preferred noble metal concentration in solution is 0.01 to 2 wt %, preferably 0.02 to 0.5 wt %. This patent therefore describes the deposition of a metal with the assistance of a binder from the solution, and not precipitation from a dispersion.

It was therefore the object of the invention to provide pastes which are in no way inferior to the known pastes as regards their technical suitability, but on the other hand do not possess the described disadvantages of the pastes of the prior art.

Pastes have now been found which meet this object. They are pastes for the production of strip conductors, resistors, capacitors or solders from pulverulent materials present in liquid dispersion from the group comprising metals, metal compounds and/or metal alloys and/or boron and/or carbon,



which are characterised in that the pulverulent materials are from one or more of the group comprising refractory metals, noble metals, transition metals, refractory metal oxides and oxide compounds, silicides and titanates and the liquid dispersions are based on water, contain water-dilutable non-ionic rheological additives in mixtures of 0.2 to 20 wt %, based on the solids content, and are free from binders and organic solvents.

The pastes according to the invention are free from organic solvents. They can be processed into well-functioning layers without the use of organic solvents and/or CFC and/or chlorinated hydrocarbon.

The pastes according to the invention are dilutable with water. All additive components which are required for adjusting the rheological properties, such as for example the viscosity of the pastes according to the invention, can either be removed completely during the production of the coatings during a heat treatment or remain as inert residues in the heat-treated layers. If necessary they can easily be removed by means of water during processing, e.g. during the cleaning of the processing equipment, and therefore do not require the use of organic solvents. In addition the pastes according to the invention are odour-neutral and not flammable. Ecological restrictions of the kind criticised in relation to the currently used pastes are not to be anticipated with the pastes according to the invention.

The pastes according to the invention are preferably mixtures consisting of the pulverulent materials and water-dilutable, rheologically active additives. Aqueous silicic acid dispersions can advantageously be involved here, preferred non-ionic rheological additives are also associative thickeners based on polyglycol ether or



polyurethane, particularly preferably those based on toluylene diisocyanates (TDI) and/or hexamethylene diisocyanates (HDI). Diphenylmethane diisocyanates (MDI) and/or isophorone diisocyanates (IPDI) are also preferred. If necessary further wetting agents and/or stabilizers can be contained in the pastes.

Typical dispersed pulverulent materials are metals, such as for example powders of the refractory metals niobium, tantalum, molybdenum, tungsten or of the transition metals such as for example iron, cobalt, nickel, chromium, copper or of the noble metals silver, gold, platinum, palladium, alloys - e.g. noble metal alloys such as silver/palladium -, oxides - such as for example the oxides of the refractory metals niobium, tantalum, molybdenum, tungsten or oxides with particular electrical properties such as for example zirconium oxide, indium-tin oxide, tantalates, niobates, titanates, rare earth oxides or oxides with magnetic properties, nitrides - such as for example titanium nitride or aluminium nitride or boron nitride, carbides and carbonitrides - such as for example tungsten carbide, tantalum carbide or tungsten titanium carbide, titanium carbintride, boron or borides, such as for example amorphous or crystalline elemental boron, aluminium boride, rare earth borides such as for example europium boride and/or gadolinium boride, silicides, such as for example molybdenum silicides or tungsten silicides in stoichiometric and non-stoichiometric form, chalcogenides such as for example zinc sulphide, molybdenum sulphide and/or tungsten sulphide and/or carbon in various modifications. The above-mentioned solids can be present individually or as any desired mixtures. The solid content of the pastes according to the invention is preferably 5 to 95 wt %, particularly preferably 50 to 90 wt %.

The range of the components present in the dispersion



should preferably be selected in such a manner that the solids of the pastes no longer contain any organic residual substances after a heat treatment to 550 °C.

The pastes according to the invention can be produced by dispersing the pulverulent materials in water and adjusting the rheological properties of the aqueous dispersions by means of the rheologically active additives. It may be advantageous at the same time to modify the rheological properties of the pastes additionally by means of wetting agents. Some conventional polyurethane thickeners already contain suitable wetting agents.

This invention also relates to the use of the pastes according to the invention. They are exceptionally suitable for coating inorganic substrates, such as for example glass, ceramics, glass ceramics, enamel and metals, and also those based on organic substances, such as for example plastics. The substrates are preferably coated by means of printing techniques, particularly preferably silk screen printing, offset printing and/or doctor-coating and/or pouring and/or immersion and/or spraying and/or electrostatic deposition processes. The required structuring of the layers can preferably be carried out by printing techniques or lithographically - also by means of UV lithography. The use of all conceivable printing techniques is possible. The pastes according to the invention are particularly suitable as metallization pastes.

The invention will be explained by examples in the following, without the latter being limiting in any way.



Examples

Example 1 (Molybdenum paste)

In order to produce a molybdenum paste, 70 wt % of molybdenum metal powder with an average particle size of approx. 2 μm (FSSS) were dispersed with 5 wt % of the associative thickener Borchigel^{*)} LW44 (HDI = hexamethylene diisocyanate, 44% emulsion in water), 8 wt % of Borchigen^{*)} DFN (polyglycol ether) and 3 wt % of the wetting agent Borchigen^{*)} ND (phosphoric acid ester amine salt) with water (to 100 wt %) with the aid of a cylinder mill. The paste produced in this way is exceptionally suitable for the production of strip conductors in ceramic multi-chip modules based on aluminium oxide and in particular also allows the plated-through holes between the individual layers to be filled in a printing step.

Example 2 (Tungsten paste)

A dispersion of 75 wt % of tungsten metal powder with FSSS = 1.4 μm and 12.5 wt % of the associative thickener Borchigel^{*)} DP40 (TDI = toluylene diisocyanate, 44% emulsion in water) was prepared with water (to 100 wt %) as a metallization paste.

Example 3 (Silicide paste)

As per example 1 a dispersion of 60 wt % of molybdenum disilicide with an average particle size of 10 μm (FSSS) and 11 wt % of the PU additive Borchigen^{*)} DFN in water (balance to 100%) was produced. The rheological properties of the paste were also adjusted by the addition of 5 wt % silicic acid dispersion (30% dispersion in water). The paste produced in this way is exceptionally suitable for the application of heating conductor layers to ceramic

*) Borchigel and Borchigen are registered trade marks of the Gebr. Borchers AG company in Goslar.



substrates, such as for example silicon nitride.

Example 4 (Oxide paste)

As per the previous examples a dispersion of 65 wt % niobium oxide with an average particle size of 2 μm (FSSS) and 5 wt % Borchigel^{*)} LW44 (HDI) together with 11 wt % Borchigen^{*)} ND in water was prepared as a paste for the production of a dielectric coating.

Example 5 (Alloy paste)

75 wt % of a powdered nickel/chromium/boron alloy with an average particle size of 15 μm and 8 wt % Borchigen^{*)} DFN together with 3 wt % Borchigen^{*)} ND were dispersed in water with the aid of a cylinder mill. A usable metallization paste was obtained.

Example 6 (Metal paste)

81.6 wt % of a silver powder with an average particle size of 0.3 - 5 μm according to FSSS and 7.4 wt % Borchigen^{*)} DFN were dispersed in water under an argon atmosphere with the aid of a dissolver. A paste was obtained which is exceptionally suitable for the application of conductive layers, such as for example the edge metallization of ceramic capacitors or for the application of resistor runs to glass.

Example 7 (Metal paste)

72.3% of nickel powder with an average particle size of < 3 μm according to FSSS and a spherical particle shape were dispersed with 8.9 wt % of Borchigen^{*)} DFN in water under an argon atmosphere using a dissolver. The nickel paste produced in this way is exceptionally suitable for the



production of conductive layers, such as for example the inner conductor tracks of ceramic capacitors.

Example 8 (Metal paste)

90.6 wt % of tantalum powder of capacitor quality was dispersed with 0.3 wt % Borchigen*) DFN and Borchigen*) ND respectively in water using a kneading device. The paste produced in this way is exceptionally suitable for the production of anodes for electrolytic capacitors.

The pastes mentioned in the examples were applied by means of silk screen printing to suitable substrates and dried at temperatures up to 550°C. Oxide-containing pastes were dried by exposure to air. Metal-containing pastes were dried under a protective gas or in vacuo. The organic additives contained in the pastes were completely removed in all cases. Additional cleaning steps were not necessary. The temperature was then increased, so that the solid sintered until it had attained the required properties.

Example 9

48 wt % of an indium tin oxide powder with an average particle size of < 800 nm and 8 wt % of Borchigen*) DFN were dissolved in water with the aid of a dissolver. A paste was obtained which is excellently suitable for the application of conductive transparent structures to glass.

Example 10

32 wt % of a niobium oxide with an average particle size of



0.3 to 0.6 μm and 3 wt % of Borchigel*) LW 44 (HDI) and 8 wt % of Borchigen*) ND were dispersed in water using a bead mill. The paste thus produced is suitable for the production of coatings for increasing the refractive index on glass.

Example 11

50 wt % of a silicon dioxide with an average particle size of 50 ... 100 nm and 4 wt % of Borchigel*) LW 44 (HDI) and 8.5 wt % of Borchigen*) ND were dispersed in water. The paste thus produced is suitable for the production of coatings for reducing reflection on glass.



Claims

1. Pastes for the production of strip conductors, resistors, capacitors or solders from pulverulent materials present in liquid dispersion from the group comprising metals, metal compounds and/or metal alloys and/or boron and/or carbon, characterised in that the pulverulent materials are one or more from the group comprising refractory metals, noble metals, transition metals, refractory metal oxides, oxide compounds silicides and titanates and the liquid dispersions involved are based on water, contain water-dilutable non-ionic rheological additives in mixtures of 0.2 to 20 wt %, based on the solids content, and are free from binders and organic solvents.
2. Pastes according to claim 1, characterised in that the quantity of the additives is 0.5 to 15 wt %.
3. Pastes according to one of claims 1 or 2, characterised in that the non-ionic rheological additives are associative thickeners based on polyglycol ether.
4. Pastes according to one of claims 1 or 2, characterised in that the non-ionic rheological additives are associative thickeners based on polyurethane.
5. Pastes according to claim 4, characterised in that the associative thickeners are based on toluylene diisocyanates (TDI) and/or hexamethylene diisocyanates (HDI).
6. Pastes according to claim 1, characterised in that the non-ionic rheological additives are aqueous silicic



acid dispersions and are present in an amount of 0.1 to 1 wt %, calculated as SiO_2 and based on the solids content.

7. Pastes according to one or more of claims 1 to 6, characterised in that they have a content of the pulverulent materials of 5 to 95 wt %.
8. Pastes according to one or more of claims 1 to 7, characterised in that they have a solids content of the pulverulent materials of 50 to 90 wt %.
9. Pastes according to one or more of claims 1 to 8, characterised in that their solids no longer contain any organic residual substances after a heat treatment at 550°C.
10. Pastes according to one or more of claims 1 to 9, characterised in that the pastes are metallization pastes, wherein the pulverulent materials are refractory metals from the group comprising niobium, tantalum, molybdenum, tungsten, rhenium, noble metals from the group comprising gold, silver, platinum, palladium and/or transition metals from the group comprising iron, chromium, cobalt, nickel and titanium.
11. Pastes according to one or more of claims 1 to 9, characterised in that the pulverulent materials belong to the group comprising refractory metal oxides, niobates and/or tantalates and/or titanates.
12. Pastes according to one or more of claims 1 to 9, characterised in that the silicides are preferably molybdenum silicide and/or tungsten silicide of varying stoichiometries.



13. Process for producing the pastes according to one or more of claims 1 to 12, characterised in that the pulverulent materials are dispersed in water and are mixed with the associative thickeners.
14. Use of the pastes according to one or more of claims 1 to 12 for coating substrates by printing techniques, preferably screen printing, offset printing and/or doctor-coating and/or pouring and/or immersion and/or spraying and/or electrostatic deposition methods.
15. Use of the pastes according to one or more of claims 1 to 12 for layers which are structured by means of printing techniques or lithography.

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