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The title of the invention is:

Flakes and their use for decorating glass, porcelain and
ceramic items whose walls are vertical

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Flakes and their use for decorating glass, porcelain and ceramic items whose walls are vertical

Description

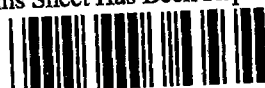
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The invention relates to flakes intended for decorating glass, porcelain and ceramic items and a decorating process making use of these flakes. This decorating process enables both the decoration of items with vertical walls and the
10 production of decorative effects which have hitherto been unobtainable with ceramic articles.

In the textile and paper industry, flakes of various materials are fixed onto the support to be decorated,
15 flakes being understood to be essentially fine particles in the form of platelets of various sizes and shapes; in the case of paper, for example, they are fixed in place by gluing or by covering the paper bearing the flakes with an organic binder forming a film.

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The decorating process for glass, porcelain and ceramic items using "pelletised" granules or glass wafers applied to the surface to be decorated and then fixing by firing is, of course, already known, the decorative effect sought,
25 material effects or appearances resembling natural rocks (for example, porphyry or marble), however, often proving inadequate or somewhat variable. Another disadvantage of this decorating process using pelletised grains or coloured wafers is that protuberances of up to 2 cm are produced and
30 so it is not suitable for vertical surfaces. Only surfaces which are flat and horizontal during the decorating procedure and during firing are suitable, essentially restricting use of the procedure to the tiling field. The present invention thus relates to flakes intended for
35 decoration which, after application to supports made of glass, porcelain or ceramic material and after firing, improve and simplify the decorating process and result in a



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more varied decorative effect on all types of support, including supports made of glass, porcelain or ceramic material, glazed or not, whose shape includes vertical walls.

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This object is achieved by flakes for decorating glass, porcelain and ceramic items, characterised in that they are essentially composed of an organic binder system and a vitrifiable inorganic substance which constitutes the decorative element.

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Use of the flakes according to the invention for decorating in the field of ceramics and glass enables the production of decorative effects which have hitherto been unobtainable with ceramic articles. In addition to tiling, it enables the decoration of items with a shape including vertical walls and thus relates to a very extended area of ceramics, for example glass, porcelain or ceramic pottery, crockery, artistic ceramics, lighting fitments, gravestones, sanitary ware, enamelled items, enamelled jewellery.

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The flakes can be obtained from a film or from sheets based on the claimed formulation which are either shredded to produce irregular shapes or are cut up to produce regular or geometric shapes. The sheets and therefore the flakes may have a thickness of 25 to 1000 x 10⁻⁶ m, preferably 25 to 500 x 10⁻⁶ m. The size of the flakes is then adjusted to 0.1 mm to 30 mm or more. In use, flakes with different sizes and different colours may be mixed, which gives an almost indefinite number of combinations. Flakes applied to the surface to be decorated, after firing, may be opaque or transparent, colourless or coloured, with a matt or gloss finish. Moreover, the decorated items may exhibit speckled, metallised, iridescent or azure effects. Moreover, the surface decorated with flakes may have a raised design.

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The two main components in the flakes according to the invention are (i) an organic binder system which burns away completely when the item decorated with flakes is fired and which vanishes without causing defects in the decoration and (ii) an inorganic material which remains in place after firing and which comprises the actual decorative element. The flakes may also contain, and this is covered by the term "essentially", processing additives and/or modifiers for adjusting the characteristics of the flake material in generally small amounts, these amounts usually being less than 20 wt.% in total, preferably less than 10 wt.%. The flakes should be very durable prior to firing and should also have a certain degree of elasticity in order to avoid fragmentation during transport and handling operations.

15

Some processing additives which may be mentioned are : drying and polymerisation accelerators for the binder such as metal compounds (for example conaphthenates) for the polymerisation of alkyd resins and photoinitiators for binder systems for UV polymerisation. Other additives may have an effect on the rheological properties of the paste from which a film or sheets (platelets) for producing the flakes is/are made in the first instance : included in this group are solvents such as for example glycols, glycol ethers, esters, terpene alcohols and aromatic hydrocarbons, thixotropic agents, agents for increasing the viscosity such as for example polyalkylene glycols, derivatives of cellulose and starch, polyvinylalcohol and polyvinylpyrrolidone, as well as wetting agents. Among the modifiers used, plasticisers must be mentioned in particular; as a general rule, classical plasticisers known to experts for their effect on the binder systems concerned may be used, in particular phthalates, dicarboxylic acids with 4 to 12 carbon atoms and fatty acids, also phosphates, polyethylene glycols and polypropylene glycols and their monoethers.

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The organic binder system must have sufficient film-forming ability to ensure, even in the presence of a large amount of inorganic material acting as decoration, the formation of a film or of sheets. The polymerised system binding the flakes is made up of one or more high molecular weight substances, these being polymerisation products, polycondensates or polyaddition products and possibly being partially cross-linked. Polymers and copolymers based on acrylic polyesters and polymethacrylates are preferably used, in particular polymers and copolymers based on butyl methacrylate, polyvinylacetate and vinylpolybutyral. In lattice-forming systems which consist of classical UV polymerisation binders, the cross-linking agents may be multifunctional vinylic compounds such as di-, tri- or tetraacrylates or methacrylates, for example mono-, di- or triethyleneglycol (meth)acrylate, hexamethylene di(meth)acrylate or trimethylolpropane tri(meth)acrylate.

The binder system may be composed, in addition to the polymers/copolymers mentioned above (polymeric or copolymeric resins), or even as an alternative to these products, other film-forming resins such as polyester or polyurethane resins or even urethane-modified acrylic or methacrylic resins.

The vitrifiable products intended for creating the decoration are various materials which may be used individually or in combination. The following should be mentioned in particular: glass frits or glazes which may be transparent, opaque, coloured or colourless and may be fired at a firing temperature between 500°C (when used for glass) and 1450°C (when used for porcelain); white or coloured inorganic pigments such as those based on metal oxides and sulphides, mixed oxide systems, silicates, phosphates, pearlised pigments (Iriodine®) based on mica, pigments with an interstitial structure (such as for example $\text{ZrSiO}_4(\text{V})$ and $\text{ZrSiO}_4(\text{Pr})$) and inclusion pigments

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- (such as for example $\text{Cd}(\text{S}, \text{Se})$ in ZrSiO_4); opacifiers such as for example ZrO_2 , ZrSiO_4 , SiO_2 , Al silicate; vitrifiable colours, decorative colours on and under glaze for decorating porcelain; a coloured clay or any other ceramic material. The material used to form the decoration preferably contains a vitrifiable material which can be fused under certain firing conditions, in particular one or more glass frits or a ceramic glaze. It is strongly recommended that the material making up the decoration is essentially composed of a mixture of white pigment and coloured pigment and/or metal oxides and a product which can be fused at a firing temperature between 500 and 1450°C.
- 15 The thickness of the flakes is preferably between 25 and 1000 x 10^{-6} m, in particular between 25 and 500 x 10^{-6} m; the flakes are essentially composed of 10 to 40 wt.% of an organic binder system and 50 to 90 wt.%, preferably 60 to 90 wt.% of an inorganic material acting as the decoration.
- 20 Additives, as mentioned above, may be present in an amount not exceeding in total about 20 wt.%, preferably 10 wt.%.

The process for manufacturing the flakes is simple. It consists of homogeneously mixing a liquid or pasty binder or a binder dissolved or emulsified in a solvent system, the binder being based on polymeric or copolymeric resins and/or polycondensation resins and/or polyaddition resins or precursors of the binder systems, such as preferably prepolymers and/or polymerisable monomers with cross-linkable compounds, with a vitrifiable inorganic substance intended to form the decoration and, if required, with additives such as plasticisers, drying accelerators, photoinitiators, solvents and viscosity regulators, converting this mixture into a film or sheets (wafers) then, after polymerisation, into flakes of the desired shape, this operation preferably being performed by crushing, cutting or shredding.

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To make the flakes, binder systems such as those described above are used in the liquid or pasty state, that is to say they are not yet polymerised, nor even cross-linked.

- 5 The binder system or precursors of these, the inorganic materials used to produce the decoration and, if required, additives such as aqueous or non-aqueous solvents and plasticisers, are mixed and homogenised in classical apparatus : blenders for intense mixing, tricylindrical
10 roller mills or other equipment. The paste resulting from the mixing procedure is converted, using classical methods such as casting, extrusion, calendering, into sheets or platelets and then polymerised. Polymerisation of the sheets or wafers may be performed by a conventional drying
15 procedure during which the greater proportion of any solvents present evaporates off, or by a cross-linking reaction between reactive groups in a prepolymer based on a polymer or a copolymer, a thermoplastic polyester or a polyurethane and appropriate cross-linking compounds, or by
20 UV polymerisation of combinations of vinylic monomers and/or oligomers in the presence of vinylic multi-functional compounds.

- The binder systems preferably used for making flakes are
25 printing media known to a person skilled in the art and generally commercially available. Media of this type contain, in a dissolved or emulsified form, a polymeric binder such as a polyacrylate, a polymethacrylate, a thermoplastic polyurethane, an acrylate/methacrylate
30 copolymer, a styrene/acrylate copolymer or a styrene/methacrylate copolymer or combinations of the groups mentioned. Among poly(meth)acrylates, the most important are poly-iso and poly-n-butyl methacrylate, polymethylmethacrylate and polymethyl, polyethyl and
35 polybutyl acrylate, individually or as a mixture. With regard to aqueous binder systems, reference is made to patent DE-C 42 19 743.



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Binder systems for UV polymerisation are also particularly suitable for manufacturing flakes. Their composition may be varied greatly; however, in this case also, polyacrylates and/or polymethacrylates or copolymers of these substances
5 are preferably used, as well as systems containing multifunctional acrylates or methacrylates. Medium U in USA-4,666,756 and EP-B 0 106 628 may be mentioned here as an example.

- 10 The flakes are used for decorating various supports made of glass and ceramics like earthenware, vitreous material, stoneware, porcelain. They may be applied, for example :
- to bisque ware and biscuit firing goods, or items glazed with non-fired or fired glaze,
 - 15 - during the course of pressing tiles from powder (double pressing),
 - by adding to paste or substance before shaping (powder, soft paste, casting slip),
 - by adding to the glaze before the glazing
20 operation,
 - by manual or mechanical dusting procedures (dusting machine),
 - by projection using a flocculating gun or by any other known method of decoration, for example a
25 silk screen process or fluidised bed.

The flakes generally adhere exceptionally well to the surfaces to be decorated, they do not fall off vertical walls during either application or firing. If required, the
30 items may first be covered with a uniform layer of adhesive (CMC or resin suspension, or any other plastic material which burns at low temperature without leaving a residue) permitting stronger adherence of the flakes to the item before firing. Items with flakes applied to the face to be
35 decorated are then fired at the requisite temperature (500 to 1450°C) to provide the decoration. Before firing, the items thus decorated with flakes may be covered with glaze,

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this latter process being preferred when the flakes do not contain sufficient flux to fix them to the surface during the firing procedure.

5 Example 1

Composition of red flakes for decorating glazed earthenware items, firing at 950°C (classical 12 hour firing cycle)

10	Transparent glaze (alkaline borosilicate)	43
	Red inclusion pigment (Zr, Si, Cd, S system)	43
	Binder : polyvinylacetate (no solvent)	14

The binder is polyvinylacetate (PVA). No solvent is used.

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Example 2

Composition of brown flakes for decorating glazed earthenware items, firing at 1050°C (12 hour firing cycle).

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	Transparent glaze (alkaline borosilicate)	33
	Ground silica (0 to 50 x 10 ⁻⁶ m)	12
	Brown inclusion pigment (Fe ; Cr ; Zn system)	25
	Ultraviolet medium	30

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(based on a copolymer of n-butyl methacrylate and methyl methacrylate, dipropyleneglycol diacrylate, photoinitiator, dibutyl phthalate and vinylpyrrolidone).

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CLAIMS

1. Flakes for decorating glass, porcelain and ceramic items, characterised in that they are essentially composed of an organic binder system and an inorganic material intended to form the decoration.
2. Flakes according to Claim 1, characterised in that the organic binder system is composed essentially of one or more polymers or copolymers from the group of polyacrylates, polymethacrylates, polyvinylacetates or vinylpolybutyrates, which may also be partially cross-linked by multifunctional vinylic compounds.
3. Flakes according to Claims 1 and 2, characterised in that the inorganic material comprising the decoration contains a substance which is fusible at the firing temperature and preferably is vitrifiable.
4. Flakes according to Claim 3, characterised in that the vitrifiable substance is present in the form of an opaque or transparent glass frit and is coloured or colourless.
5. Flakes according to Claim 3 or 4, characterised in that the inorganic substance comprising the decoration also contains one or more inorganic pigments and/or metal oxides, phosphates or silicates.
6. Flakes according to one of Claims 1 to 5, characterised in that their thickness is between 25 and 1000×10^{-6} m and that they contain essentially 10 to 40 wt.% of an organic binder, 50 to 90 wt.% of inorganic material intended for the decoration and 0 to 10 wt.% of additives.

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7. A process for manufacturing flakes for decorating glass, porcelain and ceramic items according to one of the preceding Claims, characterised in that a liquid or pasty organic binder or an organic binder dissolved or suspended in a solvent system, the binder being based on polymeric or copolymeric resins and/or polycondensation resins and/or polyaddition resins or precursors of the binder systems, is homogeneously mixed with a vitrifiable inorganic material intended to form the decoration and, if necessary, with additives such as plasticisers, drying accelerators, photoinitiators, solvents and viscosity regulators, that this mixture is converted into a film or into sheets (wafers) and that flakes of the desired shape are obtained therefrom after polymerisation.
8. A process according to Claim 7, characterised in that the inorganic material used to form the decoration is a mixture of at least one or more glass frits and one or more inorganic pigments and/or metal oxides, phosphates or silicates.
9. A process according to Claim 7 or 8, characterised in that the organic binder used is a system based on an acrylic and/or methacrylic resin and, if cross-linking is desired, a di- or trimethacrylate or a di- or triacrylate as cross-linking agent.
10. A process for decorating glass, porcelain and ceramic items by applying solid objects in the form of small particles on the surface to be decorated and by firing at a temperature between 500 and 1430°C, characterised in that the solid objects in the form of small particles used are flakes according to one of the preceding Claims.

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11. A process according to Claim 10, characterised in that
a solution of an adhesive agent which completely
evaporates during firing is first applied to the
surface to be decorated, and that the flakes are then
5 applied on top of this adhesive.

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Flakes and their use for decorating glass, porcelain and ceramic items whose walls are vertical

Abstract

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The invention relates to flakes which are suitable for decorating items made from glass, porcelain and ceramic materials with vertical walls.

- 10 The flakes are essentially composed of an organic binder system and a vitrifiable inorganic substance which forms the decoration; in general, 10 to 40 wt.% of binder, 50 to 90 wt.% of an inorganic substance based on a glass-forming product and/or pigments and/or metal oxides and 0 to 15 10 wt.% of additives.

Production of the flakes includes the production of a paste, the formation of a film or wafers, polymerisation and shredding.

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For the decorative effect, the flakes are applied to the item to be decorated and fired at temperatures between 500 and 1450°C.

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Flakes and their use for decorating glass, porcelain and ceramic items whose walls are vertical

Description

The invention relates to flakes intended for decorating glass, porcelain and ceramic items and a decorating process making use of these flakes. This decorating process enables both the decoration of items with vertical walls and the production of decorative effects which have hitherto been unobtainable with ceramic articles.

In the textile and paper industry, flakes of various materials are fixed onto the support to be decorated, flakes being understood to be essentially fine particles in the form of platelets of various sizes and shapes; in the case of paper, for example, they are fixed in place by gluing or by covering the paper bearing the flakes with an organic binder forming a film.

The decorating process for glass, porcelain and ceramic items using "pelletised" granules or glass wafers applied to the surface to be decorated and then fixing by firing is, of course, already known, the decorative effect sought, material effects or appearances resembling natural rocks (for example, porphyry or marble), however, often proving inadequate or somewhat variable. Another disadvantage of this decorating process using pelletised grains or coloured wafers is that protuberances of up to 2 cm are produced and so it is not suitable for vertical surfaces. Only surfaces which are flat and horizontal during the decorating procedure and during firing are suitable, essentially restricting use of the procedure to the tiling field. The present invention thus relates to flakes intended for decoration which, after application to supports made of glass, porcelain or ceramic material and after firing, improve and simplify the decorating process and result in a

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more varied decorative effect on all types of support, including supports made of glass, porcelain or ceramic material, glazed or not, whose shape includes vertical walls.

This object is achieved by flakes for decorating glass, porcelain and ceramic items, characterised in that they are essentially composed of an organic binder system and a vitrifiable inorganic substance which constitutes the decorative element.

Use of the flakes according to the invention for decorating in the field of ceramics and glass enables the production of decorative effects which have hitherto been unobtainable with ceramic articles. In addition to tiling, it enables the decoration of items with a shape including vertical walls and thus relates to a very extended area of ceramics, for example glass, porcelain or ceramic pottery, crockery, artistic ceramics, lighting fitments, gravestones, sanitary ware, enamelled items, enamelled jewellery.

The flakes can be obtained from a film or from sheets based on the claimed formulation which are either shredded to produce irregular shapes or are cut up to produce regular or geometric shapes. The sheets and therefore the flakes may have a thickness of 25 to 1000 x 10⁻⁶ m, preferably 25 to 500 x 10⁻⁶ m. The size of the flakes is then adjusted to 0.1 mm to 30 mm or more. In use, flakes with different sizes and different colours may be mixed, which gives an almost indefinite number of combinations. Flakes applied to the surface to be decorated, after firing, may be opaque or transparent, colourless or coloured, with a matt or gloss finish. Moreover, the decorated items may exhibit speckled, metallised, iridescent or azure effects. Moreover, the surface decorated with flakes may have a raised design.

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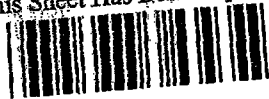
The two main components in the flakes according to the invention are (i) an organic binder system which burns away completely when the item decorated with flakes is fired and which vanishes without causing defects in the decoration and (ii) an inorganic material which remains in place after firing and which comprises the actual decorative element. The flakes may also contain, and this is covered by the term "essentially", processing additives and/or modifiers for adjusting the characteristics of the flake material in generally small amounts, these amounts usually being less than 20 wt.% in total, preferably less than 10 wt.%. The flakes should be very durable prior to firing and should also have a certain degree of elasticity in order to avoid fragmentation during transport and handling operations.

Some processing additives which may be mentioned are : drying and polymerisation accelerators for the binder such as metal compounds (for example conaphthenates) for the polymerisation of alkyd resins and photoinitiators for binder systems for UV polymerisation. Other additives may have an effect on the rheological properties of the paste from which a film or sheets (platelets) for producing the flakes is/are made in the first instance : included in this group are solvents such as for example glycols, glycol ethers, esters, terpene alcohols and aromatic hydrocarbons, thixotropic agents, agents for increasing the viscosity such as for example polyalkylene glycols, derivatives of cellulose and starch, polyvinylalcohol and polyvinylpyrrolidone, as well as wetting agents. Among the modifiers used, plasticisers must be mentioned in particular; as a general rule, classical plasticisers known to experts for their effect on the binder systems concerned may be used, in particular phthalates, dicarboxylic acids with 4 to 12 carbon atoms and fatty acids, also phosphates, polyethylene glycols and polypropylene glycols and their monoethers.

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The organic binder system must have sufficient film-forming ability to ensure, even in the presence of a large amount of inorganic material acting as decoration, the formation of a film or of sheets. The polymerised system binding the flakes is made up of one or more high molecular weight substances, these being polymerisation products, polycondensates or polyaddition products and possibly being partially cross-linked. Polymers and copolymers based on acrylic polyesters and polymethacrylates are preferably used, in particular polymers and copolymers based on butyl methacrylate, polyvinylacetate and vinylpolybutyral. In lattice-forming systems which consist of classical UV polymerisation binders, the cross-linking agents may be multifunctional vinylic compounds such as di-, tri- or tetraacrylates or methacrylates, for example mono-, di- or triethyleneglycol (meth)acrylate, hexamethylene di(meth)acrylate or trimethylolpropane tri(meth)acrylate.

The binder system may be composed, in addition to the polymers/copolymers mentioned above (polymeric or copolymeric resins), or even as an alternative to these products, other film-forming resins such as polyester or polyurethane resins or even urethane-modified acrylic or methacrylic resins.

The vitrifiable products intended for creating the decoration are various materials which may be used individually or in combination. The following should be mentioned in particular: glass frits or glazes which may be transparent, opaque, coloured or colourless and may be fired at a firing temperature between 500°C (when used for glass) and 1450°C (when used for porcelain); white or coloured inorganic pigments such as those based on metal oxides and sulphides, mixed oxide systems, silicates, phosphates, pearlised pigments (Iriodine®) based on mica, pigments with an interstitial structure (such as for example $\text{ZrSiO}_4(\text{V})$ and $\text{ZrSiO}_4(\text{Pr})$) and inclusion pigments

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(such as for example $\text{Cd}(\text{S}, \text{Se})$ in ZrSiO_4); opacifiers such as for example ZrO_2 , ZrSiO_4 , SiO_2 , Al silicate; vitrifiable colours, decorative colours on and under glaze for decorating porcelain; a coloured clay or any other ceramic material. The material used to form the decoration preferably contains a vitrifiable material which can be fused under certain firing conditions, in particular one or more glass frits or a ceramic glaze. It is strongly recommended that the material making up the decoration is essentially composed of a mixture of white pigment and coloured pigment and/or metal oxides and a product which can be fused at a firing temperature between 500 and 1450°C.

The thickness of the flakes is preferably between 25 and 1000×10^{-6} m, in particular between 25 and 500×10^{-6} m; the flakes are essentially composed of 10 to 40 wt.% of an organic binder system and 50 to 90 wt.%, preferably 60 to 90 wt.% of an inorganic material acting as the decoration. Additives, as mentioned above, may be present in an amount not exceeding in total about 20 wt.%, preferably 10 wt.%.

The process for manufacturing the flakes is simple. It consists of homogeneously mixing a liquid or pasty binder or a binder dissolved or emulsified in a solvent system, the binder being based on polymeric or copolymeric resins and/or polycondensation resins and/or polyaddition resins or precursors of the binder systems, such as preferably prepolymers and/or polymerisable monomers with cross-linkable compounds, with a vitrifiable inorganic substance intended to form the decoration and, if required, with additives such as plasticisers, drying accelerators, photoinitiators, solvents and viscosity regulators, converting this mixture into a film or sheets (wafers) then, after polymerisation, into flakes of the desired shape, this operation preferably being performed by crushing, cutting or shredding.

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To make the flakes, binder systems such as those described above are used in the liquid or pasty state, that is to say they are not yet polymerised, nor even cross-linked.

The binder system or precursors of these, the inorganic materials used to produce the decoration and, if required, additives such as aqueous or non-aqueous solvents and plasticisers, are mixed and homogenised in classical apparatus : blenders for intense mixing, tricylindrical roller mills or other equipment. The paste resulting from the mixing procedure is converted, using classical methods such as casting, extrusion, calendering, into sheets or platelets and then polymerised. Polymerisation of the sheets or wafers may be performed by a conventional drying procedure during which the greater proportion of any solvents present evaporates off, or by a cross-linking reaction between reactive groups in a prepolymer based on a polymer or a copolymer, a thermoplastic polyester or a polyurethane and appropriate cross-linking compounds, or by UV polymerisation of combinations of vinylic monomers and/or oligomers in the presence of vinylic multi-functional compounds.

The binder systems preferably used for making flakes are printing media known to a person skilled in the art and generally commercially available. Media of this type contain, in a dissolved or emulsified form, a polymeric binder such as a polyacrylate, a polymethacrylate, a thermoplastic polyurethane, an acrylate/methacrylate copolymer, a styrene/acrylate copolymer or a styrene/methacrylate copolymer or combinations of the groups mentioned. Among poly(meth)acrylates, the most important are poly-iso and poly-n-butyl methacrylate, polymethylmethacrylate and polymethyl, polyethyl and polybutyl acrylate, individually or as a mixture. With regard to aqueous binder systems, reference is made to patent DE-C 42 19 743.

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Binder systems for UV polymerisation are also particularly suitable for manufacturing flakes. Their composition may be varied greatly; however, in this case also, polyacrylates and/or polymethacrylates or copolymers of these substances are preferably used, as well as systems containing multifunctional acrylates or methacrylates. Medium U in USA-4,666,756 and EP-B 0 106 628 may be mentioned here as an example.

The flakes are used for decorating various supports made of glass and ceramics like earthenware, vitreous material, stoneware, porcelain. They may be applied, for example :

- to bisque ware and biscuit firing goods, or items glazed with non-fired or fired glaze,
- during the course of pressing tiles from powder (double pressing),
- by adding to paste or substance before shaping (powder, soft paste, casting slip),
- by adding to the glaze before the glazing operation,
- by manual or mechanical dusting procedures (dusting machine),
- by projection using a flocculating gun or by any other known method of decoration, for example a silk screen process or fluidised bed.

The flakes generally adhere exceptionally well to the surfaces to be decorated, they do not fall off vertical walls during either application or firing. If required, the items may first be covered with a uniform layer of adhesive (CMC or resin suspension, or any other plastic material which burns at low temperature without leaving a residue) permitting stronger adherence of the flakes to the item before firing. Items with flakes applied to the face to be decorated are then fired at the requisite temperature (500 to 1450°C) to provide the decoration. Before firing, the items thus decorated with flakes may be covered with glaze,

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this latter process being preferred when the flakes do not contain sufficient flux to fix them to the surface during the firing procedure.

Example 1

Composition of red flakes for decorating glazed earthenware items, firing at 950°C (classical 12 hour firing cycle)

Transparent glaze (alkaline borosilicate)	43
Red inclusion pigment (Zr, Si, Cd, S system)	43
Binder : polyvinylacetate (no solvent)	14

The binder is polyvinylacetate (PVA). No solvent is used.

Example 2

Composition of brown flakes for decorating glazed earthenware items, firing at 1050°C (12 hour firing cycle).

Transparent glaze (alkaline borosilicate)	33
Ground silica (0 to 50 x 10 ⁻⁶ m)	12
Brown inclusion pigment (Fe ; Cr ; Zn system)	25
Ultraviolet medium	30

(based on a copolymer of n-butyl methacrylate and methyl methacrylate, dipropylene glycol diacrylate, photoinitiator, dibutyl phthalate and vinylpyrrolidone).

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CLAIMS

1. Flakes for decorating glass, porcelain and ceramic items, characterised in that they are essentially composed of an organic binder system and an inorganic material intended to form the decoration.
2. Flakes according to Claim 1, characterised in that the organic binder system is composed essentially of one or more polymers or copolymers from the group of polyacrylates, polymethacrylates, polyvinylacetates or vinylpolybutyrates, which may also be partially cross-linked by multifunctional vinylic compounds.
3. Flakes according to Claims 1 and 2, characterised in that the inorganic material comprising the decoration contains a substance which is fusible at the firing temperature and preferably is vitrifiable.
4. Flakes according to Claim 3, characterised in that the vitrifiable substance is present in the form of an opaque or transparent glass frit and is coloured or colourless.
5. Flakes according to Claim 3 or 4, characterised in that the inorganic substance comprising the decoration also contains one or more inorganic pigments and/or metal oxides, phosphates or silicates.
6. Flakes according to one of Claims 1 to 5, characterised in that their thickness is between 25 and 1000×10^{-6} m and that they contain essentially 10 to 40 wt.% of an organic binder, 50 to 90 wt.% of inorganic material intended for the decoration and 0 to 10 wt.% of additives.

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7. A process for manufacturing flakes for decorating glass, porcelain and ceramic items according to one of the preceding Claims, characterised in that a liquid or pasty organic binder or an organic binder dissolved or suspended in a solvent system, the binder being based on polymeric or copolymeric resins and/or polycondensation resins and/or polyaddition resins or precursors of the binder systems, is homogeneously mixed with a vitrifiable inorganic material intended to form the decoration and, if necessary, with additives such as plasticisers, drying accelerators, photoinitiators, solvents and viscosity regulators, that this mixture is converted into a film or into sheets (wafers) and that flakes of the desired shape are obtained therefrom after polymerisation.
8. A process according to Claim 7, characterised in that the inorganic material used to form the decoration is a mixture of at least one or more glass frits and one or more inorganic pigments and/or metal oxides, phosphates or silicates.
9. A process according to Claim 7 or 8, characterised in that the organic binder used is a system based on an acrylic and/or methacrylic resin and, if cross-linking is desired, a di- or trimethacrylate or a di- or triacrylate as cross-linking agent.
10. A process for decorating glass, porcelain and ceramic items by applying solid objects in the form of small particles on the surface to be decorated and by firing at a temperature between 500 and 1430°C, characterised in that the solid objects in the form of small particles used are flakes according to one of the preceding Claims.

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11. A process according to Claim 10, characterised in that a solution of an adhesive agent which completely evaporates during firing is first applied to the surface to be decorated, and that the flakes are then applied on top of this adhesive.

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Flakes and their use for decorating glass, porcelain and ceramic items whose walls are vertical

Abstract

The invention relates to flakes which are suitable for decorating items made from glass, porcelain and ceramic materials with vertical walls.

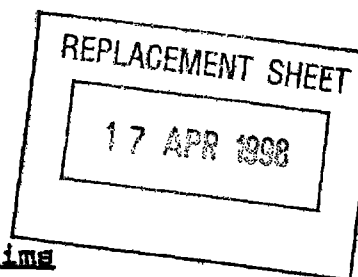
The flakes are essentially composed of an organic binder system and a vitrifiable inorganic substance which forms the decoration; in general, 10 to 40 wt.% of binder, 50 to 90 wt.% of an inorganic substance based on a glass-forming product and/or pigments and/or metal oxides and 0 to 10 wt.% of additives.

Production of the flakes includes the production of a paste, the formation of a film or wafers, polymerisation and shredding.

For the decorative effect, the flakes are applied to the item to be decorated and fired at temperatures between 500 and 1450°C.

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Claims

1. Paillettes for the decoration of glass, porcelain and ceramics,
characterised in that
they consist substantially of an organic binder system
and of a decorative vitrifiable inorganic substance
and are obtainable from a film or from sheets of the
above-mentioned composition.
2. Paillettes according to claim 1,
characterised in that
the organic binder system consists substantially of
one or more polymers or copolymers from among the
polyacrylates, polymethacrylates, polyvinyl acetates
or polyvinyl butyrates, which may also be to some
extent cross-linked by means of multifunctional vinyl
compounds.
3. Paillettes according to claim 2,
characterised in that
the vitrifiable material is in the form of an opaque
or transparent glass frit, which may be coloured or
colourless.
4. Paillettes according to claim 3,
characterised in that
the decorative inorganic substance contains in
addition one or more inorganic pigments and/or metal
oxides, metal phosphates or metal silicates.
5. Paillettes according to one of claims 1 to 4,
characterised in that
they have a thickness of from 25 to 1000 x 10⁻⁶ m and
contain substantially 10 to 40 wt.% of an organic
binder, 50 to 90 wt.% of an inorganic decorative
substance and 0 to 10 wt.% additives.

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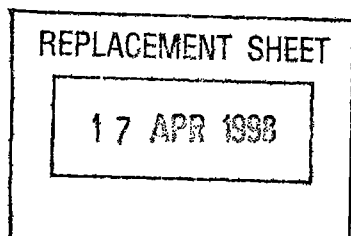
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6. Process for the production of paillettes for the decoration of glass, porcelain and ceramics according to one of the preceding claims, characterised in that an organic binder which is liquid or paste-like or dissolved or suspended in a solvent system and is based on polymer resins or copolymer resins and/or polycondensation resins and/or polyaddition resins, or intermediates of the binder systems, is or are homogeneously mixed with a decorative vitrifiable inorganic substance and, if necessary, with additives, such as plasticisers, drying accelerators, photoinitiators, solvents and agents for adjusting viscosity, this mixture is converted into a film or sheet (flakes) and from these paillettes of the required form are obtained after the polymerisation.
7. Process according to claim 6, characterised in that a mixture of at least one or more glass frits and one or more inorganic pigments and/or metal oxides, metal phosphates or metal silicates is used as the decorative inorganic substance.
8. Process according to claim 6 or 7, characterised in that a system based on acrylic resin and/or methacrylic resin is used as organic binder and, if cross-linking is required, a di- or trimethylacrylate or di- or triacrylate is used as cross-linking agent.
9. Process for decorating glass, porcelain and ceramics by application of solid substances in the form of small particles to the surface to be decorated and subsequent firing at a temperature of from 500°C up to 1430°C, characterised in that

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paillettes according to one of claims 1 to 5 are used as solid substances in the form of small particles.

10. Process according to claim 9, characterised in that first of all an adhesive solution, which is completely vaporised during the firing, is applied to the surface to be decorated, and then the paillettes are applied to the adhesive.

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Claims

1. Paillettes for the decoration of glass, porcelain and ceramics,
characterised in that
they consist substantially of an organic binder system
and of a decorative vitrifiable inorganic substance
and are obtainable from a film or from sheets of the
above-mentioned composition.
2. Paillettes according to claim 1,
characterised in that
the organic binder system consists substantially of
one or more polymers or copolymers from among the
polyacrylates, polymethacrylates, polyvinyl acetates
or polyvinyl butyrates, which may also be to some
extent cross-linked by means of multifunctional vinyl
compounds.
3. Paillettes according to claim 2,
characterised in that
the vitrifiable material is in the form of an opaque
or transparent glass frit, which may be coloured or
colourless.
4. Paillettes according to claim 3,
characterised in that
the decorative inorganic substance contains in
addition one or more inorganic pigments and/or metal
oxides, metal phosphates or metal silicates.
5. Paillettes according to one of claims 1 to 4,
characterised in that
they have a thickness of from 25 to 1000 x 10⁻⁶ m and
contain substantially 10 to 40 wt.% of an organic
binder, 50 to 90 wt.% of an inorganic decorative
substance and 0 to 10 wt.% additives.

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6. Process for the production of paillettes for the decoration of glass, porcelain and ceramics according to one of the preceding claims, characterised in that an organic binder which is liquid or paste-like or dissolved or suspended in a solvent system and is based on polymer resins or copolymer resins and/or polycondensation resins and/or polyaddition resins, or intermediates of the binder systems, is or are homogeneously mixed with a decorative vitrifiable inorganic substance and, if necessary, with additives, such as plasticisers, drying accelerators, photoinitiators, solvents and agents for adjusting viscosity, this mixture is converted into a film or sheet (flakes) and from these paillettes of the required form are obtained after the polymerisation.
7. Process according to claim 6, characterised in that a mixture of at least one or more glass frits and one or more inorganic pigments and/or metal oxides, metal phosphates or metal silicates is used as the decorative inorganic substance.
8. Process according to claim 6 or 7, characterised in that a system based on acrylic resin and/or methacrylic resin is used as organic binder and, if cross-linking is required, a di- or trimethylacrylate or di- or triacrylate is used as cross-linking agent.
9. Process for decorating glass, porcelain and ceramics by application of solid substances in the form of small particles to the surface to be decorated and subsequent firing at a temperature of from 500°C up to 1430°C, characterised in that

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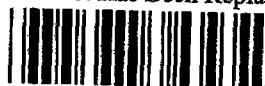
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paillettes according to one of claims 1 to 5 are used
as solid substances in the form of small particles.

10. Process according to claim 9,
characterised in that
first of all an adhesive solution, which is completely
vaporised during the firing, is applied to the surface
to be decorated, and then the paillettes are applied
to the adhesive.

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SPANGLES OR FLAKES AND THEIR USE FOR DECORATING GLASS, PORCELAIN
AND CERAMIC SURFACES WITH VERTICAL WALLS

DESCRIPTION

This patent relates to paillettes for the decoration of glass, porcelain and ceramics as well as a decoration
5 process in which these paillettes are used. This decoration process makes it possible to decorate objects having vertical walls and to achieve decorative effects hitherto unknown in ceramics.

10 In the textiles and paper industry, paillettes made of various materials are fixed to the supporting material to be decorated; by paillettes are meant mainly fine particles in the form of flakes of differing size and form. On paper, the paillettes are attached, for example, by means of a
15 film-forming organic binder pasted or applied as a coat to the paper to be provided with paillettes.

The process for decorating glass, porcelain and ceramics by means of "pelletised" granules or flakes of glass, which
20 are applied to a surface to be decorated and subsequently fired, is well-known; the decorative effect sought - textured effects or an appearance which is reminiscent of natural stones (for example, porphyry or marble) - here frequently proves to be insufficiently or only slightly
25 variable. Another disadvantage of this process of decoration with pelletised granules or coloured flakes is that they can attain an edge height of up to 2 cm and are therefore unsuitable for vertical surfaces. Only surfaces which are level and horizontal during the decoration
30 process and the firing are suitable, which in the main limits the application of this process to the sphere of tiles.

EP-A 0 565 941 discloses a catalytically active coating
35 composition. This contains an enamel frit, inert substances and flaky substrates having a coating of one or more metal oxides. The coated substrates are in particular flakes of mica coated with TiO_2 , Fe_2O_3 or other oxides and the composition is a pulverulent material.

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The present invention therefore relates to paillettes which, after application to the supporting material of glass, porcelain or ceramics and after the firing, improve and simplify the decoration process and results in a more varied decorative effect on any type of supporting material having vertical walls, including glass, porcelain or ceramics, glazed or unglazed.

This object is achieved by paillettes for the decoration of glass, porcelain and ceramics, which are characterised in that they consist substantially of an organic binder system and of a decorative vitrifiable inorganic substance and are obtainable from a film or sheets of the above-mentioned composition.

The use according to the invention of paillettes for decoration in the field of ceramics and glass makes it possible to achieve effects hitherto unknown in ceramics. In addition to the decoration of tiles, it renders possible the decoration of objects having vertical walls and therefore relates to a very extensive range of ceramics, for example, ornamental objects made of glass, porcelain or ceramics, crockery, ornamental ceramics, articles for lighting, grave furnishings, sanitary objects, enamel, decorative enamel.

The paillettes can be obtained both in irregular form and in regular or geometric form, by breaking or cutting up a film or lamellae having the claimed composition. The lamellae and hence also the paillettes may have a thickness of from 25 to 1000×10^{-6} m and preferably a thickness of from 25 to 500×10^{-6} m. The size of the paillettes is subsequently adjusted to 0.1 mm up to 30 mm or more. In the application, paillettes of varying size and of different colours can be mixed, so that the possible ways of combination are virtually unlimited. The paillettes applied to the surface to be decorated may be opaque or

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transparent, colourless or coloured, mat or shiny after the firing; in addition the decorated objects may exhibit speckled, metallic, iridescent or cloudy effects. The surface decorated with paillettes may moreover have a
5 contoured appearance.

The two main components of the paillettes according to the invention are (i) an organic binder system, which is completely burned during the firing of the objects
10 decorated with paillettes and which volatilises without causing defects in the decoration, and (ii) a vitrifiable inorganic substance, which is not burnt and which constitutes the actual decorative component. The paillettes can moreover, and this means "substantially", contain small
15 quantities of processing additives and/or modifying components, by means of which the material properties of the paillettes can be adjusted, these additives generally amounting in total to less than 20 wt.% and preferably less than 10 wt.%. Before the firing, the paillettes must
20 possess a good stability and at the same time a certain elasticity, so that they do not crumble during transport and processing.

Processing additives which may be mentioned include: drying
25 accelerators and polymerisation accelerators for the binder, such as metallic compounds (for example, Co naphthenates) for the polymerisation of alkyd resins and photoinitiators for binder systems for the UV polymerisation. Other additives can influence the
30 rheological properties of the paste from which a film or lamellae (flakes) are first of all made in order to produce the paillettes. This group includes solvents such as, for example, glycols, glycol ethers, esters, terpene alcohols and aromatic hydrocarbons, thixotropic agents, additives
35 for increasing the viscosity, such as, for example, polyalkylene glycols, cellulose compounds and starch flour compounds, polyvinyl alcohol and polyvinylpyrrolidone, and

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- wetting agents. Of the modifiers, the plasticisers in particular should be mentioned; the classical plasticisers, known to the person skilled in the art for their effect on the respective binder system, can generally be used, in particular phthalic esters, (C₄-C₁₂)-dicarboxylic esters and fatty acid esters, equally phosphate esters, polyethylene glycols and polypropylene glycols as well as their monoethers.
- 10 The organic binder system must have adequate film-forming properties in order to ensure that, even with a high proportion of decorative inorganic substance, a film or lamellae can form. The binder system of the polymerised paillettes consists of one or more substances of high
- 15 molecular weight, which can be polymerisation, polycondensation or polyaddition products and can be partly cross-linked. It is preferable to use polymers and copolymers based on polyacrylic esters and polymethacrylates, in particular polymers and copolymers
- 20 based on butyl methacrylate, polyvinyl acetate and polyvinyl butyral. In the network-forming systems, which consist of classical UV polymerisation binders, the cross-linking agents can be multifunctional vinyl compounds, such as di-, tri- or tetraacrylates or methacrylates, for
- 25 example, mono-, di- or triethylene glycol (meth)acrylate, hexamethylene di(meth)acrylate or trimethylolpropane tri(meth)acrylate.

- In addition to the above-mentioned polymers/copolymers
- 30 (polymer resins or copolymer resins) or instead of these products, the binder system may contain other film-forming resins, such as polyester resins or polyurethane resins or urethane-modified acrylic or methacrylic resins.
- 35 The vitrifiable products for the creation of the decorations consist of various substances, individually or in combination. Examples to be mentioned include glass

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frits or glazes, which are transparent, opaque, coloured or colourless and can be fired at temperatures of between 500°C (application for glass) and 1450°C (application for porcelain); white or coloured inorganic pigments based on metal oxides and metal sulphides, mixed oxide systems, silicates, phosphates, pearly lustre pigments (Iriodine®), such as those based on mica, pigments having an interstitial structure (such as, for example, ZrSiO_4 (V) and ZrSiO_4 (Pr)) and inclusion pigments (such as, for example, $\text{Cd}(\text{S}, \text{Se})$ in ZrSiO_4); opacifiers such as, for example, ZrO_2 , ZrSiO_4 , SiO_2 , aluminium silicate; enamel colours, overglaze colours and underglaze colours for decorating porcelain; engobes or any other ceramic material. The substance used for forming the decoration contains a vitrifiable and, under certain firing conditions, fusible material, in particular one or more glass frits or a ceramic glaze. It is particularly recommended that the decorative substance consist substantially of a mixture of white and coloured pigments and/or metal oxides and a product which is fusible at a firing temperature of 500°C to 1450°C.

The layer thickness of the paillettes is preferably between 25 and 1000×10^{-6} m, in particular between 25 and 500×10^{-6} m; the paillettes consist substantially to the extent of 10 to 40 wt.% of an organic binder system and to the extent of 50 to 90 wt.%, preferably 60 to 90 wt.%, of an inorganic decorative substance. Additives must not exceed 20 wt.% and preferably 10 wt.% in total, as mentioned above.

The process for producing the paillettes is simple. This process involves homogeneously mixing a binder which is liquid or paste-like or dissolved or emulsified in a solvent system and is based on polymer resins or copolymer resins and/or polycondensation resins and/or polyaddition resins, or binder intermediates such as preferably

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- prepolymers and/or polymerisable monomers and cross-linking compounds, together with a decorative vitrifiable inorganic substance and, if necessary, with additives, such as plasticisers, drying accelerators, photoinitiators,
- 5 solvents and agents for adjusting viscosity; forming a film or lamellae (flakes) from this mixture and, after the polymerisation, producing paillettes of the required form, preferably by breaking, cutting or punching out.
- 10 To produce the paillettes, binder systems in liquid or paste-like form of the type described above are used, that is, they are optionally not yet polymerised and not cross-linked either.
- 15 The binder system or its intermediates, the inorganic substances for forming the decoration and, if necessary, the additives, such as aqueous or water-insoluble solvents and plasticisers, are mixed and homogenised in conventional apparatus (for instance, in an intensive mixer or three-
- 20 cylinder roller mill). The paste resulting from the mixing is further processed with the aid of known techniques such as casting, extrusion, rolling, to form lamellae or flakes and is subsequently polymerised. The polymerisation of the lamellae or flakes can be effected by conventional drying,
- 25 while the bulk of the solvents which may be present vaporise, or by a cross-linking reaction between the reactive groups of a prepolymer based on a polymer or copolymer, on a thermoplastic polyester or on a polyurethane, and the appropriate cross-linking components,
- 30 or by UV polymerisation of monomeric and/or oligomeric vinyl compounds in the presence of multifunctional vinyl compounds.

The binder systems preferably used for the production of

35 the paillettes are printing media which are known to the person skilled in the art and are commercially available. Media of this type contain a polymeric binder in dissolved

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or emulsified form, such as polyacrylate, polymethacrylate, thermoplastic polyurethane, acrylate/methacrylate copolymer, styrene/acrylate or styrene/methacrylate copolymer or combinations of the aforementioned classes. Of the poly(meth)acrylates, examples to be mentioned in particular are poly-isobutyl methacrylate and poly-n-butyl methacrylate, polymethyl methacrylate as well as polymethyl, polybutyl and polybutyl acrylate, individually or in combination with one another. Regarding the aqueous binder systems, reference may be made to DE-C 42 19 743.

The binder systems for the UV polymerisation are also particularly suitable for the production of the paillettes. They can differ greatly in their composition; however, in this case as well one will use preferably polyacrylates and/or polymethacrylates or copolymers of these substances and in addition multifunctional acrylate or methacrylate - an example which may be given here is Medium U in US-A 4,666,756 and EP-B 0 106 628.

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The paillettes are used for decorating various supporting materials made of glass and ceramics, such as earthenware, glass composition, stoneware, porcelain. They can be applied, for example:

- 25 - on parts made of biscuit, baked material, material coated with unfired or fired glaze,
- during the pressing of tiles from powder (double-pressing process),
- as additive to the paste or composition before the shaping (powder, soft paste, casting slip),
- 30 - as additive to the glaze before the glazing process,
- for dusting by hand or mechanically (scattering machine),
- for application by means of flaking pistols or any
- 35 other known decorating technique such as, for example, screen printing or fluidised bed.

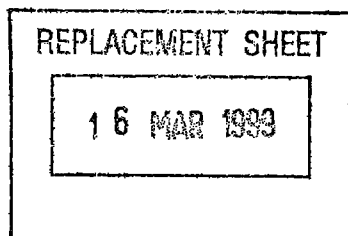
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The paillettes generally adhere very well to the surfaces being decorated; they do not fall off, either from vertical walls or during application or during firing. If desired, the parts can be coated beforehand with an adhesive layer
5 (CMC suspension or resin suspension or any other synthetic material which burns at low temperatures and leaves no residue), whereby a greater adhesion of the paillettes to the object is achieved before the firing. The parts having the paillettes applied to the decorated side are then fired
10 at the required temperature (500°C to 1450°C), in order to obtain the decoration. Before the firing, the parts decorated with the paillettes can be coated with a glaze; this process is preferably applied if the paillettes contain insufficient fluxing agent, by means of which they
15 adhere to the surface during the firing process.



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Example 1

Composition of red paillettes for decorating objects made of glazed earthenware - firing temperature 950°C

5 (traditional firing cycle 12 h)

Transparent glaze (alkali borosilicate) 43

Red inclusion pigment (system Zr, Si, Cd, S) 43

10 Binder: polyvinyl acetate (without solvent) 14

The binder is polyvinyl acetate (PVAc). No solvent is used.

15 Example 2

Composition of brown paillettes for decorating objects made of glazed earthenware - firing temperature 1050°C (firing cycle 12 h)

20

Transparent glaze (alkali borosilicate) 33

Silica, ground ($0 - 50 \times 10^{-6}$ m) 12

Brown inclusion pigment (system Fe, Cr, Zn) 25

25 UV medium 30

(based on an n-butyl methacrylate and methyl methacrylate copolymer, dipropylene glycol diacrylate, photoinitiator, dibutyl phthalate and vinyl pyrrolidone).

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Claims

1. Paillettes for the decoration of glass, porcelain and ceramics,
5 characterised in that they consist substantially of an organic binder system and of a decorative vitrifiable inorganic substance and are obtainable from a film or from sheets of the above-mentioned composition.
- 10 2. Paillettes according to claim 1, characterised in that the organic binder system consists substantially of one or more polymers or copolymers from among the
15 polyacrylates, polymethacrylates, polyvinyl acetates or polyvinyl butyrates, which may also be to some extent cross-linked by means of multifunctional vinyl compounds.
- 20 3. Paillettes according to claim 2, characterised in that the vitrifiable material is in the form of an opaque or transparent glass frit, which may be coloured or colourless.
- 25 4. Paillettes according to claim 3, characterised in that the decorative inorganic substance contains in addition one or more inorganic pigments and/or metal
30 oxides, metal phosphates or metal silicates.
5. Paillettes according to one of claims 1 to 4, characterised in that they have a thickness of from 25 to 1000 x 10⁻⁶ m and
35 contain substantially 10 to 40 wt.% of an organic binder, 50 to 90 wt.% of an inorganic decorative substance and 0 to 10 wt.% additives.



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6. Process for the production of paillettes for the decoration of glass, porcelain and ceramics according to one of the preceding claims, characterised in that
- 5 an organic binder which is liquid or paste-like or dissolved or suspended in a solvent system and is based on polymer resins or copolymer resins and/or polycondensation resins and/or polyaddition resins, or intermediates of the binder systems, is or are
- 10 homogeneously mixed with a decorative vitrifiable inorganic substance and, if necessary, with additives, such as plasticisers, drying accelerators, photoinitiators, solvents and agents for adjusting viscosity, this mixture is converted into a film or
- 15 lamellae (flakes) and from these paillettes of the required form are obtained after the polymerisation.
7. Process according to claim 6, characterised in that
- 20 a mixture of at least one or more glass frits and one or more inorganic pigments and/or metal oxides, metal phosphates or metal silicates is used as the decorative inorganic substance.
- 25 8. Process according to claim 6 or 7, characterised in that
- a system based on acrylic resin and/or methacrylic resin is used as organic binder and, if cross-linking is required, a di- or trimethylacrylate or di- or
- 30 triacrylate is used as cross-linking agent.
9. Process for decorating glass, porcelain and ceramics by application of solid substances in the form of small particles to the surface to be decorated and
- 35 subsequent firing at a temperature of from 500°C up to 1430°C, characterised in that



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paillettes according to one of claims 1 to 5 are used as solid substances in the form of small particles.

10. Process according to claim 9,
5 characterised in that
first of all an adhesive solution, which is completely vaporised during the firing, is applied to the surface to be decorated, and then the paillettes are applied to the adhesive.



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SPANGLES OR FLAKES AND THEIR USE FOR DECORATING GLASS, PORCELAIN
AND CERAMIC SURFACES WITH VERTICAL WALLS

Abstract

5

The invention relates to flakes which are suitable for decorating items made from glass, porcelain and ceramic materials with vertical walls.

- 10 The flakes are essentially composed of an organic binder system and a vitrifiable inorganic substance which forms the decoration; in general, 10 to 40 wt.% of binder, 50 to 90 wt.% of an inorganic substance based on a glass-forming product and/or pigments and/or metal oxides and 0 to 15 10 wt.% of additives.

Production of the flakes includes the production of a paste, the formation of a film or wafers, polymerisation and shredding.

20

For the decorative effect, the flakes are applied to the item to be decorated and fired at temperatures between 500 and 1450°C.

25