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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

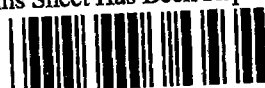
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The invention relates to flakes intended for decorating glass, porcelain and ceramic items and a decorating process making use of these flakes. This decorating process enables both the decoration of items with vertical walls and the
10 production of 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 1000×10^{-6} m, preferably 25 to 500×10^{-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.

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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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