

Description

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steps which reduce the volume/time yield and an energy-intensive sintering step are required. In addition, the non-uniformity of the pigments thus obtained is visible under a microscope.

5 There has been no shortage of attempts to improve the process described above. By precipitation of the gold purple in the presence of substances which form oxide hydrates, such as Al and Sn salts, is it possible to obtain more readily filterable co-precipitated of colloidal gold
10 and the oxide hydrates, in addition to which the color of the co-precipitates is more reproducible and resistant to ageing. However, the other steps involved in the production process correspond to steps (b), (c) and (d) mentioned above, cf. for example RO Patent 64442 B (Chemical Abstracts 98 (26): 22 07 40e), so that the overall cost of
15 the process is again considerable. Apart from this, the pigment is not uniform and the presence of the oxide can adversely affect the brilliance of the pigment and/or the properties of glazes, enamels, glass and decorative colors
20 containing such pigments.

 According to DD-PS 143 423, precipitation of the gold purple can also be carried out in the presence of inert material. The purple-colored moist deposit is then homogeneously mixed with a glass flux and, for color control,
25 with silver carbonate and the resulting mixture is wet-ground, sintered at 650 - 680°C and re-ground. The purple pigments obtained by this process are attended by the above-mentioned quality disadvantages.

 Purple-colored pearlescent pigments based on platelet-like particles coated with metal oxides, such as in particular TiO₂-coated mica, with an optically semipermeable layer of gold (cf. DE-PS 32 29 837, DE-OS 38 25 702) or a surface layer of tin oxide in which colloidal gold is incorporated (DE-OS 37 31 174) are commercially available.
35 In their case, the gold coating is always situated on a

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metal oxide layer which first has to be applied to the platelet-like substrate (besides mica, glass is also mentioned). In no case is a particulate glass directly surface-coated with colloidal gold. The presence of a metal oxide layer beneath a gold-containing coating is clearly regarded as necessary. However, application of a metal oxide layer is complicated because coating with gold has to be preceded by a calcination step to convert oxide hydrates into oxides.

In addition, the metal oxides can adversely affect the quality of the pigment and its performance properties.

Accordingly, the problem addressed by the present invention was to provide new purple pigments based on fine-particle glass, such as in particular glass frits, having a coating containing colloidal gold which would be distinguished by high brilliance and outstanding performance properties in regard to compatibility with the ceramic substrates to be decorated. The pigments would be readily adaptable to the particular substrates. In addition, the color of the new purple pigments would readily be controllable during their production. Another problem addressed by the present invention was to provide a process for the production of the new purple pigments which would be distinguished from processes for the production of known purple pigments by the fact that it could be carried out more easily, i.e. in fewer process steps, and would not involve a calcination step.

Applicants have found the purple pigments mentioned at the beginning which are characterized in that the coating essentially contains colloidal gold in a quantity of 0.05 to 5% by weight, based on the pigment, and - if desired - one or more color-modifying metals from the group consisting of Ag, Cu, Co, Ni, Sn, Ru, Rh, Pd, Os, Ir and Pt in a total quantity below that of the gold and is directly applied to the surface of glass frits of which the particle

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diameter (D_{50} value) is in the range from 0.5 to 50 μm .

In addition to the metals mentioned, the coating may contain additional substances emanating from the coating process, such as oxides for example, in small quantities of less than 20% by weight, based on the total content of metals. In a preferred embodiment, the coating consists solely of the colloidal gold and, if desired, the color-modifying metals. The color intensity of the pigments is determined by the quantity of gold. In most cases, quantities of 0.1 to 2.0% by weight and, more particularly, 0.1 to 1.0% by weight colloidal gold, based on the pigment, are sufficient. The color-modifying elements may have been deposited on the glass frit either together with the gold or in a separate step. The metals are essentially deposited on the glass frit in the form of a thin layer consisting of one or more atomic layers in such a form that the pigment particles are at least partly optically permeable.

Preferred purple pigments have a coating which consists solely of colloidal gold and silver. The color of silver-free purple pigments is tinged with violet while the color of silver-containing purple pigments is tinged more with red with increasing silver content. The silver content of these pigments is generally from 0 to 50% and preferably from 0 to 25% of the gold content.

Finely ground glass frits are used as support material for the purple pigments. Glass frits of different chemical composition can be obtained by fusing suitable glass raw materials, quenching the glass melt in water and grinding the granules or flakes obtained. In the case of pigments, the average particle diameter, the so-called D_{50} value, is generally between about 0.5 and 50 μm , although glass frits having a D_{50} value of 1 to 10 μm are preferably used. The D_{50} value may be determined by known granulometer analyses.

The composition of the frits has a crucial influence on their softening behavior, thermal expansion coefficient

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and specific color development which, in the ceramic industry, is understood to be the interaction between a pigment and a frit during firing. By selecting the glass frit from a broad commercially available range, it is possible to base the purple pigments according to the invention on a glass frit of which the properties correspond completely or at least partly to those of frits used in the decoration process in question and adapted to the substrate to be decorated. Defects in the ceramic decoration, such as flaking, flaws and opacity, are thus avoided.

The purple pigments according to the invention can be obtained by a single-stage and, in rare cases, two-stage coating process. The calcination and sintering process at temperatures above about 600°C required in the case of known purple pigments and the subsequent grinding process are unnecessary in the process according to the invention. The process according to the invention is characterized in that colloidal gold in a quantity of 0.05 to 5.0% by weight, based on the pigment, and - if desired - one or more color-modifying metals from the group consisting of Ag, Cu, Co, Ni, Sn, Ru, Rh, Pd, Os, Ir and Pt in a total quantity below that of the gold are deposited on the surface of an uncoated glass frit, of which the average particle diameter (D_{50} value) is in the range from 0.5 to 50 μm , by forming the metals to be deposited from water-soluble compounds of gold and, where present, the color-modifying metals in the presence of reducing agents in an aqueous suspension containing the glass frit, separating the pigment thus obtained from the aqueous phase and drying the pigment.

In cases where color-modifying metals are to be deposited in addition to the gold, this may be done either simultaneously or in succession. A suitable reducing agent may be used for the deposition of all metals, which is

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preferred in the case of silver-modified purple pigments, or alternatively two different reducing agents may optionally be used, one for precipitation of the gold and the other for precipitation of the color-modifying metal(s).

5 Suitable reducing agents for the deposition of colloidal gold and color-modifying metals essentially on the surface of the frit include reducing agents which are active in aqueous media, for example aldehydes, such as formaldehyde and acetaldehyde, tartaric acid, ascorbic
10 acid, reductones, reducing sugars, such as glucose, glycols, polyphenols, sulfites, dithionites, hypophosphites, hydrazine, metal hydrides, complex hydrides, tin(II) salts and hydrogen. Particularly suitable reducing agents are formaldehyde, tartrates and glucose, with which gold and
15 silver can be deposited without difficulty. To carry out the coating process, the gold solution and, accordingly, the color-modifying metal salt solution are preferably added to the aqueous suspension containing the frit and the reducing agent and adjusted to the necessary pH value with
20 stirring at a temperature of 5 to 100°C.

 In principle, however, the reducing agent may also be added to a suspension containing the metal compound and the glass frit. If desired, the actual coating step may be preceded by so-called surface activation of the glass frit
25 in which the glass frit is first treated with an aqueous SnCl_2 solution and is then washed. Where silver is used in the coating solution, the color changes from violet-tinged - without silver - to red-tinged - with silver.

 As mentioned above, the purple pigments according to
30 the invention may be used for the pigmenting of glazes, enamels, plastics, glass and decorative colors, lacquers and printing inks and hence for the production of decorative colors.

 Purple pigments specially adapted to the particular
35 application may be used, i.e. pigments based on low-melting



frits for glass colors and pigments based on relatively high-melting frits for porcelain colors and quick-fire colors and colors for wall tiles. The fact that the pigment is adapted to the glass frits of the glazes and enamels does not affect the flow behavior of the glazes and enamels during firing. Whereas known gold-containing purple pigments which contain aluminium oxide particles in addition to glass particles are not sufficiently color-stable at temperatures around 1,100°C, the purple pigments according to the invention are suitable for the rapid firing of porcelain at high temperatures. In addition, the known pigments mentioned above often led to opaque and dull decorations whereas the use of the purple pigments according to the invention enables transparent and hence brilliant decorations to be produced. Since, in the ceramic field, the frits of the pigments according to the invention are largely coordinated with those of the glazes and enamels, there are no unexpected changes in color. The use of color-modifying metals in the production of the pigments eliminates the need for subsequent color modification by the addition of, for example, silver carbonate to the decorative color.

It was not foreseeable that the gold-containing purple pigments would be able to be produced by the described process, which is considerably simplified in relation to the processes used for producing known purple pigments, would be completely uniform and would show the advantageous performance properties mentioned in the foregoing.

The invention is illustrated by the following Examples.

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Example 1

Coating of a glass frit with 0.5% by weight gold.

5 The glass frit used contains as its principal constituents PbO , SiO_2 , Al_2O_3 , SnO_2 and B_2O_3 : particle size distribution: 90% $< 8 \mu\text{m}$. For coating, 50 g of the glass frit are kept suspended by stirring in a solution of 350 ml water and 25 g D-glucose. The pH value of the reaction
10 mixture is increased with ammonia from 5.5 to 11, after which a clear solution of $0.5 \text{ g AuCl}_4 \cdot \text{H}_2\text{O}$ ($= 0.25 \text{ g Au}$) in 50 ml water is added all at once at around 25°C . After this addition, the reaction mixture is stirred in the absence of heat. After a reaction time of about 20 minutes,
15 the reaction mixture undergoes a change in color. After 120 minutes, reduction is complete. When the stirrer is switched off, the particles immediately sediment. A clear filtrate is formed above the sediment. The purple-colored pigment is filtered off under suction, washed with
20 water and ethanol and dried at 100°C .

Example 2

Coating of a glass frit with 2% by weight gold

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The lead borosilicate frit used has a particle size distribution of 90% $< 9 \mu\text{m}$. An activating solution is initially prepared. To this end, 10 g NaOH pellets are dissolved in 100 ml water. 10 g $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ are added to
30 the resulting solution. A clear solution is rapidly formed with stirring.

50 g glass frit are treated with this activating solution for 20 minutes, followed by filtration under suction and washing with water. The activated glass frit
35 is introduced into a solution of 350 ml water and 2 g H

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(AuCl₄) · H₂O (= 1 g Au). This solution is heated to 60°C and the glass particles are kept suspended by stirring. A solution of 75 g Rochelle salt in 100 ml water is added to the reaction mixture heated to 60°C. After about 30 minutes, reduction is complete and the purple-colored pigment can be filtered off under suction and washed with water. The material is dried at 100°C in a drying cabinet.

Example 3

Coating of a glass frit with 5% by weight gold

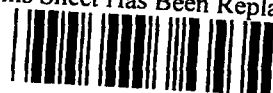
The glass frit used contains SiO₂, PbO, Al₂O₃ and B₂O₃. It has a particle size distribution of 90% <12 μm. 50 g of the glass frit are added to a solution of 75 g ascorbic acid in 350 ml water. The reaction mixture is vigorously stirred so that the particles do not sediment. A solution of 5 g HAuCl₄ · H₂O (= 2.5 g Au) in 100 ml water is then added to the mixture at room temperature. The reaction mixture as a whole is then slowly heated. The heating rate should be about 10°C per 10 minutes. After 30 minutes, the reaction is complete and the pigment can be filtered off under suction, washed and dried.

Example 4

Coating of a high-temperature quick-fire (HTQ) frit with 0.5% by weight gold and, at the same time, with 0.1% by weight silver

The HTQ frit consists of SiO₂, PbO, B₂O₃, Al₂O₃ and CaO and has a particle size distribution of 90% <15 μm. 50 g HTQ frit are added to a solution of 50 g D-glucose in 350 ml water. The pH value of the solution is increased from 5.5 to 11 with ammonia. The reaction mixture is stirred so

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vigorously that the particles are kept in suspension in the solution. A solution of 0.5 g $\text{H}(\text{AuCl}_4) \cdot \text{H}_2\text{O}$ in 50 ml water and a solution of 0.08 g AgNO_3 (= 0.05% Ag) in 50 ml water are then successively added. The reaction mixture is stirred for 2 hours at room temperature, after which the pigment is filtered off, washed and dried at 100°C.

Example 5

Coating of a glass frit with 0.5% by weight gold and 0.1% by weight silver

The glass frit used is a lead-free glass frit containing B_2O_3 , SiO_2 , Na_2O and Al_2O_3 as its principal constituents. The glass frit has a particle size distribution of 90% <5 μm . 50 g glass flux are suspended in a solution of 50 g D-glucose in 350 ml water. The pH value of the solution is increased from 6 to 11 with ammonia. The reaction mixture is stirred so vigorously that the glass particles are unable to sediment. The temperature of the reaction mixture should be approximately 25°C. A gold solution of 0.5 g $\text{H}(\text{AuCl}_4) \cdot \text{H}_2\text{O}$ and 50 ml water is added to the reaction mixture which is then left to react until it undergoes a change in color. A solution of 0.08 g AgNO_3 in 50 ml water is then added, followed by reaction for another 2 hours at room temperature. The pigment is then filtered off under suction, washed and dried at 100°C.

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Purple pigments, a process for their production and their use

Claims

1. Purple pigments based on glass frits having a coating containing colloidal gold, characterized in that the coating essentially contains colloidal gold in a quantity of 0.05 to 5% by weight, based on the pigment, and - if
5 desired - one or more color-modifying metals from the group consisting of Ag, Cu, Co, Ni, Sn, Ru, Rh, Pd, Os, Ir and Pt in a total quantity below that of the gold and is directly applied to the surface of glass frits of which the particle diameter (D_{50} value) is in the range from 0.5 to 50 μm .
- 10 2. Purple pigments as claimed in claim 1, characterized in that they contain 0.1 to 2.0% by weight colloidal gold.
3. Purple pigments as claimed in claim 1 or 2, characterized in that the coating consists solely of colloidal gold and, if desired, silver.
- 15 4. Purple pigments as claimed in any of claims 1 to 3, characterized in that the glass frit has a D_{50} value in the range from 1 to 10 μm .
5. A process for the production of purple pigments based on glass frits having a coating containing colloidal gold,
20 characterized in that colloidal gold in a quantity of 0.05 to 5.0% by weight, based on the pigment, and - if desired - one or more color-modifying metals from the group consisting of Ag, Cu, Co, Ni, Sn, Ru, Rh, Pd, Os, Ir and Pt in a total quantity below that of the gold are deposited on the
25 surface of an uncoated glass frit, of which the average particle diameter (D_{50} value) is in the range from 0.5 to 50 μm , by forming the metals to be deposited from water-soluble compounds of gold and, where present, the color-modifying metals in the presence of reducing agents in an
30 aqueous suspension containing the glass frit, separating the pigment thus obtained from the aqueous phase and drying

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the pigment.

6. A process as claimed in claim 5, characterized in that silver is used as the color-modifying metal and the gold and silver are deposited simultaneously or successively using the same reducing agent.

7. The use of the purple pigments claimed in any of claims 1 to 4 for pigmenting glazes, enamels, glass colors, decorative colors, plastics, printing inks and lacquers.

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