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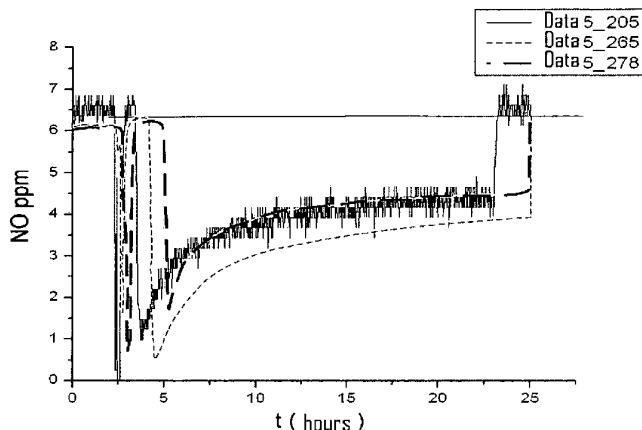
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(54) Photocatalytic ceramic glaze composition

(57) The present invention relates to a ceramic glaze composition characterized in that it comprises, in percentage by weight in relation to the total weight of the composition: a) from 50 to 90% by weight of a product, which in turn comprises from 10 to 90% by weight of a compound with photocatalytic properties, and from 10 to 90% by weight of at least one natural and/or synthetic material selected from a group of substances with feldspar or feldsparoid structure; b) from 5 to 50% by weight of at least one fluxing additive; and c) from 0.5 to 20%

by weight of sodium tripolyphosphate. It will be also an object of this invention the method for preparing said ceramic glaze, as well as its application in ceramic pieces capable of reducing NOx existing in the air. The compound with photocatalytic properties may be TiO<sub>2</sub> in the form of anatase, SrTiO<sub>3</sub>, KTaO<sub>3</sub>, ZrO<sub>2</sub>, ZnS, CdSe, GaP, SiC. The fluxing additive may comprise in wt% 30-80 PbO, 15-70 SiO<sub>2</sub>, 1-10 ZnO, 1-8 Na<sub>2</sub>O, 0.5-6 TiO<sub>2</sub>, 0.2-6 Al<sub>2</sub>O<sub>3</sub>.

FIG.1



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## Description

### Technical field

**[0001]** The present invention relates to the field of ceramic glazes and more specifically to the field of ceramic glazes with photocatalytic capacity specially applied in the manufacture of ceramic coatings. Particularly, said coatings will be characterized by comprising semiconductor materials, especially TiO<sub>2</sub>, which, under proper wavelength radiation, will be capable of causing the oxidation of nitrogen oxides contacting therewith.

### Background of the invention

**[0002]** One of the major pollution problems currently existing in large cities is derived from the emissions of nitrogen oxides to the atmosphere. Nitrogen oxides (hereinafter referred as NO<sub>x</sub>) are a mixture of gases composed by nitrogen and oxygen among which nitrogen monoxide and nitrogen dioxide should be mentioned, due to their greater toxicological impact.

**[0003]** Annually, more than 30 million tons of NO<sub>x</sub> are emitted into the atmosphere by human action. NO<sub>x</sub> are mainly produced in combustion processes, both in movable (cars, trucks, public transportation) and fixed (incinerator ovens or power plants) sources. Also, some specific chemical industries (production of nitric acid, uric acid, etc.) contribute in a lesser extent.

**[0004]** The emission of nitrogen oxides (NO<sub>x</sub>) into the atmosphere causes a variety of problems in population health as well as negative environmental impacts on the planet. In this regard, direct exposure to said oxides in concentrations higher than 3 ppm increases the possibilities of lung diseases, especially in children and elderly, and it is critical for cardiac patients.

**[0005]** Similarly, NO<sub>x</sub> react with unburned hydrocarbons to form ozone, the primary cause of photochemical smog, which causes among other health problems, eye irritation, coughing, headaches or respiratory problems.

**[0006]** In addition to the negative effects on humans and wildlife, nitrogen oxides cause damage in forestry and seriously affect the growth of certain varieties of crops and fruit crops. These, along with sulfur oxides, are the mainly responsible for acid rain. On the other hand, NO<sub>x</sub>, mainly in their forms NO<sub>2</sub> and NO, are gases that contribute to the climate change and global warming of the planet, being its influence more harmful than that of CO<sub>2</sub>. In particular, it has been calculated that NO<sub>x</sub> is about 310 times more harmful than CO<sub>2</sub>.

**[0007]** Although many technologies have been developed with the object of reducing or eliminating the emissions of said pollutant gases, yet there remains the need to design new processes, more economical and effective, in order to achieve the decontamination levels established by the laws without compromising the current level of economic development and social welfare derived from the use of fossil fuels such as oil and natural gas.

**[0008]** In this regard, the solution suggested by present invention is based on presenting a new ceramic glaze composition with photocatalytic capacity, intended for manufacturing ceramic materials capable of continuously maintaining their photocatalytic activity over time.

**[0009]** Already for some years, it is known the processing capacity of organic compounds having certain elements with photocatalytic properties. Similarly, it is well known the photocatalytic nature of compounds such as titanium dioxide, which has been widely used because it is an economic, safe and chemically stable compound. In this regard, the first known studies about the possible use of TiO<sub>2</sub> for the oxidation of organic molecules were developed by Teichner et al. (P.C. Gravelle, F. Juillet, P. Meriaudeau and S.J. Teichner, Discuss. Faraday Soc, 52, 140 (1971); M. Formenti, F. Juillet, P. Meriaudeau and S.J. Teichner, Chem Technol., 1.680 (1971)).

**[0010]** However, most part of investigations carried out so far have been focused on the study of the photodegradation mechanism, as well as the properties of the process catalysts themselves.

**[0011]** Despite of that, studies have been also developed, mainly in Japan, directed to the possibility of treating low concentrations of NO<sub>x</sub> by using photocatalysis. Thus, for example, Ichiura *et al.* works are focused on the study of photocatalytic oxidation of NO<sub>x</sub> on metal compounds modified titanium dioxide sheets (Ichiura, H., Kitaoka, T., Tanaka, H., "Photocatalytic oxidation of NO<sub>x</sub> using composite sheets containing TiO<sub>2</sub> and a metal compound", Chemosphere 51, 855 (2003)). Similarly, Dalton *et al.* have studied the photocatalytic degradation of NO<sub>x</sub> of the atmosphere, using TiO<sub>2</sub> as photocatalyst (Dalton, J.S., Janes, P.A., Nicholson J.A., Hallam K.R., Allen, G.C., "Photocatalytic oxidation of NO<sub>x</sub> gases using TiO<sub>2</sub>: a surface spectroscopic approach", Environ. Pollut. 120, 415 (2002)). Also in the literature it is possible to find works on the application of TiO<sub>2</sub> for avoiding pollution effects on buildings under solar irradiation (A. Fujishima, Taiyo Enerugi, 26 (2), 2-6 (2000)).

**[0012]** In patent literature it should be mentioned, among others, the international applications WO97/10185, WO97/10186, WO99/44954 or WO2006/030250 A2, as well as patents such as the ES2265150, wherein the photocatalytic capacity of TiO<sub>2</sub> is described, as well as its application, for example in the manufacture of coatings or in the self-cleaning of surfaces.

**[0013]** In this regard, it will be the object of this invention to present a new ceramic glaze composition capable of achieving highly effective results in terms of reducing the level of nitrogen oxides, while allowing said efficiency to be maintained over a long period of time. Thus, it is possible to provide structural elements, such as the tiles used in building coating, with a functional nature additional to the simple and merely decorative function that said ceramic elements usually have.

### Description of the invention

**[0014]** The present invention relates to a new ceramic glaze composition **characterized in that** it comprises:

- a) from 50 to 90%, preferably from 60 to 85% by weight solid of a product whose composition and obtaining method are claimed in the Spanish patent application No. 200900188 by FMC FORET SA, product that in turn comprises from 10 to 90%, preferably from 40 to 60%, of a compound with photocatalytic properties, and from 10 to 90%, preferably from 40 to 60% of at least one natural and/or synthetic material selected from a group of substances with feldspar or feldsparoid structure;
- b) from 5 to 50%, preferably from 15 to 40% by weight solid of the composition of at least one fluxing additive;
- c) from 0.5 to 20%, preferably from 1 to 10% by weight solid of the sodium tripolyphosphate composition.

**[0015]** The compound with photocatalytic properties will preferably consist of titanium dioxide in its Anatase crystalline structure. However, additionally, said compound with photocatalytic properties may be selected from a group consisting of  $\text{SrTiO}_3$ ,  $\text{KTaO}_3$ ,  $\text{ZrO}_2$ ,  $\text{ZnS}$ ,  $\text{CdSe}$ ,  $\text{GaP}$  and  $\text{SiC}$ , as well as any combination thereof.

**[0016]** In turn, natural and/or synthetic materials in the composition are characterized by being inert, nontoxic, and by having no photocatalytic activity. As it is known, feldsparoids are porous tectosilicates containing aluminum and silicon in similar proportions, which form a negatively charged three-dimensional structure balanced by cations.

**[0017]** Its main function will be to prevent photocatalytic deactivation of the titanium dioxide, thus enhancing its effectiveness and durability. In this sense, these natural and/or synthetic materials, intimately mixed with  $\text{TiO}_2$ , generate a synergistic effect through which the photocatalytic activity and durability are enhanced, so that the ceramic glaze is initially able to produce a more significant abatement of the  $\text{NO}_x$  in the surrounding atmosphere than if  $\text{TiO}_2$  were pure. Subsequently, once the steady state is reached, they allow the ceramic glaze to maintain a constant and longlasting activity, while pure  $\text{TiO}_2$  would be inactivated by poisoning. In the present invention, due to the presence of these materials, the anions derivatives from photooxidation of  $\text{NO}_x$  are reversibly deposited on the surface of feldsparoids thus maintaining the  $\text{TiO}_2$  its photocatalytic activity unchanged. In a preferred embodiment of the invention, a mixture of various feldsparoids will be used, obtained from direct combination of its components, or either by heat treatments from precursors.

**[0018]** Finally, the fluxing additive will preferably consist of frits whose chemical composition will determine the sought fluxing. Preferably, these frits will include, as

main components, fritted lead oxide ( $\text{PbO}$ ) (inert, water insoluble) at a rate between 30 and 80% by weight of frits, preferably between 50 and 70%, and silicon dioxide ( $\text{SiO}_2$ ) at a rate between 15 and 70% by weight of frits, preferably between 20 and 35%. As minor components, the frits will include zinc oxide ( $\text{ZnO}$ ) between 1 and 10% by weight of frits, sodium oxide ( $\text{Na}_2\text{O}$ ) between 1 and 8% by weight of frits, Titanium oxide ( $\text{TiO}_2$ ) between 0.5 and 6% by weight of frits, and dialuminum trioxide ( $\text{Al}_2\text{O}_3$ ) between 0.2 and 6% by weight of frits.

**[0019]** Alternatively, other types of compounds that can be used as fluxing additives are  $\text{MgO}$  or  $\text{Li}_2\text{O}$ , as well as any combination thereof.

**[0020]** The ceramic composition described containing particles of titanium dioxide ( $\text{TiO}_2$ ) in combination with feldspars and/or feldsparoids at the rates claimed in the application No. 200900188, once subjected to baking and exposed to sunlight is capable of maintaining the enhanced photocatalytic properties of  $\text{TiO}_2$  by being capable of oxidizing nitrogen oxides ( $\text{NO}_x$ ) coming into contact therewith without losing their effectiveness over time. This aspect is one of the main advantages of the present invention, being also one of the features that make it novel against the current state of the art.

**[0021]** Said oxidation process is based on the generation of hydroxyl radicals capable of degrading the pollutant compounds giving rise to substances harmless to the environment. The hydroxyl radical is a powerful oxidizing agent that oxidizes nitrogen dioxide ( $\text{NO}_2$ ), by transforming it into nitrate ion. In turn, superoxide ion is capable of transforming nitrogen monoxide ( $\text{NO}$ ) into nitrate ions.

**[0022]** In a preferred embodiment of the invention, the composition previously described will also comprise between 30 and 60%, preferably between 35 and 50% by weight of the total mixture, of at least one silk-screen carrier characterized by comprising between 60 and 90% by weight of at least one alcohol, preferably polyglycol; between 5 and 30% by weight of water and between 5 and 35% by weight of a polysaccharide-type resin.

**[0023]** For preparing the ceramic glaze made from the composition described above is not necessary to carry out any special modifications to the common processes and methods for manufacturing ceramic products. Thus, said method for preparing the ceramic glaze comprises the following steps:

- a) Mixing the constituent elements of the ceramic glaze composition;
- b) conditioning the previous mixture using a process that may consist of microbeads mill micronizing or stirring homogenization, and subsequent sieving until obtaining a mixture or solid composition with a wet rejection of 0% measured in a 45 micron sieve;
- c) mixing the solid composition of the previous step with the silk-screen carrier in a percentage between 30 and 60%, preferably between 35 and 50% by weight.

[0024] A further object of this invention is directed to the ceramic glaze made from the previous method, **characterized in that** it comprises density values (at 25°C) between 1.55 and 1.85 kg/l.

[0025] Similarly, it will be object of this invention a ceramic piece **characterized in that** at least one of its faces comprises the previously described ceramic glaze. Said ceramic piece will preferably be of porcelain type with a water absorption of less than 0.5%.

[0026] In a preferred embodiment of the invention, the method for obtaining said ceramic piece will comprise the baking and its prior decoration, followed by the application of the photocatalytic glaze on the porcelain glaze of said piece by using one of the conventional silk-screen printing systems for producing ceramics. Among said systems, silk-screen printing, gravure systems and airspray systems are preferably.

[0027] In a preferred embodiment wherein the application system is carried out by gravure, the glaze will be deposited into the cavities of a matrix located on part of a smooth cylindrical and elastically deformable surface. The excess glaze deposited on the matrix will be removed by using a blade, which will in turn allow continuously mixing again the glaze, thus producing at least a partial restocking within the matrix cavities. Finally, the transfer of the glaze contained into the matrix cavities to the ceramic piece will be performed by direct contact, i.e. by continuously rolling and without dragging said matrix on the ceramic piece surface.

[0028] Once the glaze is deposited, the decorated ceramic piece will be subjected to a baking cycle from 45 to 70 minutes in an industrial oven, according to a baking curve with a curve arrest or maximum stable temperature area from 750°C to 1150°C.

[0029] Finally, the object of this invention will be the use of said ceramic pieces in order to reduce the NOx percentage existing in the air. Thus, in case that said ceramic piece is a tile on which a layer of the glaze object of the invention has been deposited, it will be possible to degrade 3.63 mg of NOx per m<sup>2</sup> per hour, equivalent to a reduction of 18.8% of the NOx concentration in the atmosphere. Similarly, in a particular application to be applied, for example, to 200 buildings of 8 floors with an area of 4800 m<sup>2</sup> each one covered with these tiles, it will be possible to remove about 238.491.000 mg by weight of NOx/year, assuming 12 hours daily of identical sunshine 365 days a year.

[0030] Moreover, an additional advantage showed by these ceramic pieces is their regeneration by simple washing, natural or voluntary, with water. Thus, in the wash, the ions derivatives from photocatalytic oxidation are dissolved in water, being able to be completely removed and, therefore, allowing the initial photocatalytic activity of the glaze to be recovered.

#### Preferred embodiment of the invention

[0031] Three preferred embodiments of the present in-

vention are now presented by way of example and in a not limitative manner.

#### **Example 1. Composition 278BCB1**

[0032] In this first example there was used a ceramic glaze with the following composition: a solid preparation comprising 84% by weight solid of the product, whose composition and preparation method are claimed in the Spanish patent application No. 200900188, 1% by weight solid of sodium tripolyphosphate and 15% by weight solid of a fluxing additive, with the composition of said additive being as follows: 55% of lead oxide PbO, 22% of silicon dioxide SiO<sub>2</sub>, 7% of Zinc oxide ZnO, 7% of sodium oxide Na<sub>2</sub>O, 5% of titanium oxide TiO<sub>2</sub> and 4% of dialuminum trioxide Al<sub>2</sub>O<sub>3</sub>. Said solid composition was mixed and homogenized with the silk-screen carrier in a rate of 50% by weight of the total mixture, said silk-screen carrier being in turn composed of 85% of a polyglycol, 10% of water and 5% of polysaccharide-type resin. The resulting mixture showed a rejection of 0% in a 45 micron sieve and the resulting glaze was conditioned at a density of 1.68 kg/l. The referred photocatalytic glaze was applied on a porcelain-type ceramic piece (with water absorption of less than 0.5%), previously decorated and baked. The piece with the photocatalytic glaze was then subjected to a baking cycle for 50 minutes at a maximum baking temperature of 910°C. The photocatalytic piece thus obtained was tested according to ISO 22197-1:2007 in order to determine its activity degree, providing a value of 0.68 ppm/hour of NOx decomposition.

#### **Example 2. Composition 205SBB1**

[0033] In this example there was used a ceramic glaze with the following composition: a solid preparation comprising 60% by weight solid of the product, whose composition and preparation method are claimed in the Spanish patent application No. 200900188, 5% by weight solid of sodium tripolyphosphate and 35% by weight solid of a fluxing additive, with the composition of said additive being as follows: 50% of lead oxide PbO, 35% of silicon dioxide SiO<sub>2</sub>, 2% of Zinc oxide ZnO, 5% of sodium oxide Na<sub>2</sub>O, 5% of titanium oxide TiO<sub>2</sub> and 3% of dialuminum trioxide Al<sub>2</sub>O<sub>3</sub>. Said solid composition was mixed and homogenized with the silk-screen carrier in a rate of 55% by weight of the total mixture, said silk-screen carrier being in turn composed of 80% of a polyglycol, 10% of water and 10% of polysaccharide-type resin. The resulting mixture showed a rejection of 0% in a 45 micron sieve, and the resulting glaze was conditioned at a density of 1.58 kg/l. The referred photocatalytic glaze was applied on a porcelain-type ceramic piece (with water absorption of less than 0.5%), previously decorated and baked. The piece with the photocatalytic glaze was then subjected to a baking cycle for 68 minutes at a maximum baking temperature of 875°C. The photocatalytic piece thus obtained was tested according to ISO 22197-1:2007 in or-

der to determine its activity degree, providing a value of 0.59 ppm/hour of NOx decomposition.

### Example 3. Composition 265BCB1

[0034] In this example there was used a ceramic glaze with the following composition: a solid preparation comprising 75% by weight solid of the product, whose composition and preparation method are claimed in the Spanish patent application No. 200900188, 1% by weight solid of sodium tripolyphosphate and 24% by weight solid of a fluxing additive, with the composition of said additive being as follows: 60% of lead oxide PbO, 25% of silicon dioxide SiO<sub>2</sub>, 6% of Zinc oxide ZnO, 4% of sodium oxide Na<sub>2</sub>O, 3% of titanium oxide TiO<sub>2</sub> and 2% of dialuminum trioxide Al<sub>2</sub>O<sub>3</sub>. Said solid composition was mixed and homogenized with the silk-screen carrier in a rate of 45% by weight of the total mixture, said silk-screen carrier being in turn composed of 85% of a polyglycol, 6% of water and 9% of polysaccharide-type resin. The resulting mixture showed a rejection of 0% in a 45 micron sieve, and the resulting glaze was conditioned at a density of 1.62 kg/l. The referred photocatalytic glaze was applied on a porcelain-type ceramic piece (with water absorption of less than 0.5%), previously decorated and baked. The piece with the photocatalytic glaze was then subjected to a baking cycle for 60 minutes with a maximum baking temperature of 800°C. The photocatalytic piece thus obtained was tested according to ISO 22197-1:2007 to determine its activity degree, providing a value of 0.85 ppm/hour of NOx decomposition.

[0035] In the figure accompanying this description (FIG. 1) the comparative results of the three previous examples, according to the ISO 22197-1 2007 STANDARD, are represented.

### Claims

1. Ceramic glaze composition **characterized in that** it comprises, in percentage by weight in relation to the total weight of the composition:
  - a) from 50 to 90% by weight of a product, which in turn comprises from 10 to 90% by weight of a compound with photocatalytic properties, and from 10 to 90% by weight of at least one natural and/or synthetic material selected from a group of substances with feldspar or feldsparoid structure;
  - b) from 5 to 50% by weight of at least one fluxing additive;
  - c) from 0.5 to 20% by weight of sodium tripolyphosphate.
2. Composition, according to claim 1, wherein the compound with photocatalytic properties consist of titanium dioxide in the form of Anatase.
3. Composition, according to claim 1, wherein said compound with photocatalytic properties is selected from a group consisting of SrTiO<sub>3</sub>, KTaO<sub>3</sub>, ZrO<sub>2</sub>, ZnS, CdSe, GaP and SiC, as well as any combination thereof.
4. Composition, according to any one of claims 1 to 3, wherein the fluxing additive consists of ceramic frits **characterized by** comprising from 30 to 80% by weight of fritted lead oxide, from 15 to 70% by weight of silicon dioxide (SiO<sub>2</sub>), from 1 to 10% by weight of Zinc oxide (ZnO), from 1 to 8% by weight of sodium oxide (Na<sub>2</sub>O), from 0.5 to 6% by weight of titanium oxide (TiO<sub>2</sub>), and from 0.2 to 6% by weight of dialuminum trioxide (Al<sub>2</sub>O<sub>3</sub>).
5. Composition, according to any one of claims 1 to 4, wherein the fluxing additive is selected from a group consisting of MgO y Li<sub>2</sub>O, as well as any combination thereof.
6. Composition, according to any one of the preceding claims, **characterized in that** it additionally comprises between 30 and 60% by weight of the total mixture of at least one silk-screen carrier.
7. Composition, according to claim 6, wherein said silk-screen carrier is **characterized in that** it comprises from 60 to 90% by weight of an alcohol, from 5 to 30% by weight of water, and from 5 and to 35% by weight of a polysaccharide-type resin.
8. Method for preparing a ceramic glaze from a composition according to any one of claims 1 to 7, **characterized in that** it comprises the following steps:
  - a) mixing the constituent elements of the ceramic glaze composition;
  - b) conditioning the previous mixture by microbeads mill micronizing or stirring homogenization, and subsequent sieving until obtaining a mixture or solid composition with a wet rejection of 0% measured in a 45 micron sieve;
  - c) mixing the solid composition of the previous step with a silk-screen carrier in a percentage by weight between 30 and 60%.
9. Ceramic glaze obtained from the method of preparation according to claim 8, **characterized in that** it comprises a density value at 25°C from 1.55 to 1.85 Kg/l.
10. Ceramic piece subjected to baking between 45 and 70 minutes with a maximum temperature area between 750°C and 1150°C, **characterized in that** at least one of its faces comprises a ceramic glaze according to claim 9.

11. Ceramic piece, according to claim 10, wherein at least one of its faces comprises a ceramic glaze obtained from a ceramic glaze composition **characterized in** turn by comprising:

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a) from 50 to 90% by weight of a product which in turn comprises from 10 to 90% by weight of a compound with photocatalytic properties, and from 10 to 90% by weight of at least one natural and/or synthetic material selected from a group of substances with feldspar or feldsparoid structure;

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b) from 5 to 50% by weight of at least one fluxing additive;

c) from 0.5 to 20% by weight of sodium tripolyphosphate.

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12. Use of a ceramic piece according to any of claims 10 or 11 in order to continuously reduce photocatalytically the  $\text{NO}_2$  and NO existing in the air.

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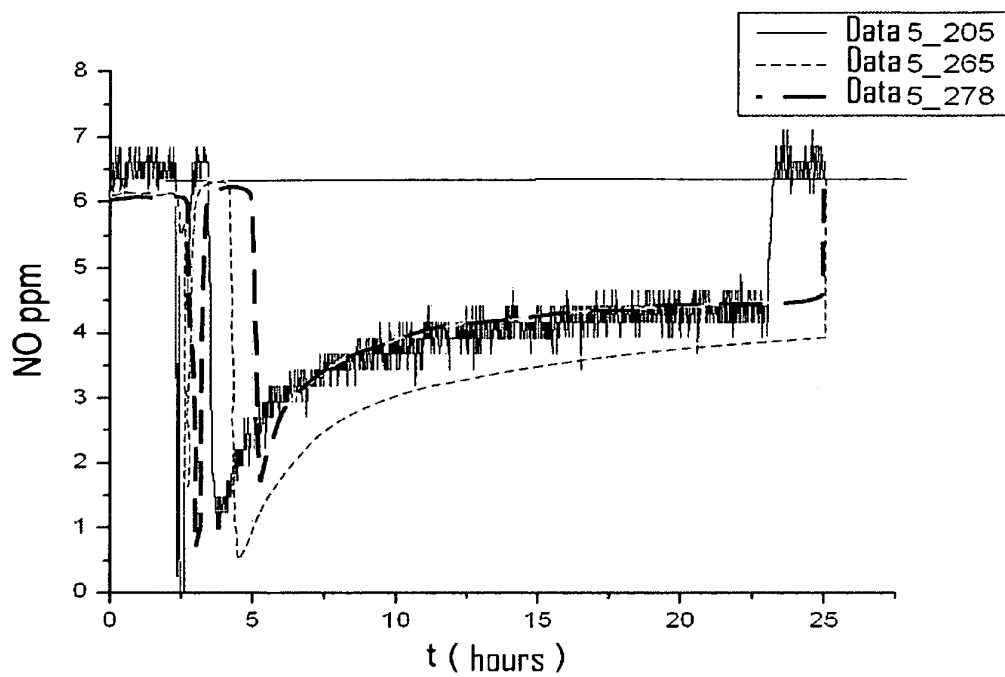
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FIG.1



REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 9710185 A [0012]
- WO 9710186 A [0012]
- WO 9944954 A [0012]
- WO 2006030250 A2 [0012]
- ES 2265150 [0012]
- ES 200900188 [0014] [0032] [0033] [0034]
- WO 200900188 A [0020]

Non-patent literature cited in the description

- TEICHNER ; P.C. GRAVELLE ; F. JUILLET ; P. MERIAUDEAU ; S.J. TEICHNER et al. *Discuss. Faraday Soc*, 1971, vol. 52, 140 [0009]
- M. FORMENTI ; F. JUILLET ; P. MERIAUDEAU ; S.J. TEICHNER. *Chem Technol.*, 1971, 1.680 [0009]
- ICHIURA, H. ; KITAOKA, T. ; TANAKA, H. Photocatalytic oxidation of NO<sub>x</sub> using composite sheets containing TiO<sub>2</sub> and a metal compound. *Chemosphere*, 2003, vol. 51, 855 [0011]
- DALTON, J.S. ; JANES, P.A. ; NICHOLSON J.A. ; HALLAM K.R. ; ALLEN, G.C. Photocatalytic oxidation of NO<sub>x</sub> gases using TiO<sub>2</sub>: a surface spectroscopic approach. *Environ. Pollut.*, 2002, vol. 120, 415 [0011]
- A. FUJISHIMA. *Taiyo Enerugi*, 2000, vol. 26 (2), 2-6 [0011]