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(54) Method for reducing defects in ceramic tile production

(57) This invention is directed to a method for reducing product defects in the production of ceramic products during the firing process of the ceramic products. An oxidizing atmosphere is provided in a roller kiln furnace at the vicinity of the heating elements to sustain a heated oxidizing atmosphere. The ceramic product is passed through the vicinity of the oxidizing atmosphere for firing. The ceramic products are fired in the presence of the oxidizing atmosphere.

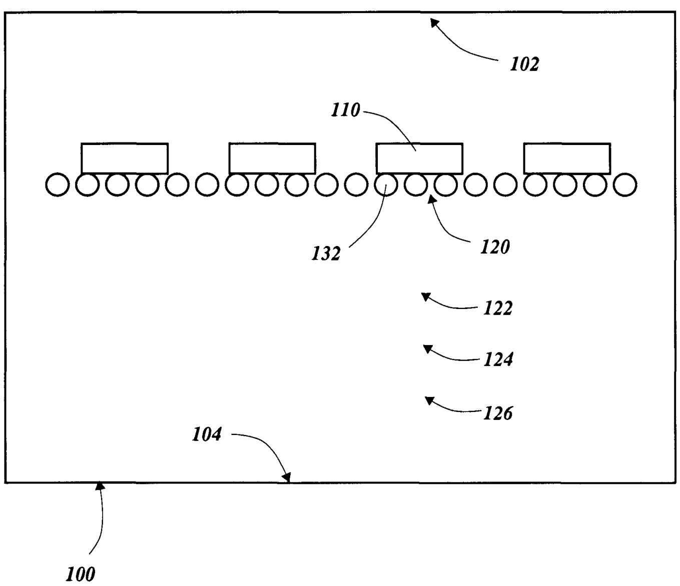

Fig. 1

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Description

Field of the Invention

[0001] This invention is generally related to a method for reducing the defects associated with heating of ceramic materials. More specifically, this invention relates to the use of oxygen to reduce or eliminate the black core defects during the production of enameled ceramic tiles in the roller hearth kiln.

Background of the Invention

[0002] The argillaceous minerals used in the formulation of the primary compounds in enameled tiles contain frequently a high quantity of substances that are susceptible to chemical reactions with oxygen at high temperatures. The argillaceous minerals contain substantial quantities of carbon and organic materials, sulfur and its compounds, and some oxides of transition metals (particularly iron) which can generate defects in the sintered ceramic products in their lower valence state. Accordingly, it is necessary to use an oxygen rich atmosphere to have these materials oxidized, in a stage prior to the firing process.

[0003] Incomplete oxidation during the firing phase results in certain burned products in the ceramic product, and causes certain textural changes (and imperfections), which lowers the quality of the ceramic products and the mechanical resistance characteristics of the final ceramic product. A dark core known as "black core" will likely develop during the firing, which is formed by carbon residues from the thermal decomposition of the organic material contained in the clays. Particularly, the dark color in the center is believed to be caused by iron, which is present in a reduced condition. The main source of reduction of the ferric oxide (Fe_2O_3) to ferrous oxide (FeO), and/or metallic iron (Fe) is the presence of a carbonaceous residue which results from the carbonization of organic impurities. This reduction is dependent on the oxidation rate of these transition metals contained in the clay and the oxidation velocity is dependent on various factors including: 1) the nature and quantity of oxidizible and reducible substances; 2) the particle size of these substances; 3) the heating rate; 4) the atmosphere concentration surrounding the oxidizible and reducible substances on oxygen, carbon monoxide and sulfur dioxide; 5) the composition and textural variation of the pieces during each step of the burning cycle; and 6) the enamel fusibility deposited in the "green body". Generally, the black core defect occurs with greater frequency in the single firing process. A slow firing cycle is preferred over a faster firing cycle in order to obtain a better quality product, although such a slow firing cycle may not be practical in the industry.

[0004] The addition of oxygen significantly benefits the ceramic production process including 1) reducing or eliminating the defects formed from the firing process; 2) maintaining or increasing the production rate; and 3) allowing the use of lower quality raw materials (i.e., rich in transition metals and/or organic compounds). Oxygen enrichment also allows the process, at a constant or higher production rate, to produce a final product having superior quality compared with the traditional method which does not use additional oxygen.

[0005] A number of attempts have been made to prevent the formation of black core. However, each of these methods presents certain disadvantageous.

[0006] Improvements to the quality of the raw material have been considered. However, this increases the production costs and requires additional expense to make such raw material improvements.

[0007] Reduction in the compacting pressure has also been attempted. However, the difficulty relating to "green compact" manipulation prior to the firing process reduces the facility of this process. Additionally, reduction in compacting pressure raises the porosity in the final product, which reduces the intrinsic product quality (dimensional variation, mechanical resistance etc.) and which will reduce the product competitiveness in the marketplace.

[0008] Increasing the enameled tile residence time in the furnace reduces the productivity of the available equipment.

[0009] The use of additives/flux agents enable the liberation of oxygen when heated, thus improving the oxidation of the organic compounds. As these materials have low melting temperatures during the enameled tiles pre-heating, promotes a rapid reduction of the opened porosity. This will avoid the interactions with the furnace atmosphere at a defined temperature. Additionally, the additive/flux agents promote further darkening of burned products.

[0010] The use of powders with fine particles may facilitate the elimination of volatiles. However, it is difficult to work with fine powder as a significantly higher compacting pressure is required, thus reducing the properties in the ceramic body (i.e., particles distribution homogeneity), affecting mainly the porosity and the final mechanical resistance. As a result, the product quality may be affected.

[0011] The use of higher melting temperature vitrifying enamels raises the residence time of the "green compact" into the oxidizing furnace atmosphere to better oxidize the organic compounds. The porous area remains open for a longer period of time. As a result, the aesthetics of the final product is compromised.

[0012] The lower moisture content of the enamel tiles provides a lower volume of gases to be extracted from the green compact. Lower content of moisture represents fewer opened channels for gases to exit, thus, greater difficulty of the oxidant atmosphere to penetrate into the green body.

[0013] Processing the enameled ceramic tiles with a thin enamel layer may compromise the abrasion resistance of the final product. Reducing the thickness of the green compact enables a reduction in the mechanic stress. The higher content of moisture provides a higher quantity of open channels, thus enhancing the green body oxidation but requiring an increase in green body residence time into the kiln for moisture extraction.

[0014] U.S. patent No. 4,329,142 relates to the reduction of defects caused by the incomplete oxidation of the carbonaceous materials and sulfur compounds present in the raw material.

[0015] None of the above reference teaches or suggests the claimed invention for using oxygen in the production of enameled ceramics by minimizing the transition metal state valence reduction. It is necessary, therefore, to provide a method for producing enameled ceramics which minimizes incomplete oxidation, by avoiding the transition metal state valence reduction.

Summary of the Invention

[0016] One aspect of this invention is directed to a method for reducing product defects in the production of ceramic products during the firing process and for increasing the production rate of the ceramic products, the method comprising the steps of providing an enriched oxidizing atmosphere in a furnace at the vicinity of the ceramic products to maintain a heated oxidizing atmosphere; passing the ceramic products for firing in the vicinity of the oxidizing atmosphere; and firing the ceramic products in the presence of the oxidizing atmosphere.

[0017] As used herein, the term "enriched oxidizing atmosphere" shall mean an atmospheric gas having an oxygen content of equal or greater than air. The concentration of oxygen in the enriched oxidizing atmosphere may range from that found in air to pure oxygen.

Detailed Description of the Invention

[0018] This invention provides a method for maintaining the characteristic of the raw material such as grain sizes, moisture content, compacting pressure, porosity, dimensions, thickness, enamel type and enameling process during the manufacturing of the ceramic material. An enameled tile product using this process may be obtained with little or no defects, such as black core. Better mechanical resistance and high production rate are maintained. Further, this invention is directed to optimizing other process parameters such as higher compacting pressure, the use of lower quality raw material, higher moisture contents, larger raw materials, greater green compact thickness, enamel with lower temperature of fusibility, capacity for using low BTU gas fuel, such as gasogene, and reducing the specific consumption while increasing production. This process is adaptable to any roller kiln, thus minimizing initial investments.

[0019] The quality of the ceramic products processed in roller kilns depends mainly on the furnace conditions. The kiln atmosphere composition is one of the most important factors that characterizes the burning conditions. The kiln furnace atmosphere must provide an oxidizing condition to eliminate or reduce the occurrence of defects in the tile, such as black core.

[0020] The process of this invention is to locally control the kiln atmosphere composition by adding oxygen. Oxygen may be added to the kiln in an ambient temperature or preheated outside of the kiln to provide a higher oxidant atmosphere, mainly in the temperature where the defects can occur. Thus, the material must be characterized in a ceramic specialized laboratory to determine these temperatures, as well as the composition of oxidizable substances.

[0021] The addition of oxygen raises the oxygen concentration available to react with the oxidizable compounds of the ceramic compact. Several spin rolls (for transporting the pieces of ceramic product into the furnace) were substituted by static rolls (without spin movement), through which the oxygen was introduced into the furnace. This process enables the oxygen to be added to the furnace in close proximity to the ceramic materials, increasing the oxygen concentration at this point and the oxidation efficiency, without being wasted in the enrichment of the total furnace gases volume. This invention also enables the oxygen to be heated directly into the ceramic rolls, thus improving the oxygen reactivity with the compound materials to be oxidized.

[0022] In this invention, any atmosphere having more available oxygen than the existing oxygen concentration in the furnace atmosphere will prevent black core defects. The lowest measured concentration in the furnace atmosphere without oxygen added was about 1%. Thus, pure oxygen and/or oxygen mixture capable of enriching the furnace atmosphere at an oxygen concentration of greater than about 1% will prevent the core defects and increase the production rate of the ceramic products.

[0023] Because the furnace rolls are hot through continuously heating, the addition of oxygen in the process uses this available source of heat to promote the heating of the oxygen added to the furnace, thus improving the oxidation process reaction. Increasing the oxygen concentration or increasing the oxidizing atmosphere temperature increases the oxidation process efficiency. Alternatively, the oxygen may be preheated outside of the kiln furnace.

[0024] A variety of methods may be used to add oxygen to the furnace. Instead of adding the oxygen directly below or above the tiles and/or both below and above the tiles, an oxygenated atmosphere may be added in the kiln atmosphere to react with the tiles.

[0025] A typical method of injecting oxygen is by removing the rotating rolls to install static roll without the rotating movement for oxygen injection. A variation of such oxygen injecting is by using small static rolls (or tubes) installed among the existing rolls for oxygen addition.

[0026] Another variation of oxygen injection comprises using some of the existing spin rolls to be drilled through its length longitudinally across the rolls and to equip them with rotating union, thus enabling oxygen to be fed into the rolls. The drilling through the spin rolls is applicable to other types of rolls as well.

[0027] A control system is needed to feed oxygen only when the holes drilled in the rotating rolls have a good approximation of gas flow with the ceramic materials. Further, the oxygen rolls may be added above the tiles, below the tiles, or both above and below the tiles. In all cases, lower black core defect results when oxygen is fed close to the tiles undergoing treatment.

[0028] Preferably, the oxidizing atmosphere is added into the furnace in the pre-heating zone (or the oxidizing zone). The temperature of the furnace for the oxidizing atmosphere may range from about 200°C to about 1000°C, preferably from about 400°C to about 900°C.

EXAMPLE A

[0029] In one embodiment of this invention, a roller kiln for a single firing process was provided in which the acceleration of the burning cycle and the nominal production was increased from about 4300 m^2/day to about 4900 m^2/day for ceramic tiles with low softening enamel temperature, and from about 4500 m^2/day to about 5000 m^2/day for ceramic tiles with refractory enamel. This was accomplished due to the oxygen utilization to accelerate the reactions of the oxidation of the ceramic materials. The addition of oxygen was done by the substitution of one roll with spin movement by one static roll (without spin movement) in each of the three existing rolls, in a defined kiln section. These rolls (without spin movement) were built with the same sillimanite materials as the existing rolls, where several holes were drilled on its length and directed to the inferior piece surfaces to enable the added oxygen to distribute uniformly in the kiln transversal section.

EXAMPLE B

[0030] Trials were performed to analyze the influence of an oxygen-enriched atmosphere on the black core defect. Samples of ceramic materials were characterized using x-ray diffraction (DRX) and chemical analysis by x-ray fluorescence. The temperatures of reactions and the oxidant atmosphere were determined by differential thermal analysis (DTA) and thermogravimetric analysis (TG).

[0031] Ceramic material samples were ignited in a laboratory scale furnace, simulating the industrial burning cycle. Additions of oxygen and oxygen/nitrogen mixture were made by furnace atmosphere enrichment and addition of oxygen directly in the ceramic material samples. A scanning electron microscope was used to examine the structures of the oxidized layers and the non-oxidized layers (black core).

[0032] The results of this trial demonstrated that oxygen addition, under the prescribed conditions, completely prevented the black core formation.

EXAMPLE C

[0033] A trial was conducted to determine the oxygen consumption in the process that prevented black core formation. Roller kilns are the most technologically advanced and widely used for enameled tile production and are very versatile as compared to conventional methods for introducing ceramic materials for firing. Some advantages for the use of roller kiln are its ability for good burning uniformity, bigger production with reduced burning cycles, lower production losses and lower fuel consumption. Another type of furnace is the tunnel kiln. The roller kiln furnace is preferred because it uses a single stage burning cycle, while the tunnel kiln furnaces uses a two stage burning cycle.

[0034] For this trial, a roller kiln produced by Enaplic Engenharia was used. The total width was 93 m, the useful width was 2.2 m. There were 35 rolls in each module, the burning cycle for low softening temperature enamel tiles was 43 min., and the burning cycle for refractory enamel tiles was 41 min. The tile production for low softening temperature enamel was 4500 m^2/day. The tile production for the refractory enamel tiles was about 4850 m^2/day. The fuel consumed in this trial was relatively low at about HHV 1480 kcal/Nm^3. Fuel consumption was about 26,000 Nm^3, and the temperature of the off gases at the kiln was from about 250°C to about 400°C. The tile mass in the kiln inlet was about 16.6 ± 0.4 kg/m^2, and the mass tile in the kiln outlet was about 16.2 ± 0.4 kg/m^2. The tile density in the furnace inlet was about 1.85 ± 0.02 g/cm^3. The moisture content in the tile at the furnace was about 2.00 ± 0.50% by mass. The water absorption of the tiles at the kiln outlet was about 4.5 ± 1.5% by volume. The tiles size at the furnace inlet was 360.2 mm x 360.2 mm and the tiles size at the furnace outlet was about 335.8 mm x 335.8 mm.

Oxygen addition in the kiln:

[0035] Oxygen was added directly to the ceramic tiles. Some of the spin rolls in the roller kiln furnace were replaced by static rolls at the positions where the oxygen was fed. During the trial, one static roll was replaced, and two spin rolls were maintained. Drilled rolls were made to feed oxygen into the kiln. One of the extremities was closed with refractory mortar, while oxygen was fed into the other extremity. Thirty (30) holes of 1.2 mm diameter (1900 mm in length) were drilled to distribute the oxygen flow to the ceramic tile pieces.
[0036] Thermogravimetric analysis and differential thermal analysis of the raw ceramic tile material showed mass loss and endothermic reaction in the temperature showed a range of from about 400°C to about 900°C. Oxygen was directed to the pre-heating zone in the temperature range of from about 400°C to about 900°C.
[0037] One hundred twenty spin rolls were substituted by an equal number of static rolls. Oxygen distributors were used to control the flow of oxygen to feed the four rolls in each module of the furnace. Each oxygen distributor was equipped with critical orifice system to measure the oxygen flow. Thirty oxygen distributors were installed in the kiln furnace. An oxygen rotameter was installed in to measure the total oxygen flow fed to the kiln furnace.
[0038] Measurements were performed in the field to determine the extent of black core defects. The kiln atmosphere was analyzed with the addition of oxygen in the static rolls and without oxygen addition. Fig. 1 provides a transverse view of the kiln furnace 100. Ceramic tiles 110 were passed through the furnace 100, preferably roller kiln furnace, at a position between the kiln roof 102 and kiln bottom 104. The static roll 132 used for oxygen addition was placed transversally across the kiln furnace. Monitor probes were placed at various positions 120, 122, 124 and 126 to measure the atmospheric measurements in the kiln.
[0039] Table I below provides the results of the trials using certain modules under specific oxygen flow for each roll in the furnace, and the resulting oxygen and carbon dioxide concentration at the various position resulting therefrom.

Cell	Probe Position	O_2 Conc.(%)	CO_2 Conc.(%)	O_2 added O_2 Conc.(%)	O_2 added CO_2Conc.(%)
A	122	4.30	13.00	17.80	10.10
	124	4.10	12.60	6.80	11.30
	126	4.20	12.40	7.70	10.70
	128	4.50	12.60	6.80	10.80
B	122	1.40	15.40	11.60	11.60
	124	1.90	14.90	7.80	12.10
	126	2.00	15.10	7.90	12.10
	128	1.90	14.40	7.80	11.50
C	122	1.10	15.30	12.40	11.20
	124	2.20	15.90	8.50	11.60
	126	1.30	16.30	8.20	12.40
	128	1.80	15.20	8.20	12.10

The above data were taken under the following trial conditions: the oxygen flow rate for each roll in cell A was 2.5 Nm^3/h @ fce; the oxygen flow rate for each roll in cell B was 1.8 Nm^3/h @ fce; and the oxygen flow rate for each roll in cell C was 1.3 Nm^3/h @ fce. Where oxygen was not added, the production rate was 4500 m^2/day of high softening temperature enamel; and where oxygen was added, the production rate was 4850 m^2/day of the same high softening temperature enamel. The total oxygen added by the rotameter was 138 Nm^3/h @ fce.
[0040] It is shown that the oxygen concentration is highest at position 122 (nearest the product) due to the way the oxygen is added in the furnace through the rolls.

EXAMPLE D

[0041] A trial to determine the formation of black core defect was performed using the procedure in Example C. The baseline conditions, as determined without oxygen, for high temperature softening enamel tiles was 4500 m^2/day without black core defects, with the compacting pressure of 280 bar. Results of this trial show that a production of 5020 m^2/day was achieved without formation of black core defects even when oxygen was provided at 2.25 Nm^3/h of oxygen for each roll. The total oxygen flow rate was 81 Nm^3/h.
[0042] The furnace temperature was from about 400°C to about 900°C, and the optimal temperature was from about 700°C to about 900°C. It was determined that at a furnace temperature of 700°C, the tile surface temperature was about 45°C lower than the furnace temperature. At a furnace temperature of about 900°C, the tile temperature was

about 15°C lower than the furnace temperature.

EXAMPLE E

[0043] A trial on the formation of black core in tiles with low softening temperature enamels was performed based on lead oxides. The performance of this type of tiles present difficulties because these enamel melts at a lower temperature, thus closing the pores in lower temperature and becoming more difficult for the interaction of the oxidant atmosphere with the organic compounds of the clay. As a result, the production rate of this kind of tiles is lower than, for example, the tiles used for trial in Example D.

[0044] The production rate was about 4540 m^2/day without the addition of oxygen, and at a compacting pressure of 343 bar. Very high black core defect results in the absence of oxygen, other than ambient oxygen. Comparatively, the addition of oxygen to the kiln furnace of about 185 Nm^3/h showed the increased production to about 5200 m^2/day, and decreased in black core defects to near trace amounts.

[0045] Specific features of the invention are shown in one or more of the drawings for convenience only, as each feature may be combined with other features in accordance with the invention. Alternative embodiments will be recognized by those skilled in the art and are intended to be included within the scope of the claims.

Claims

1. A method for reducing product defects in the production of ceramic products during the firing process and for increasing the production rate of said ceramic products, said method comprising

a. providing an enriched oxidizing atmosphere in a furnace at the vicinity of the ceramic products to maintain a heated oxidizing atmosphere;
b. passing said ceramic products for firing in the vicinity of said enriched oxidizing atmosphere; and
c. firing said ceramic products in the presence of said enriched oxidizing atmosphere.

2. The method of claim 1 which comprises adding an enriched oxygen-containing gas to said oxidizing atmosphere.

3. The method of claim 2 which comprises adding an enriched oxygen-containing gas to said oxidizing atmosphere at ambient temperature.

4. The method of claim 2 which comprises heating said enriched oxygen-containing gas prior to firing through a static roll.

5. The method of claim 2 which comprises preheating said enriched oxygen-containing gas outside of a kiln furnace.

6. The method of claim 2 wherein said oxygen-containing gas comprises adding an oxidizing atmosphere having an oxygen concentration of greater than about 1%.

7. The method of claim 1 wherein said enriched oxidizing atmosphere comprises pure oxygen.

8. The method of claim 1 which comprises passing said ceramic products for firing in a plurality of static rolls.

9. The method of claim 8 which comprises passing said ceramic products for firing in a plurality of static rolls drilled through its length in a longitudinal direction.

10. The method of claim 1 which comprises passing said enriched oxidizing atmosphere to the furnace through static rolls in said furnace.

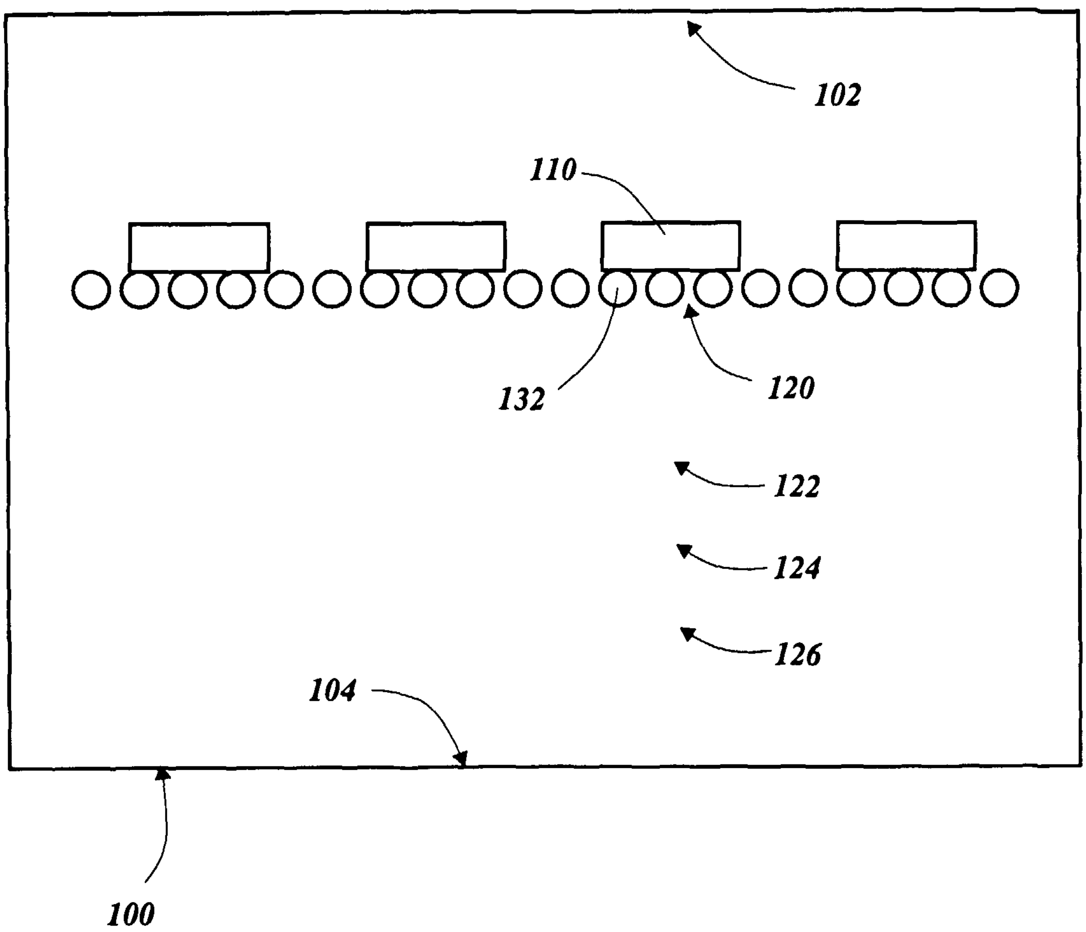

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 00 50 0199

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 391 585 A (E.K.RILEY) 5 July 1983 (1983-07-05) * claims; figures *	1,2,6,7	F27B9/36 F27B9/24
X	US 4 329 142 A (A.O.DYER) 11 May 1982 (1982-05-11) * claims; figures *	1,2,6,7	
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 203 (M-1590), 11 April 1994 (1994-04-11) & JP 06 003070 A (MURATA MFG CO LTD), 11 January 1994 (1994-01-11) * abstract *	4,8-10	
A	EP 0 184 749 A (LINDE AG) 18 June 1986 (1986-06-18)		
A	EP 0 184 175 A (LINDE AG) 11 June 1986 (1986-06-11)		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			F27B F27D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 December 2000	Coulomb, J

CATEGORY OF CITED DOCUMENTS

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19-12-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4391585 A	05-07-1983	GB 2073384 A	14-10-1981
		AR 226451 A	15-07-1982
		BR 8101675 A	29-09-1981
		CA 1144742 A	19-04-1983
		DE 3163948 D	12-07-1984
		EP 0036748 A	30-09-1981
		JP 1428744 C	09-03-1988
		JP 56149576 A	19-11-1981
		JP 62039357 B	22-08-1987
		KR 8501138 B	09-08-1985
		ZA 8102001 A	28-04-1982
US 4329142 A	11-05-1982	AU 537107 B	07-06-1984
		AU 5938580 A	08-01-1981
		CA 1138178 A	28-12-1982
		DE 3067743 D	14-06-1984
		DK 258380 A	19-12-1980
		EP 0021768 A	07-01-1981
		ES 492496 D	16-05-1981
		ES 8104974 A	01-08-1981
		GB 2057650 A,B	01-04-1981
		IE 49915 B	08-01-1986
		JP 1445124 C	30-06-1988
		JP 56045863 A	25-04-1981
		JP 62057592 B	01-12-1987
		ZA 8003595 A	28-04-1982
JP 06003070 A	11-01-1994	NONE	
EP 184749 A	18-06-1986	DE 3444542 A	19-06-1986
		AT 72894 T	15-03-1992
		DE 3585432 A	02-04-1992
		ZA 8509313 A	27-08-1986
EP 184175 A	11-06-1986	DE 3444536 A	12-06-1986
		DE 3585431 A	02-04-1992

EPO FORM P0459

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