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(54) **Modified coke lumps for mineral melting furnaces**

(57) The present application discloses modified coke lumps as fuel in mineral melting furnaces (cupola furnaces), for the production of stone wool, as well as the preparation thereof. The coke lump may carry an ablative coating of a carbon material or a non-volatile carbon-forming material and a non-volatile silicon material; or a substantial portion of the pores of a coke lump may comprise salts or precursor compound(s), which leave a non-volatile substance when heated to a temperature in the range of 1200-2000°C in inert or reducing atmosphere.

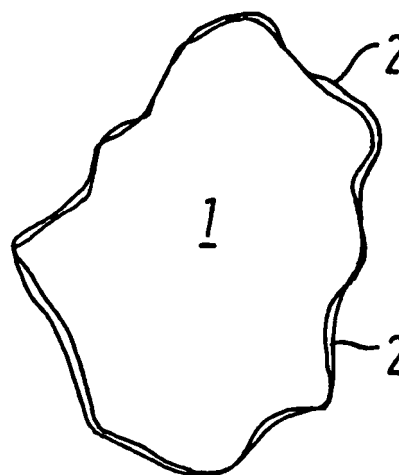


FIG. 1

Description

FIELD OF THE INVENTION

[0001] The present invention relates to modified, and thereby improved, coke lumps useful as fuel in mineral melting furnaces, in particular for the production of stone wool. The present invention also relates to the preparation of such modified coke lumps.

BACKGROUND OF THE INVENTION

[0002] The production of stone wool and, e.g., metal smelting are important industrial processes. The mineral melting in the production process for stone wool is typically conducted in a so-called cupola furnace in which the raw materials, e.g. coke and mineral materials such as rocks (e.g. of basalt, diabase, gabbro), briquettes (e.g. containing olivine, basalt, diabase, gabbro, slag, limestone, waste stone wool, etc.), are charged to the upper part of the furnace. Air is blasted through a number of nozzles near the bottom of the cupola. Most of the coke combusts at a very high temperature in the lower region just above the nozzles. The hot flue gas from the combustion containing carbon dioxide and water vapour flows up through the cupola and leaves the top at a significantly reduced temperature. The upward flowing flue gas transfers its energy to the down flowing raw materials that melt and to the coke. The raw materials melt in the region above the nozzles. The melt runs to the bottom of the cupola furnace and is collected in a melt bath located below the nozzles. The molten mineral material is found in the lower region of the furnace, and coke is predominantly found in a region just above the lower region.

[0003] A problem realised in conventional cupola furnaces is that a considerable amount of the fuel, i.e. in particular coke, is partly pyrolysed or gasified with carbon dioxide or water vapour in the furnace. Hereby a significant fraction of the thermal energy is lost from the cupola furnace and a significant amount of potentially problematic CO (carbon monoxide) and H₂ (hydrogen) is formed.

[0004] One way of reducing the gasification of coke is by use of a less reactive coke (normally related to a larger density of the carbon and a lower porosity of the lump) or by use of larger lumps of coke. A third alternative is by covering the coke surface with a solid surface layer as e.g. GB 1,409,971 disclosing a method of preparing a molten mineral mass in a coke-fired shaft furnace, wherein coke lumps are coated with a solid surface layer.

[0005] The present invention provides new solutions to the above problems.

BRIEF DESCRIPTION OF THE INVENTION

[0006] One main aspect of the present invention relates to coke lumps carrying an ablative coating. Hence, the present invention provides a coke lump carrying an ablative coating of a composition comprising (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon material(s), preferably having a weight average particle size of at the most 500 µm.

[0007] Another main aspect of the present invention relates to coke lumps wherein a substantial portion of the pores comprises a non-volatile substance. Hence, the present invention also provides a coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or (ii) precursor compound(s), which leave a non-volatile substance when heated to a temperature in the range of 1200-2000°C in inert or reducing atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

Figure 1 illustrates a coke lump (1) coated with a surface coating (2), in particular an ablative coating.

Figure 2 illustrates a coke lump (1) with an open pores system (3). For illustrative purposes, a pore (4) is filled with a solution of a salt and/or precursor compound (i.e. prior to heating to a temperature in the range of 1200-2000°C), whereas another pore (5) has a reduced diameter due to deposition of a non-volatile substance (e.g. a salt) resulting from heating of the salt or precursor compound to a temperature in the range of 1200-2000°C.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention relates to modified coke lumps.

[0010] In the present context, the term "coke" represents solid carbonaceous fuels with a predominant part of the available energy present in the form of a solid, non-volatile, but reactive above 800°C. Coke is typically a hard, dry

carbon substance produced by heating coal to a high temperature in the absence of air.

[0011] In the present context, the term "lump" reflects a block or a particle of material which will be held back by a grid or mesh having a spacing of 50 mm. Preferably, the block or particle will also be held back by a grid or mesh having a spacing of 90 mm. It should be understood that the before-mentioned definition relates to the modified coke lump.

Ablative coating

[0012] As mentioned above, the present invention provides a coke lump carrying an ablative coating of a composition comprising (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon material(s), preferably having a weight average particle size of at the most 500 μm .

[0013] In the present context, the term "ablative coating" in connection with coke lumps is intended to mean a coating which, when the coke lump is subjected to a temperature exceeding 1200°C, is capable of removing the heat energy from the coke to reduce the reactivity of the coke towards e.g. CO₂. Ablation is a process in which heat energy is consumed by a material through melting, vaporization or thermal decomposition and then dissipated as the material vaporizes or erodes. These ablative materials may be chemically constructed or made from natural materials.

[0014] Preferably, the ablative coating is present on the entire surface of the coke lump, however, in a cost efficient industrial process, it may not be possible to ensure that the entire surface of all (or just substantially all) of the coke lumps are fully covered. Hence, it should be understood that the term "carrying an ablative coating" in connection with a coke lump refers to a situation where at least 80% of the surface of the coke lump is covered by the ablative coating. More particular, at least 90%, or even more preferable, the entire surface, of the surface of the coke lump is covered by the ablative coating.

[0015] For a population of coke lumps, it should be understood that the term "carrying an ablative coating" refers to a situation where at least 80% of the surface of 90% of the coke lumps in a population of coke lumps is covered by the ablative coating. Thus, the present invention also relates to such a population of coke lumps.

[0016] The ablative coating of the coke lumps plays an important role and consists of a composition comprising of (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon material(s).

[0017] In the present context, the term "non-volatile" is intended to mean the fraction of a material which does not (significantly) evaporate, decompose or in any other way disappear from the surface where deposited, as the material is heated to a temperature of 1200°C in an inert or reducing atmosphere at standard pressure (101.3 kPa; 1 atm.).

[0018] It should be understood that the ablative coating may comprise minor amounts of volatile materials, e.g. up to 15% by weight, due to the presence of water, solvents, volatiles in the commercial products corresponding to the carbon/ carbon-forming and silicon materials.

[0019] The carbon/carbon-forming material(s) and the silicon material(s) will form the ablative coating when these materials are in intimate contact when heated.

[0020] It is believed that the relative weight ratio between the carbon/carbon-forming material(s) and the silicon material (s) is not particularly critical when the coke lump is used as fuel in a mineral melting furnace, because excess of the carbon material(s) will be consumed as fuel in the furnace, and because excess of the silicon material(s) will form part of the mineral melt. However, it is typically preferred that the composition comprises 10-90% by weight of the carbon or carbon-forming material(s) and 90-10% by weight of the silicon material(s), more particularly 20-80% by weight of the carbon or carbon-forming material(s) and 80-20% by weight of the silicon material(s). One, two or more carbon/carbon-forming materials may be combined with one, two or more silicon materials.

[0021] The carbon or carbon-forming materials can be selected from a plethora of materials, but the carbon materials are typically selected from tar, granulated coke, coke powder and carbon powder, whereas the carbon-forming materials are typically selected from sugars, carbohydrate syrups, molasses, polyurethanes, and phenol urea formaldehyde.

[0022] More particular, the one or more carbon or carbon-forming material(s) are selected from the group consisting of tar, carbohydrate syrups, molasses, and phenol urea formaldehyde.

[0023] The silicon materials can also be selected from a wide range of materials, but are typically selected from the group consisting of silica, silica fumes, silicones, siloxanes (including polysiloxanes), and silicate rich oxides and minerals, in particular from silica and silica fumes.

[0024] The silicon materials should preferably have a weight average particle size of at the most 500 μm in order to ensure a suitable contact between the carbon/carbon-forming material and the silicon material. Preferably, the weight average particle size is at the most 250 μm , especially at the most 100 μm . It is also preferred that at least 5% by weight of the particles of the silicon material(s) have a particle size exceeding 2 mm.

[0025] The "weight average particle size" can be determined by available particle size measurements (e.g. laser diffraction) and corresponding trivial recalculation to identify the diameter at which an equal weight is present as larger and smaller particles. It is of course understood that particles so atypically large that removal of a few particles will significantly alter the weight average particle size are not included in this measurement.

[0026] It should be understood that the composition may also comprise other constituents, e.g. up to 50% by weight of other materials, e.g. mineral materials, and binders, etc. When present, such mineral materials preferably constitute 3-50% by weight, in particular 5-25% by weight. Suitable examples of such mineral materials are those selected from the group consisting of bauxite, alundross, olivine, mullite, magnesite, lime, kaolin, dolomite, plastic clay, flyash and bentonite, although other similar, useful mineral materials may also be contemplated.

[0027] The thickness of the coating should be sufficient to suitably protect the inner coke lump. Hence, average thickness of the ablative coating is typically in the range of 0.1-10 mm, such as in the range of 0.5-2.5 mm.

[0028] The average thickness can be determined by examining a number of cross sections by an element sensitive method of higher spatial resolution; e.g. EDX in a SEM.

[0029] Based on the initial considerations, it is believed that the following compositions will be particularly useful as ablative coatings for coke lumps: (1) Tar with silica fumes or fine silica sand, and (2) molasses with silica fumes or fine silica sand.

[0030] The present invention also provides a process for the preparation of a coke lump carrying an ablative coating of a composition comprising (I) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (i) one or more non-volatile silicon material(s) as defined above, said process comprising the steps of:

(i) providing the coke lump,

(ii) spraying or soaking the coke lump with a coating composition comprising the one or more carbon or carbon-forming material(s) and the one or more silicon material(s), and

(iii) optionally drying and/or curing the coke lump.

[0031] In the first step, the coke lump is provided in such a way that it can be suitably sprayed. For example, the coke lump may be placed on a conveyer belt, or the like. Alternatively, the coke may be held in a rotating drum-shaped grid to allow spraying of all surfaces. A third option is placing the coke temporarily in a mesh cage suitable for dipping in said coating.

[0032] In the second step, the coke lump is sprayed with or soaked in a coating composition comprising the one or more carbon or carbon-forming material(s) and the one or more silicon material(s). The coating composition may either be the composition as such, but more preferably the coating composition comprises the carbon/carbon-forming materials) and the silicon material(s) of the final composition in combination with volatiles (e.g. diluents, wetting agents), mineral materials, binders, etc.

[0033] In one embodiment, the coating composition further comprises a binder. Examples of binders are those selected from the group consisting of plastic clay, flyash, bentonite, (Na,Al)PO₄, phosphate compounds, methyl cellulose, and other cellulose derivatives.

[0034] As mentioned above, the coating composition may further comprise 3-50% by weight (calculated on the basis of the non-volatiles) of mineral material(s).

[0035] After spraying or soaking, the coke lump may be dried or cured, or charged directly into the top of a mineral melting furnace, e.g. a cupola.

Impregnation of pores

[0036] The present invention also provides a coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or (ii) precursor compound(s), which leave a non-volatile substance when heated to a temperature in the range of 1200-2000°C in inert or reducing atmosphere.

[0037] The motivation for impregnation of pores relates to the well-known reaction rate of coke lump gasification. At low temperatures (e.g. 800-1000°C), the kinetics of coke gasification are limiting, i.e. the entire internal surface of the porous lump contributes to the reaction rate. As temperature increases, diffusional transport in pores of CO and CO₂ from and to the internal surface becomes limiting, and an increasing central volume of the coke lump is thus relatively inert to gasification; only the outer "shell" contributes significantly to the reaction rate. At even higher temperatures only the outmost surface of the lump is reacting, as diffusion in pores prevents significant reaction inside the coke lump. If the pore size distribution (and consequently the overall porosity) in the outmost part of the coke lump is lowered, diffusion limitation will be more pronounced at any temperature, and consequently the reactivity of the internal surface of the coke lump will be reduced at any intermediate temperature.

[0038] In the present context, the term "substantial portion" is intended to mean at least 50% of the pores within a distance of 5 mm from the surface of the coke lump, in particular at least 70% of such pores, such as at least 80%, or at least 90%, of such pores.

[0039] The one or more salt(s) and/or precursor compound(s) are, when leaving a non-volatile substance (e.g. a salt,

in particular the salt in non-decomposed form), believed to efficiently reduce the gas transport by diffusion, so that a lower gasification rate of the coke lump may be achieved (see, e.g., Figure 2). This effect is obtained either upon thermal conversion of the one or more precursor compound(s) at a temperature in the range of 1200-2000°C, whereby a suitable material, e.g. carbon, is deposited in the pores of the coke lump, or by simple deposition of a salt (with or without thermal decomposition/conversion) within the pores of the coke lump upon evaporation of the solvent for the salt.

[0040] The term "inert or reducing atmosphere" should be understood as not oxidizing relative to the deposited carbon at the temperatures being considered.

[0041] Also in the present context, the term "non-volatile" is intended to mean the fraction of a material which does not significantly evaporate, decompose or in any other way disappear from the surface where deposited, as the material is heated to a temperature of 1200°C in an inert or reducing atmosphere at standard pressure (101.3 kPa; 1 atm.)

[0042] Examples of useful precursor compounds are those selected from the groups consisting of tar, polyurethanes, phenol urea formaldehyde, sugars, carbohydrate syrups, and molasses.

[0043] Examples of useful salts are those selected from the group consisting of $\text{Ca}(\text{MnO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$ nitrates or chlorides of Al, Fe, Mg and Ca, and sodium silicate (water glass). Such salts will typically (which is also preferred) not undergo thermal decomposition/conversion upon heating to 1200°C.

[0044] Hence, the one or more salt(s) and/or precursor compound(s) are preferably selected from the groups consisting of tar, polyurethanes, and phenol urea formaldehyde, sugars, carbohydrate syrups, molasses, $\text{Ca}(\text{MnO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$, nitrates or chlorides of Al, Fe, Mg and Ca, and sodium silicate (water glass).

[0045] In particular, precursor compounds such as sugars and carbohydrate syrups with high carbon content as well as salts such as $\text{Ca}(\text{MnO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$ and water glass are expected to be advantageous.

[0046] As mentioned above, the portion of the pores of particular concern is pores within a distance of 5 mm from the surface of the coke lump. More particular, pores within a distance of 10 mm, especially pores within a distance of 20 mm, from the surface of the coke lump are considered and filled with the salt(s) and/or precursor compound(s).

[0047] The present Invention also provides a process for the preparation of a coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or (ii) precursor compound(s) as defined above, said process comprising the steps of:

(i) providing the coke lump,

(ii) optionally establishing a lower pressure around the coke lump to facilitate impregnation by re-establishing the ambient pressure after step (iii)

(iii) spraying or soaking the coke lump with a solution or dispersion comprising the one or more salt(s) and/or precursor compound(s), and

(iv) optionally drying and/or curing the coke lump.

[0048] Water is a suitable and useful solvent or dispersing agent for the solution or dispersion used in step (iii).

[0049] The solution or dispersion preferably comprises a wetting agent, e.g. a surfactant lowering the surface tension of water and/or enhancing penetration of water into the coke porosity.

[0050] The salts and/or precursor compounds may be applied to the coke lump in the form of a solution or a dispersion, preferably a colloidal dispersion. The salts are, however, preferably applied in the form of a solution in order to facilitate a suitable penetration into the pores of the coke lump.

[0051] After spraying or soaking, the coke lump may be dried or cured, or charged directly into the top of a mineral melting furnace, e.g. a cupola.

Surface Coating

[0052] The present application also provides a coke lump on which at least 80%, more particular at least 90%, or even more preferable the entire surface, of the surface is coated with a composition comprising one or more substances which remain essentially on the surface of the coke lump at temperatures above 1200°C, more particular above 1300°C, and especially above 1500°C. In particular, the composition include (i) a high melting particle material and optionally (ii) a lower melting material, the higher melting material being selected from the group of silica, bauxite, aludross, calcined bauxite, olivine, mullite, magnesite, lime, dolomite, kaolin, aluminium phosphate, sodium-aluminium phosphate, anorthosite, iron oxide and iron, and the optional lower melting material being selected from the group of bentonite, flyash, clay, cements, Portland cement, phosphates, crushed glass, crushed glass cullets or recycle glass, crushed stone wool fibres or glass wool fibres and sodium silicates (water glass). Alternatively, any subselection of the aforementioned materials may be applied.

[0053] The present invention also provides a process for the preparation of a coke lump as defined above, said process comprising the steps of:

(i) providing the coke lump,

(ii) spraying or soaking the coke lump with a suspension comprising the solid substance(s), and

(iii) optionally drying and/or curing the coke lump.

[0054] The suspension preferably comprises a wetting agent, in particular a surfactant lowering the surface tension of water.

[0055] The suspension may preferably further comprise a viscosity modifying agent, e.g. selected from the group consisting of plastic clay, flyash, bentonite, methyl cellulose and other cellulose derivatives.

[0056] The high melting particle material may in particular be selected among the substances silica, silica fumes, aludross, bauxite and olivine, the optional lower melting may in particular be selected among the substances Portland cement, clay and crushed stone wool fibres. The viscosity modifying additive may in particular be a cellulose derivate.

[0057] Another type of surface coating is so-called intumescent paints.

[0058] After spraying or soaking, the coke lump may be dried or cured, or charged directly into the top of a mineral melting furnace, e.g. a cupola.

EXPERIMENTALS

Example 1

[0059] The surface of coke may be provided with an ablative coating.

[0060] An ablative coating may be prepared, e.g., as a combination of silica and carbon. Silicate may be applied in the form of sand, silica fumes or other fine particles rich in silica. Carbon may be applied in the form of tar, sugar, molasses or other organic polymers or compounds with a substantial content of non-volatile carbon. Silicone or siloxane may be applied to provide one or both components by decomposition or partial combustion.

[0061] The ablative coating may be applied in the form of a suspension or solution or liquid, by methods such as e.g. dipping or spraying or passing a lacquer-blanket of the fluid.

Example 2

[0062] The pore structure in a coke lump may be partially blocked by application of a salt or a non-volatile substance.

[0063] The non-volatile substance may be present in the form of an organic or inorganic material which has been left upon heating of a precursor compound to 1200°C. The salt or precursor compound may be dissolved, molten or in other way liquefied, or as a gel or dispersion of particles with a predominant diameter which allows for a significant level of penetration into the porous structure of the selected coke. A wetting agent may be applied to ensure sufficient penetration into the porous structure of the coke. The medium for e.g. dissolution is preferentially water but other media may be used, e.g. organic solvents or fuels. Examples of salts and precursor compounds are given in Table 1.

Table 1 - Examples of salts and precursor compounds which may be applied to reduce activity of coke.

	Salts and precursor compounds
# 1	Tar
# 2	Sugar
# 3	Molasses
#4	$\text{Ca}(\text{MnO}_4)_2$
# 5	$\text{Ca}(\text{NO}_3)_2$
# 6	Water glass
# 7	Phenolic binder resin, e.g. phenol urea formaldehyde

[0064] The one or more salts and/or precursor compounds may be applied by methods such as e.g. dipping or spraying or passing a lacquer-blanket of the fluid. The applied fluid may or may not form a continuous film on the surface of the

coke after impregnation. The salts and/or precursor compounds may dry, decompose, crystallise or otherwise react before or during the passing down through the cupola to leave a non-volatile substance above 1200°C.

Example 3

[0065] A coke lump may be provided with a surface coating by application of a suspension.

[0066] The suspension may contain one or more high-melting oxides or minerals, one or more lower melting oxides or minerals or glasses as well as one or more viscosity regulating additives, or any subselection of the aforementioned materials. A binder serving to increase the adhesion of the dry coating on the coke may be used. Examples are given in Table 2. The particle sizes must be selected to match the application process. Materials are preferably suspended in water or a water-based liquid system, but organic based systems may be applied. Another specific example is use of so called intumescent paints.

Table 2 - Examples of coating materials and combinations of these which may be applied to reduce activity of coke.

	High melting material	Low melting material	Viscosity regulating material
Suspension 1	AlPO ₄	Glass cullet	Methylcellulose
Suspension 2	Olivine sand	Portland cement	bentonite
Suspension 3	Quartz sand	Water glass	Methylcellulose
Suspension 4	Portland cement	Crushed stone wool fibre waste	
Suspension 5	Kaolin		
Suspension 6	Iron oxide		Plastic clay
Suspension 7	Lime		Methylcellulose

[0067] Coke lumps are coated by methods such as e.g. dipping or spraying or passing a lacquer-blanket of the suspension. The coating dries before or during the passing down through the cupola.

Claims

1. A coke lump carrying an ablative coating of a composition comprising (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon material(s).
2. The coke lump according to claim 1, wherein the one or more silicon material(s) have a weight average particle size of at the most 500 µm.
3. The coke lump according to any one of the preceding claims, wherein the composition comprises 10-90% by weight of the one or more carbon or carbon-forming material(s) and 90-10% by weight of the one or more silicon material(s).
4. The coke lump according to any one of the preceding claims, wherein the one or more carbon or carbon-forming material(s) are selected from the group consisting of tar, granulated coke, coke powder, carbon powder, sugars, carbohydrate syrups, molasses, polyurethanes, and phenol urea formaldehyde.
5. The coke lump according to claim 4, wherein the one or more carbon or carbon-forming material(s) are selected from the group consisting of tar, carbohydrate syrups, molasses, and phenol urea formaldehyde.
6. The coke lump according to any one of the preceding claims, wherein the one or more silicon material(s) are selected from the group consisting of silica, silica fumes, silicones, siloxanes, and silicate rich oxides and minerals.
7. The coke lump according to claim 6, wherein the one or more silicon material(s) are selected from the group consisting of silica and silica fumes.
8. A process for the preparation of a coke lump carrying an ablative coating of a composition comprising (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon

material(s) as defined in any one of claims 1-7, said process comprising the steps of:

- (i) providing the coke lump,
- (ii) spraying or soaking the coke lump with a coating composition comprising the one or more carbon or carbon-forming material(s) and the one or more silicon material(s), and
- (iii) optionally drying and/or curing the coke lump.

9. A coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or (ii) precursor compound(s), which leave a non-volatile substance when heated to a temperature in the range of 1200-2000°C in inert or reducing atmosphere.

10. A process for the preparation of a coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or (ii) precursor compound(s) as defined in claim 9, said process comprising the steps of:

- (i) providing the coke lump,
- (ii) optionally establishing a lower pressure around the coke lump to facilitate impregnation by re-establishing the ambient pressure after step (iii),
- (iii) spraying or soaking the coke lump with a solution or dispersion comprising the one or more salt(s) and/or precursor compound(s), and
- (iv) optionally drying and/or curing the coke lump.

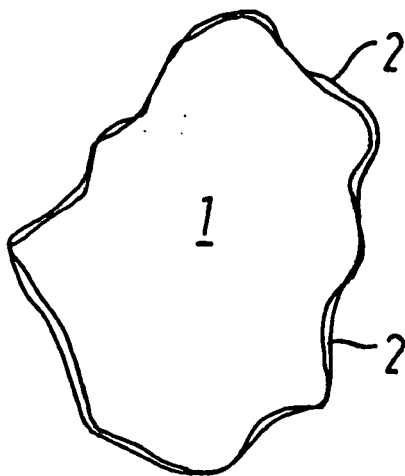


FIG. 1

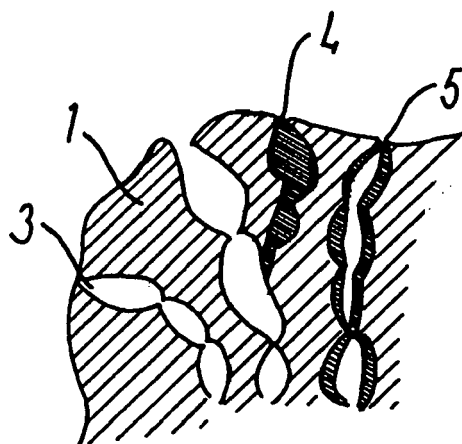


FIG. 2

EPO FORM 1503 03.82 (P04C01) 3

**CLAIMS INCURRING FEES**

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-8



The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-8

Coke lump carrying an ablative coating of a composition comprising (i) one or more carbon material(s) and/or non-volatile carbon-forming material(s) and (ii) one or more non-volatile silicon material(s). Method for producing the same comprising the step of spraying or soaking the coke lump with the afore-mentioned coating composition.

2. claims: 9-10

A coke lump wherein a substantial portion of the pores comprises one or more (i) salt(s) and/or precursor compound(s), which leave a non-volatile substance when heated to a temperature in the range of 1200-2000°C in inert or reducing atmosphere. Method for producing the same comprising the step of spraying or soaking the coke lump with a solution or a dispersion comprising the afore-mentioned salt(s).

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 07 5346

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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