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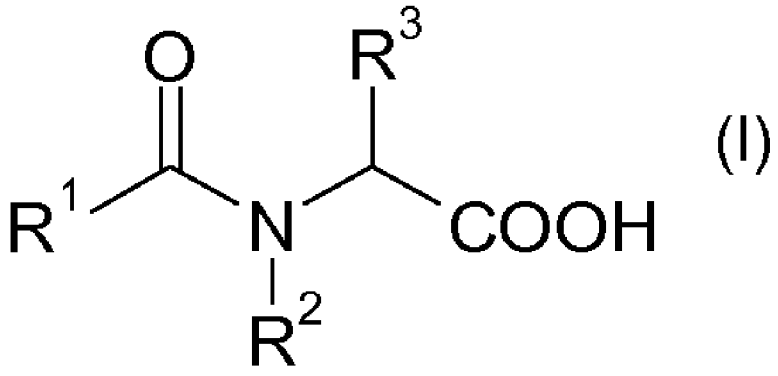
(54) Title: NON-CORROSIVE SOFT-MAGNETIC POWDER



(I)

(57) Abstract: The invention concerns a process for coating soft-magnetic powder, which comprises the step of treating the soft-magnetic powder with a solution containing: A) at least one inhibitor, which is a 5- to 12-membred heterocyclic compound containing at least one substituted or unsubstituted ring-nitrogen atom and at least one ring-carbon atom, wherein one ring atom is substituted with C_2 - C_{28} alkyl, C_2 - C_{28} alkenyl or C_2 - C_{28} alkynyl; and optionally B) at least one inhibitor, which is a compound with general formula (I), wherein R^1 indicates C_2 - C_{28} alkyl, C_2 - C_{28} alkenyl or C_2 - C_{28} alkynyl; R^2 and R^3 independently of each other indicate H, C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_1 - C_6 alkynyl, C_3 - C_7 cycloalkyl or C_6 - C_{12} aryl. The invention further relates to a soft-magnetic powder containing inhibitors of class A) and class B), use of such powder as well as an electronic component comprising such powder.

Non-corrosive Soft-Magnetic Powder

Description

The invention relates to a process of preparing non-corrosive soft-magnetic powder. The invention further relates to a product prepared by the process as well as the use of such a soft-magnetic powder.

Iron-based powders have long been used as a base material in the manufacture of electronic components. Other uses of such powders include metal injection molded parts, powder metallurgy, and various specialty products, such as food supplements.

A popular application of soft-magnetic powder includes magnetic core components, which serve as piece of magnetic material with a high permeability used to confine and guide magnetic fields in electrical, electromechanical and magnetic devices such as electromagnets, transformers, electric motors, inductors and magnetic assemblies. These components are usually produced in different shapes and sizes by molding soft-magnetic powder in a die under high pressure.

In electronic applications, particularly in alternating current (AC) applications, the two key characteristics of the magnetic core component are the magnetic permeability and the core loss characteristic. In this context, the magnetic permeability of a material provides an indication of its ability to become magnetized or its ability to carry a magnetic flux. Permeability is defined as the ratio of the induced magnetic flux to the magnetizing force or field intensity. When a magnetic material is exposed to a rapidly varying field, the total energy of the core is reduced by the occurrence of hysteresis losses and/or eddy current losses. The hysteresis loss is caused by the necessary expenditure of energy to overcome the retained magnetic forces within the core component. The eddy current loss is caused by the production of electric currents in the core component due to the changing flux caused by AC conditions and basically results in a resistive loss.

Generally, devices for high frequency applications are sensitive to core losses and in order to reduce losses due to eddy currents an improved insulating property is desired. The simplest way of achieving this is thickening the insulating layer for each particle. Furthermore, it has been found that rust causes reduction in resistance and a rust inhibiting layer can reduce such losses. However, the thicker the insulation layer is, the lower the core density of soft-magnetic particles gets and the magnetic flux density decreases. Furthermore, an attempt to increase the magnetic flux density by compression-molding under high pressure may lead to larger strain in the core and, hence, to a higher hysteresis loss.

In order to manufacture a soft-magnetic powder core having optimal key characteristics, it is necessary to increase the resistivity and the density of the core simultaneously. For this reason, particles would ideally be covered with a thin insulating layer having a high insulating property. In the field of magnetic powders different approaches to this problem exist.

WO 2007/084 363 A2 relates to a method for preparing metallurgical powder compositions and compacted articles made thereof. The metallurgical powder composition comprises a base-metal powder, which is at least partially coated by metal phosphate and a particulate internal lubricant. The internal lubricants used include, for example, polyamides, C_5 to C_{30} fatty acids, metal salts of polyamides, metal salts of C_5 to C_{30} fatty acids, ammonium salts of C_5 to C_{30} fatty acids, lithium stearate, zinc stearate, manganese stearate, calcium stearate, ethylene bis-stearamide, polyethylene waxes, polyolefins, and combinations thereof. Through the combination of phosphate coating and internal lubricant the lubricity of the metal particles and the compacted parts can be increased, while reducing the amount of organic compounds present.

EP 0 810 615 B1 describes a soft-magnetic powder composite core, which comprises particles with insulating layers. In particular, the soft-magnetic particles are treated by a solution comprising a phosphating solution, which comprises a solvent and phosphate salts. Additionally, the solution comprises a surfactant and a rust inhibitor, which is an organic compound containing nitrogen and/or sulfur having a lone pair of electrons suppressing the formation of iron oxide.

EP 0 765 199 B1 discloses admixing powder compositions of iron-based particles with a thermoplastic material and a lubricant selected from the group of stearates, waxes, paraffins, natural and synthetic fat derivatives and oligomers of polyamide type. The obtained mixture is compacted at a temperature below the glass-transition temperature or melting point of the thermo-plastic resin and the compacted product is heated in order to cure the thermoplastic resin. With the lubricant added to the thermoplastic material the process is less time consuming, but an essential improvement in the soft-magnetic properties cannot be reached.

Furthermore, in the field of metal processing, especially metal surface structures, different insulating layers are utilized to eliminate corrosion. CN 101 525 563 A for example refers to an after polishing detergent including a corrosion inhibitor that is used to protect the surface of a processing object from corrosion, when the chemical-mechanical polishing-cleaning is carried out. CN 100 588 743 A discloses an acid solution for treating magnesium alloy surfaces, which comprises two acids, a corrosion in-

hibitor and a wetting agent for activation of magnesium alloy surface to form a compact film.

US 5,415,805 A describes a composition and method for inhibiting corrosion of iron and iron containing metals in sulfur mines. The composition comprises an aqueous solution of an alcohol, an acid, a fatty imidazoline, and an ethoxylated fatty diamine, and an aqueous solution of a molybdate compound or salt thereof.

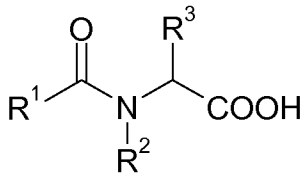
Known processes for forming insulating layers on magnetic particles typically tackle one of the key characteristics, i.e. the density or the insulation properties, while keeping the other constant. Therefore, the resistivity and magnetic permeability obtainable are limited. Hence, there is still a need in the art to further improve the process of treating soft-magnetic powders in order to reach optimal results for magnetic core components prepared from such powders.

Therefore, it is an object of the invention to provide a process for coating soft-magnetic powder and a corresponding soft-magnetic powder that facilitates to achieve high resistivity, high permeability and non-corrosive properties when utilized in magnetic core components. Furthermore, it is an object of the invention to provide a process which allows to achieve aforementioned goals in a simple, cost-effective and uncomplicated manner. Another object of the invention is to provide electronics components including soft-magnetic powder, which require no further corrosion protection. In this context, one object of the invention is to provide soft-magnetic powder that allows producing electronic components without further corrosion protection layers.

These objects are achieved by a process for coating a soft-magnetic powder comprising the step of treating the soft-magnetic powder with a solution containing:

(A) at least one first inhibitor, which is a 5- to 12-, preferably 5- to 9-, particularly preferably 5- to 7-membred heterocyclic compound containing at least one substituted or unsubstituted ring-nitrogen atom and at least one ring-carbon atom, wherein one ring atom, preferably one ring-carbon atom, is substituted with $C_2 - C_{28}$ alkyl, $C_2 - C_{28}$ alkenyl or $C_2 - C_{28}$ alkynyl, preferably $C_8 - C_{26}$ alkyl, $C_8 - C_{26}$ alkenyl or $C_8 - C_{26}$ alkynyl, more preferably $C_{12} - C_{22}$ alkyl, $C_{12} - C_{22}$ alkenyl or $C_{12} - C_{22}$ alkynyl and most preferably $C_{14} - C_{18}$ alkyl, $C_{14} - C_{18}$ alkenyl or $C_{14} - C_{18}$ alkynyl; and optionally

(B) at least one second inhibitor, which is a compound with general formula (I),



(I)

wherein

R^1 indicates C_2 – C_{28} alkyl, C_2 – C_{28} alkenyl or C_2 – C_{28} alkynyl, preferably C_8 – C_{26} alkyl, C_8 – C_{26} alkenyl or C_8 – C_{26} alkynyl, more preferably C_{12} – C_{22} alkyl, C_{12} – C_{22} alkenyl or C_{12} – C_{22} alkynyl and most preferably C_{14} – C_{18} alkyl, C_{14} – C_{18} alkenyl or C_{14} – C_{18} alkynyl;
R^2 and R^3 independently of each other indicate H, C_1 – C_6 alkyl, C_2 – C_6 alkenyl, C_1 – C_6 alkynyl, C_3 – C_7 cycloalkyl or C_6 – C_{12} aryl.

For the purposes of the present invention, -COOH also includes carboxylate which are preferably derivatives of a carboxylic acid function, in particular a metal carboxylate, a carboxylic ester function or a carboxamide or function. These include, for example, the esters with C_1-C_4-alkanoles such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol and tert-butanol.

The invention further pertains to a soft-magnetic powder containing at least one first inhibitor of class (A) as specified above and optionally at least one second inhibitor of class (B) as specified above, a soft-magnetic powder obtained by aforementioned process and uses of such powder in electronic components. The following description concerns the process as well as the product proposed by the invention. In particular, preferred embodiments of the inhibitor classes (A) and (B), the inhibitor composition and the soft-magnetic powder apply to the process for treating the soft-magnetic powder and the treated soft-magnetic powder alike.

The invention also concerns the use of the treated soft-magnetic powder for manufacturing electronic components, in particular magnetic core components as used in electrical, electro-mechanical and magnetic devices such as electromagnets, transformers, electric motors, inductors and magnetic assemblies. Further uses of the coated soft-magnetic powder include manufacture of Radio-Frequency Identification (RFID) tags and manufacture of elements reflecting or shielding electromagnetic radiation.

The invention provides a process for coating soft-magnetic powder and the corresponding treated powder which is optimally suitable for manufacturing electronic components. In particular, the soft-magnetic powder coated according to the invention allows to achieve high resistivity, high permeability and non-corrosive properties when

used for manufacture of electronic components, such as magnetic core components. The invention further allows to flexibly adapt such characteristics by modifying the treatment solution and the inhibitor content used therein. Furthermore, owing to the simple and uncomplicated manner of the proposed method, a high batch-to-batch consistency can be achieved, which again allows for reliable production of electronic components. Overall, the soft-magnetic powder coated according to the invention facilitates to prepare electronic components with unique electromagnetic performance characteristics. Additionally, electronic components comprising the soft-magnetic powder coated according to the invention do not require further layers for corrosion protection saving space and production costs.

A soft-magnetic powder of the present invention includes a plurality of particles composed of a soft-magnetic material. Such powders comprise particles with a mean size between 0.5 and 250 µm, preferably between 2 and 150 µm, more preferably between 2 and 10 µm. These particles may vary in shape. In respect of the shape, numerous variants known to the person skilled in the art are possible. The shape of the powder particles may, for example, be needle-shaped, cylindrical, plate-shaped, teardrop-shaped, flattened or spherical. Soft-magnetic particles with various particle shapes are commercially available. Preferred is a spherical shape as such particles can be coated more easily, which in fact results in a more effective insulation against electrical current.

As soft-magnetic material an elemental metal, an alloy or a mixture of one or more elemental metal(s) with one or more alloy(s) may be employed. Typical elemental metals comprise Fe, Co and Ni. Alloys may include Fe-based alloys, such as Fe-Si alloy, Fe-Si-Cr alloy, Fe-Si-Ni-Cr alloy, Fe-Al alloy, Fe-N alloy, Fe-Ni alloy, Fe-C alloy, Fe-B alloy, Fe-Co alloy, Fe- P alloy, Fe-Ni-Co alloy, Fe-Cr alloy, Fe-Mn alloy, Fe-Al-Si alloy and ferrites, or rare earth Fe-based alloy, such as Nd-Fe-B alloy, Sn-Fe-N alloy, Sm-Co alloy, Sm-Co-Fe-Cu-Zr alloy and Sr-ferrite. In a preferred embodiment Fe or Fe-based alloys, such as Fe-Si-Cr, Fe-Si or Fe-Al-Si, serve as soft-magnetic material.

In a particularly preferred embodiment Fe serves as soft-magnetic material and the soft-magnetic powder is a carbonyl iron powder. Carbonyl iron can be obtained according to known processes by thermal decomposition of iron pentacarbonyl in a gas phase, as described, for example, in *Ullmann's Encyclopedia of Industrial Chemistry, 5th Edition, Vol. A 14, page 599 or in DE 3 428 121 or in DE 3 940 347*, and contains particularly pure metallic iron.

Carbonyl iron powder is a gray, finely divided powder of metallic iron having a low content of secondary constituents and consisting essentially of spherical particles having a

mean particle diameter of up to 10 µm. Unreduced carbonyl iron powder, which is preferred in the present context, has an iron content of >97% by weight (here based on the total weight of the powder), a carbon content of <1.5% by weight, a nitrogen content of <1.5% by weight and an oxygen content of <1.5% by weight. Reduced carbonyl iron powder, which is particularly preferred in the process of the present invention, havs an iron content of >99.5% by weight (here based on the total weight of the powder), a carbon content of <0.1% by weight, a nitrogen content of <0.01% by weight and an oxygen content of <0.5% by weight. The mean diameter of the powder particles is preferably from 1 to 10 µm and their specific surface area (BET of the powder particles) is preferably from 0.2 to 2.5 m^2/g.

In a further embodiment of the invention the soft-magnetic powder is pre-treated, preferably phosphated. Phosphating may include coating the soft-magnetic material with an insulating amorphous compound, such as phosphoric acid or salts thereof with at least one element selected from the group consisting of Al, Si, Mg, Y, Ca, B, Zr, and Fe. Since these materials provide reasonably good insulation properties and sufficiently couple a metal to an organic compound, they are particularly suitable for pre-treating particles of the soft-magnetic powder. Furthermore, the pre-treatment prepares the surface of the powder particles such that the inhibitor(s) contained in the solution adhere more easily.

The average thickness of the coating stemming from the pre-treatment may lie between 1 nm to 1 µm, preferred between 1 and 50 nm. In addition, the amount of the coating with respect to the soft-magnetic material is not higher than 4 wt%, thus, a significant decrease in magnetic flux density of the magnetic core obtained by molding the soft-magnetic powder can be prevented.

One method of pre-treating the soft-magnetic particles includes mixing the soft-magnetic powder with phosphoric acid or salts thereof optionally mixed with an organic solvent. The person skilled in the art may choose an appropriate time and appropriate temperature conditions to form an iron phosphate layer. The pre-treatment may for example be carried out at room temperature for a period of 10 min to 10 hours. The solvent may then be evaporated by elevating the temperature to form dry powder. After phosphating the phosphor content typically varies between 0.01 and 1 %, preferably between 0.02 and 1 % by weight of the dry powder.

According to the invention, the at least one first inhibitor of class (A) is a 5- to 12-, preferably 5- to 9-, particularly preferably 5- to 7-membred heterocyclic compound containing at least one substituted or unsubstituted ring-nitrogen atom and at least one ring-carbon atom, wherein one ring atom, preferably one ring-carbon atom, is substituted

with C_2 – C_{28} alkyl, C_2 – C_{28} alkenyl or C_2 – C_{28} alkynyl, preferably C_8 – C_{26} alkyl, C_8 – C_{26} alkenyl or C_8 – C_{26} alkynyl, more preferably C_{12} – C_{22} alkyl, C_{12} – C_{22} alkenyl or C_{12} – C_{22} alkynyl and most preferably C_{14} – C_{18} alkyl, C_{14} – C_{18} alkenyl or C_{14} – C_{18} alkynyl.

Preferred heterocyclic compounds are imidazole, imidazoline, imidazolidine, benzimidazole, benzimidazoline, benzimidazolidine, thiazole, thiazoline, thiazolidine, benzthiazole, benzthiazoline, benzthiazolidine, oxazole, oxazoline, oxazolidine, benzoxazole, benzoxazoline, benzoxazolidine, pyridine, collidine, pyrimidine, triazole, benzotriazole, triazoline or tetrazole. More preferred heterocycles are imidazole, imidazoline, imidazolidine, benzimidazole, benzimidazoline or benzimidazolidine. Most preferred heterocycles are imidazole, imidazoline, imidazolidine.

In one embodiment the ring-nitrogen atom may be substituted by a monovalent straight or branched carbon chain R_{chain} having from 2 to 10, preferably from 2 to 6 carbon atoms, wherein the chain is substituted by at least one of the groups NH_2, OH, OR_Y, $OC(O)R_Y$, $OC(O)R_Z$, COOH, CO_2R_Y,

wherein R_Y means a monovalent straight or branched chain including from 1 to 10 carbon atoms, wherein R_Y may also be substituted by one or more substituents selected from R_Y, R_Z, F, Cl, Br, I, OH, CN, NO_2, CF_3, NH_2, NHR_Y, NHR_Z, NO_2, CO_2H, CO_2R_Y, CO_2R_Z, CO_2NH_2, SH, SO_3H, SO_2NH_2, CHO, $COCH_3$, CH_2OH,

wherein R_Z means aromatic hydrocarbon radicals having from 6 to 8 ring carbons, wherein R_Z may also be substituted by one or more substituents selected from R_Y, F, Cl, Br, I, CN, NO_2, CF_3, NH_2, NHR_Y, NO_2, CO_2H, CO_2R_Y, CO_2NH_2, SH, SO_3H, SO_2NH_2, CHO, $COCH_3$, CH_2OH.

Preferably R_Y means methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, 1-methylbutyl, tert-pentyl, neopentyl, n-hexyl, 3-hexyl, 2-methyl-1-pentyl, 3-methyl-1-pentyl, 4-methyl-1-pentyl, 2-methyl-2-pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, 2-methyl-3-pentyl, 3-methyl-3-pentyl, 2,2-dimethyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-ethyl-1-butyl, 2,3-dimethyl-2-butyl, 3,3-dimethyl-2-butyl, n-heptyl, n-octyl, 1-methylheptyl, 2-ethylhexyl, 2,4,4-trimethyl-pentyl, 1,1,3,3-tetramethylbutyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl.

R_Z is preferably unsubstituted or substituted phenyl, naphthyl, anthracenyl, phenanthrenyl, naphthacenyl, chrysenyl, pyrenyl, and particularly preferably phenyl or naphthyl.

Substituted R_Z is for example, 2-, 3- and 4-methylphenyl, 2,4-, 2,5-, 3,5- and 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2-, 3- and 4-ethylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diethylphenyl, 2,4,6-triethylphenyl, 2-, 3- and 4-propylphenyl, 2,4-, 2,5-, 3,5- and 2,6-dipropylphenyl, 2,4,6-tripropylphenyl, 2-, 3- and 4-isopropylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisopropylphenyl, 2,4,6-triisopropylphenyl, 2-, 3- and 4-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-dibutylphenyl, 2,4,6-tributylphenyl, 2-, 3- and 4-isobutylphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisobutylphenyl, 2,4,6-triisobutylphenyl, 2-, 3- and 4-sec-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-di-sec-butylphenyl, 2,4,6-tri-sec-butylphenyl, 2-, 3- and 4-tert-butylphenyl, 2,4-, 2,5-, 3,5- and 2,6-di-tert-butylphenyl, 2,4,6-tri-tert-butylphenyl and 2-, 3-, 4-dodecylphenyl; 2-, 3- and 4-methoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-dimethoxyphenyl, 2,4,6-trimethoxyphenyl, 2-, 3- and 4-ethoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-diethoxyphenyl, 2,4,6-triethoxyphenyl, 2-, 3- and 4-propoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-dipropoxyphenyl, 2-, 3- and 4-isopropoxyphenyl, 2,4-, 2,5-, 3,5- and 2,6-diisopropoxyphenyl, 2-, 3- and 4-butoxyphenyl, 2-, 3-, 4-hexyloxyphenyl; 2-, 3-, 4-chlorophenyl, 2,4-, 2,5-, 3,5- and 2,6-dichlorophenyl, trichlorophenyl, 2-, 3-, 4-fluorophenyl, 2,4-, 2,5-, 3,5- and 2,6-difluorophenyl, trifluorophenyl such as 2,4,6-trifluorophenyl, tetrafluorophenyl, pentafluorophenyl, 2-, 3- and 4-cyanophenyl; 2-nitrophenyl, 4-nitrophenyl, 2,4-dinitrophenyl, 2,6-dinitrophenyl; 4-dimethylaminophenyl; 4-acetylphenyl; methoxyethylphenyl, ethoxymethylphenyl.

Preferably R_{chain} is a monovalent straight or branched carbon chain having from 2 to 10 carbon atoms wherein the chain is substituted by at least one of group –OH, for example 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl, 2-hydroxy-2,2-dimethylethyl, 5-hydroxy-3-oxapentyl, 6-hydroxyhexyl, 7-hydroxy-4-oxaheptyl, 8-hydroxy-4-oxaoctyl, 8-hydroxy-3,6-dioxaoctyl, and the like.

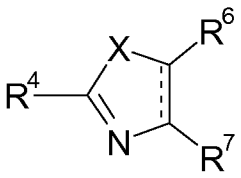
Preferably R_{chain} is a monovalent straight or branched carbon chain having from 2 to 10 carbon atoms wherein the chain is substituted by at least one of group –COOH, for example carboxymethyl, 2-carboxyethyl, 3-carboxypropyl, 4-carboxybutyl, 5-carboxypentyl, 6-carboxyhexyl, 7-carboxyheptyl, 8-carboxyoctyl, 9-carboxynonyl, 10-carboxydecyl, 12-carboxydodecyl and 14-carboxytetradecyl.

Preferably R_{chain} is a monovalent straight or branched carbon chain having from 2 to 10 carbon atoms wherein the chain is substituted by at least one amino group, e.g. 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl and the like.

Optionally the heterocyclic compound, particularly at least one carbon-ring atom, is further substituted with H, $C_1 – C_6$ alkyl, $C_2 – C_6$ alkenyl, $C_1 – C_6$ alkynyl, $C_3 – C_7$ cycloalkyl or $C_6 – C_{12}$ aryl, preferably $C_1 – C_6$ alkyl and more preferably methyl.

In a preferred embodiment of the invention, the compound of formula (I) is derived from a fatty acid. In this context, the fatty acid may be saturated or unsaturated, preferably unsaturated, and may be chosen from the group consisting of myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α-linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, docosahexaenoic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid and cerotic acid. Preferred fatty acids are palmitoleic acid, oleic acid, linoleic acid, linoelaidic acid, α-linolenic acid, lauric acid, lalmitic acid, ricinoleic acid or stearic acid. Particularly preferred fatty acids have 12 to 18 carbon atoms and 1 to 4 double bonds in the fatty acid, such as oleic acid, lauric acid, ricinoleic acid and stearic acid.

In a preferred embodiment the at least one second inhibitor of class (A) is a compound of the general formula (II):



(II)

In formula (II) R^4 indicates C_2 – C_{28} alkyl, C_2 – C_{28} alkenyl or C_2 – C_{28} alkynyl, preferably C_8 – C_{26} alkyl, C_8 – C_{26} alkenyl or C_8 – C_{26} alkynyl, more preferably C_{12} – C_{22} alkyl, C_{12} – C_{22} alkenyl or C_{12} – C_{22} alkynyl and most preferably C_{14} – C_{18} alkyl, C_{14} – C_{18} alkenyl or C_{14} – C_{18} alkynyl.

Here X can be chosen from the group consisting of O, S, NR^5. In a preferred embodiment X may be S or NR^5 and in a more preferred embodiment X is NR^5.

In this context, R^5 indicates H, C_1 – C_6 alkyl, C_2 – C_6 alkenyl, C_1 – C_6 alkynyl, C_3 – C_7 cycloalkyl or C_6 – C_{12} aryl, preferably H, C_1 – C_6 alkyl optionally substituted with 1 or 2 substituents from the group consisting of OH, COOH or NH_2.

Furthermore, the alkyl in R^5 is optionally substituted with 1 to 3 substituents from the group consisting of F, Cl, Br, C, OH, C_1 to C_4 alkoxy, C_6 to C_{10} aryl, CF_3, CN, NH_2.

R^6 and R^7 may be connected through a single or double bond and independently of each other indicate H, C_1 – C_6 alkyl, C_2 – C_6 alkenyl, C_1 – C_6 alkynyl, C_3 – C_7 cycloalkyl or C_6 – C_{12} aryl. Preferably R^6 and R^7 independently of each other indicate H, C_1 to C_6 alkyl, more preferably H or methyl.

In a preferred embodiment of the invention, the compound of formula (II) is derived from a fatty acid. In this context, the fatty acid may be saturated or unsaturated, preferably unsaturated, and may be chosen from the group consisting of myristoleic acid, palmitoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α-linolenic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, docosahexaenoic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, ….. Preferred fatty acids are palmitoleic acid, oleic acid, linoleic acid, linoelaidic acid, α-linolenic acid, lauric acid, lalmitic acid, ricinoleic acid and stearic acid. Particularly preferred fatty acids have 12 to 18 carbon atoms and 1 to 4 double bonds in the fatty acid, such as oleic acid, lauric acid, ricinoleic acid and stearic acid.

In the context of the present invention specifications in % by weight (wt %) refer to the fraction of the total weight of soft-magnetic powder unless otherwise specified. For instance, the solution for treating soft-magnetic powder includes first inhibitor(s) of class (A) as specified above, optionally second inhibitor(s) of class (B) and optionally further components such as a solvent. Here wt% refers to the fraction of total weight of soft-magnetic powder to be treated with the solution, unless explicitly stated. Hence the indication wt% is based on the total weight of soft-magnetic powder excluding other components e.g. from the solution.

The solution utilized in the method according to the invention preferably contains at least one inhibitor of each class (A) and (B) as specified above. In one embodiment the solution contains more than 0.05 wt%, preferably between 0.1 and 1.0 wt% and particularly preferably between 0.10 and 0.8 wt% of the at least one first inhibitor of class (A). Additionally, the solution may contain more than 0.03 wt%, preferably between 0.05 and 0.6 wt% and particularly preferably between 0.1 and 0.5 wt% of the at least one second inhibitor of class (B). The total fraction of inhibitor(s) contained in the solution may vary between 0.05 and 1 wt%, preferably between 0.1 and 0.5 wt%.

The weight ratio of inhibitor(s) of class (A) to inhibitor(s) of class (B) may lie between 0.5 and 10, preferably between 0.8 and 5 and particularly preferably between 1 and 3.

Furthermore, the solution may contain a solvent. Particularly suitable solvents are water, acetone, acetic acid, aceton-nitrile, glycerin, hexane, methyl *t*-butyl ether, propanol, benzene, ethanol or methanol. Examples of other suitable solvents are aromatic hydrocarbons, such as toluene or xylene; alkyl esters, such as methyl acetate, ethyl acetate, propyl acetate, butyl acetate, isobutyl acetate, isopropyl acetate, and 3-methylbutanol; alkoxy alcohols, such as methoxypropanol, methoxybutanol, ethoxypropanol; alkylbenzenes, such as ethylbenzene, isopropylbenzene; butyl glycol, butyl diglycol, alkyl glycol

acetates, such as butyl glycol acetate and butyl diglycol acetate; 2-methoxy-1-methylethyl acetate, diglycol dialkyl ethers, diglycol monoalkyl ethers, dipropylene glycol dialkyl ethers, dipropylene glycol monoalkyl ethers, diglycol alkyl ether acetates, dipropylene glycol alkyl ether acetates, ethers, such as dioxane and tetrahydrofuran, lactones, such as butyrolactone; ketones, such as acetone, 2-butanone, cyclohexanone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK); methylphenol (ortho-, meta-, or para-cresol), pyrrolidones, such as N-methyl-2-pyrrolidone; dimethylformamide, and also mixtures made of two or more of these solvents.

The solvent content in the solution may amount up to 50 wt%. Preferably the solvent content lies between 20 and 5 wt%.

The solution may be prepared by mixing at least one first inhibitor of class (A) and optionally at least one second inhibitor of class (B) with the solvent. The prepared solution may then be mixed with the soft magnetic powder. The method of mixing these components is not limited, and the mixing may be effected by a mixer, e.g. stirred tank, planetary mixer, paddle mixer or a kneader. After mixing the soft-magnetic powder and the solution including a solvent the mixture may be heated for the solvent to evaporate. In this manner a dry soft-magnetic powder is provided, that includes a non-corrosive thin coating.

The average thickness of the inhibitor coating may lie between 0.5 nm to 20 nm. In addition, the ratio of inhibitor coating to the soft-magnetic material is not higher than 0.1 and preferably not higher than 0.01. Thus a significant decrease in magnetic flux density of the magnetic core obtained by molding the soft-magnetic powder can be prevented.

The soft-magnetic powder treated according to the process described above and the treated soft-magnetic iron powder are particularly suitable for the manufacture of electronic components. Electronic components such as magnetic cores may be obtained by e.g. press molding or injection molding the soft-magnetic powder. To manufacture such electronic components, the soft-magnetic powder is typically incorporated with one or more types of resin, such as epoxy resin, urethane resin, polyurethane resin, phenolic resin, amino resin, silicon resin, polyamide resin, polyimide resin, acrylic resin, polyester resin, polycarbonate resin, norbornene resin, styrene resin, polyether sulfone resin, silicon resin, polysiloxane resin, fluororesin, polybutadiene resin, vinyl ether resin, polyvinyl chloride resin or vinyl ester resin. The method of mixing these components is not limited, and the mixing may be effected by a mixer, e.g. ribbon blender, tumbler, Nauta mixer, Henschel mixer or supermixer or kneading machine, e.g., Banbury mixer,

kneader, roll, kneader-ruder, paddle mixer, planetary mixer or monoaxial or biaxial extruder.

The composition is used to produce a magnetic or magnetisable molding. Particular moldings of this type are coil cores or coil formers, as used in electrical engineering. Coils with corresponding coil cores or coil formers are used by way of example as electromagnets, in generators, in laptop computers, in netbooks, in mobile telephones, in electric motors, in AC inverters, in electronic components in the automobile industry, in toys, and in the electronics industry. The composition can moreover be used to produce magnetic-field concentrators.

To produce a molding, the composition of soft-magnetic powder and resin is heated and molten at a melting point of the resein, preferably the thermoplastic resin, component, and then formed into an electronic component, such as a magnetic core of desired shape. Then the composition is compressed in a mold to give a molding. The compression produces a molding which has high strength.

Another method to produce the molding includes the composition of soft-magnetic powder and resin, which is pressed in a mold at pressures up to 1000 MPa, preferably up to 500 MPa with or without heating. After compression the molding is left to cure.

The soft-magnetic powder treated according to the process described above or containing at least one first inhibitor of class (A) and optionally at least one second inhibitor of class (B) as described above may be used in electronic components, in particular magnetic core components as used in electrical, electro-mechanical and magnetic devices such as electromagnets, transformers, electric motors, inductors, and magnetic assemblies, manufacture of Radio-Frequency Identification (RFID) tags and for reflecting or shielding electromagnetic radiation.

Powder injection molding allows to produce complex metal parts cost effectively and efficiently. Powder injection molding typically includes pressing the soft-magnetic powders together with a polymer as adhesive into the desired shape, the adhesive is then removed and the powder is compacted into a solid metal part in the sintering phase. This works particularly well with carbonyl-iron powder because the spherical iron particles can be packed together very tightly.

In the production of RFID tags (Radio-Frequency Identification), which are labels in the size of rice grains for automatic object localization or identification, soft-magnetic powder may be employed in printing the RFID structure.

Lastly, electronic components manufactured of soft-magnetic powder may be used for shielding electronic devices. In such applications, alternating magnetic field of the radiation causes the powder particles to continuously rearrange themselves. Due to the resulting friction, the powder particles convert the energy of the electromagnetic waves into heat.

Examples

Preparation of carbonyl iron powder

In the examples, 2,2kg of phosphated carbonyl iron powder (CIP) were filled into a 1,2L coated tinplate beaker, which was placed into a planetary mixer. After inerting by flushing with $N_2$190mL of acetone containing the corresponding chemicals was added. The inhibitors used in these examples are oleyl-imidazoline as first inhibitor of class A and oleyl-sarcosine as second inhibitor of class B. The composition of respective solutions are given in Tables 1 and 3.

After stirring the slurry with paddle mixers by 30-100 r/min for 30min at room temperature, the temperature was raised above the boiling point of acetone. After 3 to 4 hours of heat treatment the dry powder was ready to use.

Table 1 specifies the solutions prepared in examples 1 to 11 with oleyl-imidazoline as first inhibitor of class A and oleyl-sarcosine as second inhibitor of class B.

Example no.	Inhibitor A [wt%]	Inhibitor B [wt%]	total content of inhibitors A and B [wt%]	ratio inhibitor A to inhibitor B
1	0,100%	0,050%	0,15%	2,0
2	0,200%	0,100%	0,30%	2,0
3	0,333%	0,167%	0,50%	2,0
4	0,300%	0,000%	0,30%	Inhibtor A only
5	0,000%	0,300%	0,30%	Inhibitor B only
6	0,066%	0,033%	0,10%	2,0
7	0,033%	0,017%	0,05%	2,0
8	0,667%	0,333%	1,00%	2,0
9	0,250%	0,250%	0,50%	1,0
10	0,375%	0,125%	0,50%	3,0
11	0,262%	0,238%	0,50%	1,1

Table 2 specifies the solution prepared in example 12 with oleyl-imidazoline as first inhibitor of class A and stearoyl sarcosine as second inhibitor of class B.

Example no.	Inhibitor A [wt%]	Inhibitor B [wt%]	total content of inhibitors A and B [wt%]	ratio inhibitor A to inhibitor B
12	0,100%	0,20%	0,3%	2,0

Mixing with epoxy resin

The coated CIP powder (100g) was mixed with epoxy resin (Epikote 1004, Momentive) by dissolving the epoxy resin (2.8g) in a solvent (20mL; e.g. acetone, methylethylketone). In a glass beaker the coated CIP is stirred together with the epoxy solution using a dissolver mixer (IKA, RW20 D2M, 1000 R/min). After mixing the slurry is poured in an aluminum plate, which is then put in a fume hood for 8h. The resulting dry CIP epoxy plate is milled in a knife mill (Kinematica, Microtron MB550) for 10 seconds to yield the ready to press powder.

Molding and wiring of ring core

6.8g (±0.1g) of the ready to press powder is put into a steel mold (ring type: outer diameter 20.1mm; inner diameter 12.5mm; resulting height approximately 5-6mm) and

molded at 440MPa for a couple of seconds. From the exact mass and height of the ring the density of the ring core is calculated. The ring core is wired (20 windings) with an isolated 0.85mm copper wire (Isodraht, Multogan 2000MH 62) for determination of the permeability and resistivity.

Measurement of Permeability and Resistivity

An LRC meter (E4980A Agilent) was used to measure permeability of a ring core. All measurements were done at 100kHz with 0V DC bias. The test AC current of 10mA was applied to the ring core.

To measure the resistivity of the pressed parts, a power supply was connected in series to a voltmeter and a sample. 300 Volts were applied to a multimeter and the sample connected in series. Voltage reading of a multimeter was used to estimate the resistance of the sample using following equation.

$$R_{sample} = R_{meter} \times (V_{PS} - V_{meter})/V_{meter},$$

where R_{sample} is the resistance of the cylinder, R_{meter} is the internal resistance of the meter, V_{PS} is the applied voltage from power supply (=300V), and V_{meter} is the reading from the voltmeter.

Corrosion test

A filter paper (Macherey-Nagel, MN640W) was placed in a plastic petri dish (Ø 33mm, 12mm height).1g of the coated powder (without epoxy) was placed on the filter paper. 2mL of destilled water was added onto the powder and the petri dish was closed. The closed petri dish was put into a climate chamber set to 85°C and 85% relative humidity. After 24h the petri dish was removed from the climate chamber and opened. The filter paper was rinsed with water to remove the iron powder and rinsed a second time with acetone before drying. If iron oxides or hydoxides are formed the filter paper turns orange to brown or orange to brown spots are observed. The corrosion resistance was evaluated by inspection of the dried filter paper: ++ corresponds to no traces of corrosion; + corresponds some small (<2mm) orange/brown dots or a thin (<2mm) line around the powder; - corresponds some (>2mm) orange/brown dots or a (>2mm) line around the powder; -- complete paper is orange/brown colored.

Test Results

After treatment of the carbonyl iron powder and formation of the compacted samples the permeability, resistivity and the corrosion characteristics were determined as described above. The results for examples 1 to 11 are given in Table 2.

In comparison Table 3 specifies in line 1 the permeability, resistivity and corrosion resistance for phosphated carbonyl iron powder that has not been treated with inhibitors A or B. In this context, examples no. 4 and no. 5 including either inhibitor A or B illustrate the effect of each inhibitor individually on the permeability, resistivity and corrosion resistance. Whereas a treatment with inhibitor A (example no. 11) results in a high corrosion resistance, a reasonably high permeability but a small resistivity, treatment with inhibitor B (example no. 5) yields a high permeability and a high resistivity, but only intermediate corrosion resistance.

Examples 1 to 3 and 6 to 11 including phosphated carbonyl iron powder treated with both inhibitors show that the characteristic parameters of a compacted device, such as a magnetic core, may be optimized by adapting the contents. In particular an increasing content of inhibitor A reveals better corrosion resistance and higher resistivity. On the other hand a higher content of inhibitor B leads to an increase in permeability up to a threshold of about 0.3 wt%. An optimal inhibitor composition is reached in example 2, where the solution for treating phosphated carbonyl iron powder contains around 0.2 wt% of inhibitor A and 0.1 wt% of inhibitor B. Such a composition leads to a compacted sample core, which exhibits high permeability as well as resistivity values and a high corrosion resistance.

Table 3 specifies the characteristic properties of compacted samples of magnetic cores prepared of the mixtures specified in Table 1.

Example no	density [g/cm^3]	permeability	resistivity [MΩ]	corrosion characteristics
1	5,8925	23,0	900	+
2	5,9656	24,5	2500	++
3	5,8764	24,4	2000	+
4	5,8853	24,5	280	++
5	5,8910	25,1	1000	--
6	5,8485	24,4	540	-
7	5,8593	22,9	540	--
8	5,8732	23,8	2100	++
9	5,8529	24,0	600	+
10	5,9117	23,8	1900	++
11	5,9055	23,8	640	++

Table 4 specifies a comparative example for phosphated carbonyl iron powder without further coating.

Example no.	Corrosion	Permeability	Resitivity [MΩ]
13	--	22.7	40

Table 5 specifies the characteristic properties of compacted samples of magnetic cores prepared with the mixture specified in Table 2.

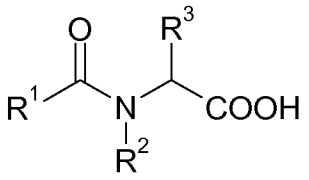
Example no.	density [g/cm^3]	permeability	resistivity [MΩ]	corrosion characteristics
12	5,94	23,0	1100	+

Claims

1. A process for coating soft-magnetic powder, which comprises the step of treating the soft-magnetic powder with a solution containing:

A) at least one first inhibitor, which is a 5- to 12-membred heterocyclic compound containing at least one substituted or unsubstituted ring-nitrogen atom and at least one ring-carbon atom, wherein one ring atom is substituted with $C_2 – C_{28}$ alkyl, $C_2 – C_{28}$ alkenyl or $C_2 – C_{28}$ alkynyl; and optionally

B) at least one second inhibitor, which is a compound with general formula (I),



(I)

wherein

R^1 indicates $C_2 – C_{28}$ alkyl, $C_2 – C_{28}$ alkenyl or $C_2 – C_{28}$ alkynyl;
R^2 and R^3 independently of each other indicate H, $C_1 – C_6$ alkyl, $C_2 – C_6$ alkenyl, $C_1 – C_6$ alkynyl, $C_3 – C_7$ cycloalkyl or $C_6 – C_{12}$ aryl.

2. The process of claim 1, wherein the heterocyclic compound of the at least one first inhibitor of class (A) is chosen from the group consisting of imidazole, imidazoline, imidazolidine, benzimidazol, benzimidazoline, benzimidazolidine, thiazole, thiazoline, thiazolidine, benzthiazole, benzthiazoline, benzthiazolidine, oxazole, oxazoline, oxazolidine, benzoxazole, benzoxazoline, benzoxazolidine, pyridine, collidine, pyrimidine, triazole, triazoline, benzotriazole, tetrazole.

3. The process of claim 1 or 2, wherein the heterocyclic compound is further substituted with H, $C_1 – C_6$ alkyl, $C_2 – C_6$ alkenyl, $C_1 – C_6$ alkynyl, $C_3 – C_7$ cycloalkyl or $C_6 – C_{12}$ aryl.

4. The process of claims 1 to 3, wherein the compound of formula (I) is derived from a fatty acid.

5. The process of claims 1 to 4, wherein the solution contains at least one inhibitor of each class A) and B).

6. The process of claims 1 to 5, wherein the solution contains more than 0.05 wt % of the first inhibitor of class A).

7. The process of claims 1 to 6, wherein the solution contains more than 0.03 wt% of the second inhibitor of class B).

8. The process of claims 1 to 7, wherein the weight ratio of one or more inhibitor(s) of class A) to one or more inhibitor(s) of class B) is higher than 1.

9. The process of claims 1 to 8, wherein the soft-magnetic powder is a carbonyl iron powder.

10. The process of claims 1 to 9, wherein the soft-magnetic powder is pre-treated.

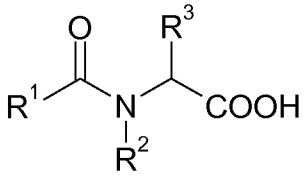
11. The process of claim 10, wherein the soft-magnetic powder is phosphated.

12. A soft magnetic powder obtained by the process according to claims 1 to 11.

13. A soft-magnetic powder containing:

A) at least one inhibitor, which is a 5- to 12-membred heterocyclic compound containing at least one substituted or unsubstituted ring-nitrogen atom and at least one ring-carbon atom, wherein one ring atom is substituted with $C_2 - C_{28}$ alkyl, $C_2 - C_{28}$ alkenyl or $C_2 - C_{28}$ alkynyl; and optionally

B) at least one inhibitor, which is a compound with general formula (I),



(I)

wherein

R^1 indicates C_2 – C_{28} alkyl, C_2 – C_{28} alkenyl or C_2 – C_{28} alkynyl;
R^2 and R^3 independently of each other indicate H, C_1 – C_6 alkyl, C_2 – C_6 alkenyl, C_1 – C_6 alkynyl, C_3 – C_7 cycloalkyl or C_6 – C_{12} aryl.

14. Use of the soft-magnetic powder of claims 12 or 13 for the manufacture of electronic components.

15. An electronic component comprising the soft-magnetic powder of claims 12 or 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/070008

A. CLASSIFICATION OF SUBJECT MATTER
INV. B22F1/00 H01F1/24 H01F1/26 H01F41/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B22F H01F C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/233811 A1 (BLETTNER CARSTEN [DE] ET AL) 29 September 2011 (2011-09-29) paragraph [0022] - paragraph [0028] paragraph [0035] paragraph [0046]	1-15
X	US 2009/087684 A1 (OMURA KAZUFUMI [JP] ET AL) 2 April 2009 (2009-04-02) paragraph [0002] paragraph [0038] - paragraph [0041] paragraph [0096]	1-15
X	US 5 160 447 A (ISHIKAWA MASAYUKI [JP] ET AL) 3 November 1992 (1992-11-03) column 17, line 52 - column 18, line 2	1-15

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 January 2014	27/01/2014

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Morra, Valentina

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/220837 A1 (TOKUMITSU SHUZO [JP] ET AL) 15 September 2011 (2011-09-15) the whole document	1-15
A	US 5 415 805 A (BROWN J MICHAEL [US] ET AL) 16 May 1995 (1995-05-16) cited in the application the whole document	1-15

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/070008

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1, 3-15(all partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1, 3-15(all partially)

Present claims 1, 3-15 relate to an extremely large number of possible compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds claimed, see examples.
The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1, 3-15 (PCT Guidelines 9.19 and 9.23).
The search of claims 1, 3-15 was restricted to those claimed compounds which appear to be supported and a generalisation of their structural formulae, i.e. the compunds wherein the heterocyclic compound of the at least one first inhibitor of class (A) is chosen from the group consisting of imidazole, imidazoline, imidazolidine, benzimidazol, benzimidazoline, benzimidazolidine, thiazole, thiazoline, thiazolidine, benzthiazole, benzthiazoline, benzthiazolidine, oxazole, oxazoline, oxazolidine, benzoxazole, benzoxazoline, benzoxazolidine, pyridine, collidine, pyrimidine, triazole, triazoline, benzotriazole, tetrazole.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/070008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011233811 A1	29-09-2011	NONE	
US 2009087684 A1	02-04-2009	JP 5219715 B2	26-06-2013
		JP 2009259371 A	05-11-2009
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