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(54) METHOD FOR STRONGLY REDUCING THE SIZE OF GRANULAR MATERIALS

(57) This invention provides a process for reducing the average particle size of a granular material by a factor of at least 20 by:
- providing a mixing vessel equipped with (A) a high speed disperser and (B) a rotor stator mixer,
- providing a liquid medium to the mixing vessel,
- switching on the high speed disperser (A) at a speed ranging from 1 to 50 m/s,
- adding to the mixing vessel a granular material having an average particle size ranging from 1 to 5 mm,
- operating the high speed disperser (A) for a period of time sufficient to reduce the average size of the granular material by a factor of at least about 10, thus producing granules of an intermediate average size ranging from 0.1 to 0.5 mm, and
- switching on the rotor stator mixer (B) and operating it for a period of time sufficient to reduce the average size of the intermediate granules by a factor of at least about 2.

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Description

Field of the Invention

[0001] The present invention relates to aqueous systems. More specifically the present invention relates to that can be safely manufactured while using equipment standard in the art of dispersion technology.

Background of the Invention

[0002] Various processes have been described for significantly reducing the particle size, i.e. the average particle size, of granular chemical materials of various types.

[0003] For instance, EP 2 586 849 discloses reducing the particle size of a granular mono-ammonium phosphate (MAP), by means of a method comprising the steps of:

a. providing a mixing vessel equipped with internal agitating means and optionally with internal wall scraping means, said mixing vessel (i) having an internal high speed rotor/stator mixer and/or being externally connected to a high speed inline rotor/stator mixer,
b. providing to said mixing vessel (1) water, (2) a defoamer, (3) MAP in the form of granules or particles with an average diameter ranging from 50 μm to 5 mm, in such proportions that the resulting water/MAP blend contains, per 100 parts by weight, 20% to 65% MAP and 35% to 80% water;
c. mixing the water/MAP blend in the presence of the foamer (2) until the MAP granules or particles provided in step (b) are disintegrated into both optically detectable solid particles and non-optically detectable solid particles; and
d. adding a thickener to set the viscosity of the aqueous system between 100 cps and 200 cps.

[0004] However, this method has proved to be far from ideal. One issue is that the granules of any chemical, tend to settle down very quickly, when added to the liquid medium or vehicle (whether water or another), in case only a rotor stator system is connected to the mixing vessel. The rotor stator inline mixer or the rotor stator batch mixer may well be blocked by a too high feed rate of added granules. For instance, if a mixing vessel connected to the rotor stator system, is filled with 50% water, it may be noticed that when adding granules to the water, these granules go immediately to the bottom of the vessel and thus create a high concentration of granules vs. Water at the bottom of the mixing vessel. The inline rotor stator mixer receives an input of a too much granule concentration and will block. In the event of a batch type rotor stator mixer, the rotor will aspire the granules and gets blocked because the distribution of the granules is not homogenous. Thus, as a whole and despite the apparent advantage of a one-step operation, the above mentioned method was found too difficult to be safely and continuously operated, i.e. too complicated in practice for large scale production.

[0005] There is a need in the art for designing a process that:

- is applicable to a very wide range of granular chemical materials, whether natural or synthetic, mineral or organic;
- makes use of commercial standard, easy to maintain, manufacturing equipment;
- makes use of inexpensive liquid vehicles (in particular water) and, if need be, inexpensive optional grinding aids;
- is versatile by nature, its main operating parameters being tailored at will by the skilled person, depending upon the kind of granular material to be reduced in size, without performing vast experimentation;
- provides a significantly high specific surface area of fine and very fine particles; and
- can provide a fine particle size distribution that, despite a huge proportion of very fine particles, can be adequately and readily measured and monitored by quantitative determination methods well known to the skilled person, in particular for the purpose of quality production control in a manufacturing plant.

Summary of the invention

[0006] The above needs in the art are met by a process wherein size reduction is performed in at least two steps, the first step being performed by operating a high speed disperser having a mixing disk, and the second step being performed by operating a rotor stator mixer, for instance the type of rotor stator mixer disclosed in EP 2 586 849, the content of which is incorporated by reference. We have found that a combination of a rotor stator system (inline or batch type), combined with any type of high speed disperser having a disk preferably having tooth shapes at the edge of the disk, whether with a closed disk or an open disk, whether with 1, 2 or 3 levels or teeth, can keep the granules in a homogenous state in the liquid medium, and thus avoid entrance of a non-homogenous feed of granules into the rotor stator system, and avoid the risk of consequently blocking the stator. More specifically the process of the present invention is as defined in claim 1, i.e. a process for reducing the average particle size of a granular material by a factor of at least 20, said process comprising the steps of:

- providing a mixing vessel equipped with (A) a high speed disperser having a mixing disk and (B) a rotor stator mixer,
- providing a liquid medium to the mixing vessel,
- switching on the high speed disperser (A) at a circumferential speed of the mixing disk ranging from 1 to 50 m/s,
- adding to the mixing vessel a granular material hav-

ing an average particle size ranging from 1 to 5 mm, said mineral granular material being compatible with the liquid medium,

- operating the high speed disperser (A) for a period of time sufficient to reduce the average size of the granular material by a factor of at least about 10, thus producing granules of an intermediate average size ranging from 0.1 to 0.5 mm,
- switching on the rotor stator mixer (B) and operating said rotor stator mixer for a period of time sufficient to reduce the average size of the intermediate granules by a factor of at least about 2, thus producing fine particles having an average size ranging from 0.001 to 50 μm, as determined by a laser diffraction system.

[0007] Additional optional or preferred features of the process in accordance with the present invention are apparent from the dependent claims. In particular, the process in accordance with the present invention may comprise the use of one or more thickeners, which may be of different types, e.g. thickeners that are able to swell in water during the initial stage of the process, and/or thickeners which are able to control and adjust the desired viscosity in the final stage of the process. The process in accordance with the present invention may also comprise the use of one or more dispersing agents for aqueous systems.

Definitions

[0008] Unless stated otherwise herein, the term "rotor stator mixer" refers to an equipment substantially as described in EP 2 586 849.

[0009] Unless stated otherwise herein, the term " high speed disperser having a mixing disk" refers to a so-called high speed disperser (or dissolver) having a mixing disk, either closed or open, preferably having 1, 2 or 3 levels of tooth shapes at the edge of the disk. Examples of such, or funcionally equivalent, are available from various suppliers, including but without limitation:

- Morehouse Cowles (13930 Magnolia Ave., Chino, CA 91710, United States of America); for details of specifications, including the fundamentals of dispersions, basics and principles of dispersion technology, mode of operation of the impeller, and so on, reference is made to the publicly available documentation of this company;
- Siehe Industry, Hongqiao District, Shanghai, China;
- TMBA Europe b.v., Noordwijkerhout, The Netherlands; and
- G. Ferrari Fils sprl, Parc Industriel, 7822 Ghislenghien, Belgium.

Detailed description of the Invention

[0010] We herein describe various embodiments or preferred embodiments of each aspect of the present invention, which may be combined at will and without limitation, as long as the functional goal of the invention is achieved. Unless explicitly specified herein, narrower ranges of certain features within the above described broad expression of the present invention are not intended to be preferred but merely illustrative.

[0011] In accordance with an embodiment of the present invention, the granular material may be mineral, e.g. selected from the group consisting of phosphates, sulfates (for instance aluminum sulfate), borates, hydrates (for instance aluminum hydrate), zeolites, hypophosphites, alkaline earth carbonates (for instance calcium carbonate), and alkaline earth oxides and hydroxides (for instance magnesium oxide, magnesium hydroxide). In accordance with another embodiment of the present invention, the granular material may be organic such as, but not limited to, peroxydicarbonic acid, bis[4-(1,1-dimethylethyl)cyclohexyl] ester (commercially available under the trade name Perkadox® 16).

[0012] In accordance with another embodiment of the present invention, the rotor stator mixer (B) is either an internal batch-type rotor stator mixer (B1) or an inline rotor stator mixer (B2) externally connected to the mixing vessel (A).

[0013] In accordance with another embodiment of the present invention, the high speed disperser (A) is one of the type of a single shaft high speed disperser having a closed or open disk and having at least one set of teeth at the edge of said disk.

[0014] In accordance with another embodiment of the present invention, the liquid medium (or vehicle) provided to the mixing vessel may be selected from various chemical groups, especially from the group consisting of:

- mono-ethanolamine (MEA), di-ethanolamine (DEA), tri-ethanolamine (TEA),
- water, or water optionally admixed with ammonia,
- resorcinol bis(diphenyl phosphate), and other phosphate based plasticizers, and
- mixtures of the above species in any suitable proportions.

[0015] In accordance with another embodiment of the present invention, the process may further comprise the step of providing to the mixing vessel a first type thickening agent prior to, or simultaneously with, providing the liquid medium (or vehicle) to the mixing vessel. The first type thickening agent is preferably one acting as a swelling agent in an aqueous system, and may be an organic material such as, but not limited to, xanthane gum or carboxymethylcellulose. The type and useful amount of thickening/swelling agents may depend upon the granular material chemical and upon the solids content of the dispersion, but are well known to the person skilled in dispersion technology.

[0016] In accordance with another embodiment of the present invention, the process may further comprise the step of providing to the mixing vessel a dispersing agent such as an alkali neutralized acrylic polymer. The type and useful amount of dispersing agents may depend upon the granular material chemical and upon the solids content of the dispersion, but are well known to the person skilled in dispersion technology.

[0017] In accordance with another embodiment of the present invention, the process may further comprise the step of providing to the mixing vessel a second type thickening agent after operation of the high speed dispenser (A) and/or during operation of the rotor stator mixer (B). Such a second type thickening agent may be a mineral material such as, but not limited to, fumed silica or a phyllosilicate such as sepiolite (a complex magnesium silicate which can be found in fibrous or fine particulate solid forms from various commercial sources), or any other inorganic material capable to adjust the final viscosity of the dispersion to a predefined or desirable viscosity target. The type and useful amount of such mineral thickening agents may depend upon the granular material chemical and upon the solids content of the dispersion, but are well known to the person skilled in dispersion technology. The proper selection of the amount of thickener added at this step is also based on its capacity to afford the target final viscosity of the liquid (aqueous) aqueous system without negatively interfering with the other physical and chemical characteristics of the fine particles produced in the final stage. Usually an amount of thickener from 0.2% to 1% by weight, is well sufficient for meeting this requirement.

[0018] In accordance with another embodiment of the present invention, the liquid medium (or vehicle) provided to the mixing vessel may further include, dissolved or suspended therein, a grinding aid chemical. The grinding aid chemical may be, but without limitation, selected from the group consisting of sand, silicate powder, phosphoric acid, sulfuric acid, nitric acid, and other weak or strong acids. In the case of an acidic grinding aid, after obtaining the final desired particle size, the medium (vehicle) may be brought back to normal by the addition of a suitable alkaline chemical, in a manner well known to the person skilled in the art. Consequently also, a salt may then be formed be formed by the acid, the partially dissolved granular/medium blend and the added alkaline chemical. This salt should be considered as a co-product, usually present in an amount limited to 1% - 5% mole/mole, and in such limited amount is normally not detrimental to the main product quality.

[0019] Since, when used pure, some vehicles (e.g. DEA and TEA) are not liquid at ambient temperature, it may be necessary to perform the process at normal pressure but above their melting point. In accordance with another embodiment of the present invention, the process may thus be performed at a temperature between about 15°C and 50°C, for instance between about 20°C and 40°C.

[0020] In accordance with another embodiment of the present invention, the amount of granular material added to the mixing vessel may be such that the solid contents of the dispersion comprising the liquid medium and the granular material ranges between about 20% and 70% by weight, for instance between about 35% and 65% by weight, or between about 40% and 50% by weight.

[0021] In accordance with another embodiment of the present invention, the period of time of operating the high speed disperser (A) may range from about 5 to 60 minutes, preferably from about 10 to 30 minutes.

[0022] In accordance with another embodiment of the present invention, the period of time of operating the rotor stator mixer (B) may range from about 10 to 60 minutes, preferably from about 15 to 30 minutes.

[0023] Determination of the average particle size throughout the sequence of process steps can be made by the skilled person by reference to the current limits and precision of optical methods for determining the presence and size of particles present in a liquid medium (or vehicle), preferably an aqueous or water-based medium. The standard reference in this respect is currently laser diffraction particle size analysis. A laser diffraction particle size analyzer currently does not easily detect or quantifies with reasonable accurateness particles which are in aqueous solution, i.e. particles with a size below 0.1 μm. If need be, in particular for product quality control and regulations, the quantification of the amount of non-optically detectable particles present in the dispersed aqueous medium of the present invention can thus be carried out by indirect methods. Just as an example, and without a pretention to be exhaustive, a suitable determination method includes the steps of:

(i) optically measuring the average particle size corresponding to 50% of optically detectable solid particles of the aqueous system obtained in the final stage,
(ii) diluting with water in a recipient, using a dilution ratio X, the aqueous system of step (i) thereby reducing its viscosity, thus determining a total solid content of 50/X % in the diluted aqueous system,
(iii) leaving the diluted aqueous system of step (ii) settle until all of the solid particles are visually situated on the bottom of the recipient, thus leaving a clear colorless liquid on the top of the recipient,
(iv) taking a sample of said clear colorless liquid on the top of the recipient,
(v) measuring the solid content of the sample of step (iv) by means of a gravimetric infrared moisture analyzer, and
(vi) proportionating the solid content measured in step (v) to the total solid content of step (ii).

[0024] Within the above determination method, the higher the dilution ratio X, the higher the viscosity reduction of the aqueous system, therefore the lower the settling time of step (iii). Depending upon the time period allowed for global determination, the skilled person will readily select an appropriate dilution ratio X. It has thus been found that the above determination method can be carried out within a reasonable period of time (say not more than a few hours) by selecting a dilution ratio X ranging from about 5 to about 20.

[0025] Laser diffraction particle size analysis is herein given as a non limiting example of an easy-to-use method suitable for performing step (i) of the above determination method.

[0026] Gravimetric infrared moisture analysis is herein given as a non limiting example of an easy-to-use method suitable for determining the presence and amount of particles with a size below 0.1 μm within an aqueous liquid solution. Such a method may be performed for instance by using a precision weighing balance from the company Sartorius (Germany).

[0027] Thus another specific, most preferred, embodiment of the present invention relates to a process wherein the respective amounts and sizes of optically detectable particles and non-optically detectable particles are determined through a combination of laser diffraction particle size analysis and gravimetric infrared moisture analysis.

[0028] By using the above-described determination methods, it is possible to determine the proportion of non-optically detectable particles in the final process stage. By applying a correction factor derived from the proportion of non-optically detectable particles in the total solid particles of an aqueous system, it is then possible to calculate the average particle size of both optically detectable and non-optically detectable particles.

[0029] In accordance with another embodiment of the present invention, the process is performed, in contrast with the teaching of EP 2 586 849, in the absence of a defoamer.

[0030] The present invention produces significant advantages over the traditional processes for finely comminuting granular materials. In particular:

- it is applicable to a very wide range of granular chemical materials, whether natural or synthetic, mineral or organic;
- it makes use of commercial standard manufacturing equipment, and of inexpensive liquid vehicles (in particular water) and optional grinding aids;
- it is versatile by nature, and its main operating parameters can be tailored at will by the skilled person, depending upon the kind of granular material to be reduced in size, without performing vast experimentation;
- it provides a significantly high specific surface area of fine and very fine particles; and
- it can provide a fine particle size distribution that, despite a huge proportion of very fine particles, can be adequately and readily measured and monitored by the skilled person, in particular for the purpose of quality production control in a manufacturing plant.

[0031] The following examples are provided only for the purpose of illustrating one of the numerous possible embodiments of the invention, and should in no way be construed or interpreted as limiting the scope of the invention, which is defined by the appended claims.

EXAMPLE 1 - Reducing the particle size of coarse aluminium trihydrate (ATH).

[0032] Commercially available aluminium trihydrate_(ATH) with an average particle size of 5 microns is suitable to make stable dispersions with standard mixing equipment. However, a 5 micron ATH grade can be 2-3 times more expensive than a coarse grade with average particle size above 50 microns. The latter particle size is too high to make stable dispersions with low viscosity by standard mixing equipment.

[0033] In order to make a dispersion of 50% ATH in water, based on coarse ATH, with a final average particle size of 5 microns or 10 microns, the 2 stage refining process of described herein is used with an acid grinding aid.

[0034] Specifically, in order to produce 1000 kg, the process provides a mixing tank equipped with a high speed disperser having a mixing disk, and with a rotor atstor mixer. The sequence of process steps is as follows:

i. Fill the mixing tank with 450 litres of water
ii. Add 5 kg of phosphoric acid (85% solution) and mix with a standard high speed disperser (commercially available from the company Morehouse Cowles, 13930 Magnolia Ave., Chino, CA 91710, United States of America), hereinafter designated as "standard mixer", until a homogenous state is achieved.
iii. Add 2 kg of a dispersing agent, e.g. an alkali neutralized acrylic polymer like DISPEX AA4140NS commercially available from BASF, Germany. Mix with standard mixer until a homogenous state is achieved.
iv. Add 500 kg of coarse type ATH and mix with the standard mixer during 10 minutes. The ATH is chemically attacked and slowly "softened", due to the presence of the phosphoric acid.
v. Switch on the rotor stator mixer, whether an inline type or a batch type, and run it for 15 to 30 minutes. During this stage, the ATH particles will reduce in size down to 5-10 microns.
vi. Due to the acid, a negligible quantity of aluminium phosphate is formed.
vii. Measuring solid content and pH:

    1. Eventually add some ammonia solution to adjust the pH to a range of 7.5 - 8.0.
    2. Add water until the solid content is 50% by weight.

EXAMPLE 2 - Reducing the particle size of coarse aluminium sulfate (1-3 mm)

[0035] Aluminium sulfate is available in the form granules, with a particle size ranging from 1 to 3 mm. It can be dissolved using hot water, but after cooling, crystallization will occur.

[0036] With the 2 stage process of the invention, combining standard mixing and rotor stator mixing, a stable solution can be made quickly starting from cold water (5-20°C).

[0037] In order to produce 1000 kg, of a 40% by weight suspension of fine aluminium sulfate, the sequence of process steps is as follows:

i. Fill the mixing tank with 575 litres of water
ii. Add 5 kg of sulfuric acid (75% solution) and mix with a standard high speed disperser (commercially available from the company Morehouse Cowles, 13930 Magnolia Ave., Chino, CA 91710, United States of America), hereinafter designated as standard mixer until a homogenous state is achieved.
iii. Add 2 kg of a dispersing agent, type e.g. an alkali neutralized acrylic polymer like DISPEX AA4140NS commercially from

[0038] BASF, Germany. Mix with the standard mixer until a homogenous state is achieved.

iv. Add 400 kg of aluminium sulfate granules (size 1-3 mm) and mix with standard mixer during 10 minutes. The aluminium sulfate will be chemically attacked and "softened", slowly, by the presence of the acid.
v. Switch on the rotor stator mixer, whether an inline type or a batch type, and run it for 15-30 minutes. During this stage, the aluminium sulfate particles will reduce in size down to an average of 5 to 10 microns.
vi. To neutralize the sulfuric acid, add 5 to 10 kg of aluminium trihydrate (ATH) until pH returns to the original pH of aluminium sulfate in water. This way, the final chemical composition will not, or only slightly, differ from a pure aluminium sulfate in water mixture.
vii. Measuring solid content and pH:

    1. Eventually add water until total solid content is 40%
    2. Adjust pH by adding whether some ATH if too acidic, or some sulfuric acid if pH is too high.

[0039] The result is a stable suspension of aluminium sulfate, without the need of heating sources.

Claims

1. A process for reducing the average particle size of a granular material by a factor of at least 20, said process comprising the steps of:

    - providing a mixing vessel equipped with (A) a high speed disperser having a mixing disk and (B) a rotor stator mixer,
    - providing a liquid medium to the mixing vessel,
    - switching on the high speed disperser (A) at a circumferential speed of the mixing disk ranging from 1 to 50 m/s,
    - adding to the mixing vessel a granular material having an average particle size ranging from 1 to 5 mm, said mineral granular material being compatible with the liquid medium,
    - operating the high speed disperser (A) for a period of time sufficient to reduce the average size of the granular material by a factor of at least about 10, thus producing granules of an intermediate average size ranging from 0.1 to 0.5 mm,
    - switching on the rotor stator mixer (B) and operating said rotor stator mixer for a period of time sufficient to reduce the average size of the intermediate granules by a factor of at least about 2, thus producing fine particles having an average size ranging from 0.001 to 50 μm, as determined by a laser diffraction system.

2. A process as defined in claim 1, **characterized in that** the granular material is selected from the group consisting of phosphates, sulfates, borates, hydrates, zeolites, hypophosphites, alkaline earth carbonates, and alkaline earth oxides and hydroxides.

3. A process as defined in claim 1 or claim 2, **characterized in that** the rotor stator mixer (B) is either an internal batch-type rotor stator mixer (B1) or an inline rotor stator mixer (B2) externally connected to the mixing vessel (A).

4. A process as defined in any one of claims 1 to 3, **characterized in that** the high speed disperser (A) is one of the type of a single shaft high speed disperser having a closed or open disk and having at least one set of teeth at the edge of said disk.

5. A process as defined in any one of claims 1 to 4, **characterized in that** the liquid medium provided to the mixing vessel is selected from the group consisting of:

    - mono-ethanolamine (MEA), di-ethanolamine (DEA), tri-ethanolamine (TEA),
    - water optionally admixed with ammonia,
    - resorcinol bis(diphenyl phosphate), and other phosphate based plasticizers, and
    - mixtures thereof in any suitable proportions.

6. A process as defined in any one of claims 1 to 5, further comprising the step of providing to the mixing vessel a first type thickening agent prior to, or simultaneously with, providing the liquid medium to the mixing vessel.

7. A process as defined in claim 6, **characterized in that** the first type thickening agent is xanthane gum or carboxymethylcellulose.

8. A process as defined in any one of claims 1 to 7, further comprising the step of providing to the mixing vessel a second type thickening agent after operation of the high speed dispenser (A) and/or during operation of the rotor stator mixer (B).

9. A process as defined in claim 8, **characterized in that** the second type thickening agent is fumed silica or sepiolite.

10. A process as defined in any one of claims 1 to 9, **characterized in that** the liquid medium provided to the mixing vessel further includes, dissolved or suspended therein, a grinding aid chemical.

11. A process as defined in claim 10, **characterized in that** the grinding aid chemical is selected from the group consisting of sand, silicate powder, phosphoric acid, sulfuric acid, nitric acid, and other weak or strong acids.

12. A process as defined in any one of claims 1 to 11, being performed at a temperature between about 15°C and 50°C.

13. A process as defined in any one of claims 1 to 6, **characterized in that** the amount of granular material added to the mixing vessel is such that the solid contents of the dispersion comprising the liquid medium and the granular material ranges between about 20% and 70% by weight.

14. A process as defined in any one of claims 1 to 13, **characterized in that** the period of time of operating the high speed disperser (A) ranges from about 5 to 60 minutes.

15. A process as defined in any one of claims 1 to 14, **characterized in that** the period of time of operating the rotor stator mixer (B) ranges from about 10 to 60 minutes.

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EUROPEAN SEARCH REPORT

Application Number
EP 16 18 8026

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A,D	EP 2 586 849 A2 (FR MASTER BVBA [BE]) 1 May 2013 (2013-05-01) * paragraph [0013] - paragraph [0061] *	1-15	INV. B02C17/16 B02C18/08 B02C23/06
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TECHNICAL FIELDS SEARCHED (IPC)

B02C
B01F

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	14 February 2017	Swiderski, Piotr

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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T : theory or principle underlying the invention
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L : document cited for other reasons
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 16 18 8026

14-02-2017

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