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(54) Title: SULFUR FERTILIZER

(57) Abstract: The present invention refers to a sulfur fertilizer composition, the process for preparing the same and its use.



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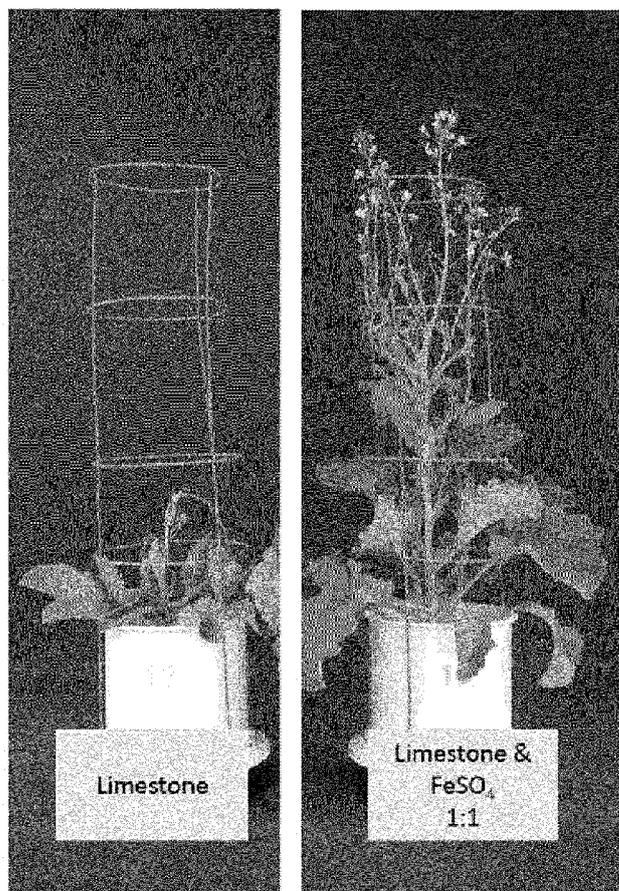


Figure 1



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## SULFUR FERTILIZER

The present invention refers to a sulfur fertilizer composition, the process for preparing the same and its use.

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Sulfur (S) is an important plant nutrient. It is required by plants in amounts similar to phosphorus (P), thus it is grouped with nitrogen (N), potassium (K) and P as the fourth major plant nutrient. Sulfur is an important component of several essential amino acids and thus, sulfur is important for both protein quality and quantity. It is also involved in nitrogen metabolism, photosynthesis, synthesis of oils in oilseed crops such as canola, and in synthesis and function of enzymes, amino acids and other organic compounds.

10

Due to increasing removal of sulfur compounds from flue gas, especially of power plants, waste and biomass incineration plants, in the last three decades the intake of sulfur compounds into soil has decreased significantly in many regions. In Germany for example the SO<sub>2</sub> emissions have come down from ca. 5 million tons per year to ca. 0.5 million tons per year. Accordingly, the average intake of S into the soil has changed from ca. 500 kg S / (ha \* a) to less than 50 kg S / (ha \* a).

20

Sulfur deficiencies can have a major impact on crop yield and quality. Sulfur deficiencies mainly arise on acid sandy soils where sulfate has been leached, especially in such areas with high winter rainfall.

25

Naturally, deficiencies of sulfur mainly occur for cultures with high demand for sulfur, like alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, wheat, barley, maize, sunflowers, soybean, navy beans, sorghum, oats and triticale, furthermore cruciferous plants like brassicas, radish, rocket and allium crops like onion, leek and garlic.

30

Deficiencies of sulfur result in lower yield and worse quality of cultures. Fertilizing with sulfur may overcome those problems. Fertilizing with sulfur may not only

affect sulfur content of plants but also positively affect the storability of the products (e.g. garlic).

In the state of art commonly used sulfur fertilizers are: Ammonium sulfate,  
5 potassium sulfate, magnesium sulfate, gypsum or elemental sulfur.

Elemental sulfur and ammonium sulfate result in acidification of soil and therefore, they can be used without negative impact on soils with high pH only. On the other hand,  $\text{NH}_3$  volatilization can be a problem with ammonium sulfate in case of high pH of soil.

10 Ammonium sulfate, potassium sulfate, magnesium sulfate have very high solubilities and sulfate may be washed out in case of strong rainfall. Elemental sulfur has a very low solubility. Elemental sulfur applied during winter is ineffective for overcoming sulfur deficiency because the S is oxidized too slowly by soil  
15 microorganisms. Gypsum exhibits a useful solubility, but usually is not available in form of stable granulates and does not raise soil pH.

Other source of sulfur might be ferrous sulfate obtained as by-product from  $\text{TiO}_2$  production. So far, the use of ferrous sulfate is known for waste water treatment,  
20 for iron oxide pigments, or as chromate reducing agent.

In the state of art, iron sulfate has not been mentioned or suggested as sulfur fertilizer. Some applications mention iron sulfate as moss killer or as Fe source in case of Fe deficiency (chlorosis) or as phosphorus and heavy metal absorber in  
25 polluted soils. However, the use of iron sulfate results in acidification of soil.

In several patent applications, agricultural uses of iron sulfate are described.

30 GB 1 473 403 discloses a method for preparing compositions useful as soil modifiers or fertilizers by thoroughly mixing ferrous sulfate heptahydrate (copperas) with compounds chosen from oxides, hydroxides or carbonates of alkaline or earth alkaline elements thereby obtaining reaction products consisting of alkaline or earth alkaline sulfates and ferrous hydroxide. Subsequently, the

ferrous hydroxide is converted into ferric hydroxide by oxidation with oxygen or air. No application as sulfur fertilizer is disclosed in GB 1 473 403.

5 DE 42 19 351 discloses an additive for agriculture obtained from ferrous sulfate (not ferrous sulfate heptahydrate!) obtained as by-product from titanium dioxide manufacture optionally blended with earth alkaline compounds and an organic material. Use of this material is for treating Fe, Mn and Zn deficiencies. No application as sulfur fertilizer is disclosed in DE 42 19 351.

10 EP 0 093 204 discloses a process for granulating Fe containing fertilizing mixtures comprising ferrous sulfate and fertilizing agents by use of hydrophilic additives. Also admixing of other fertilizing agents like ammonium sulfate, NPK compounds, micronutrients or natural fertilizers is disclosed. No application as sulfur fertilizer is disclosed in EP 0 093 204.

15 EP 2 165 976 discloses a method for pressure compacting of compositions based on ferrous sulfate heptahydrate. Use of this material is as Fe source for agriculture. No application as sulfur fertilizer is disclosed in EP 2 165 976.

20 In the state of art, there is still the need for an improved sulfur fertilizer composition which provides sufficient sulfur to the soil upon application of the composition to the soil.

25 For solving the problem of the invention, the inventors have considered the disadvantages of the prior art compositions and came to the inventive solution by providing a sulfur fertilizer without detrimental impact on soil pH and plant nutrition, preferably in form of stable granulates, without expensive additives or processes for granulation, and a process for preparing the same as well as its use as fertilizer.

30 Therefore, the present invention is directed to a process for manufacturing a fertilizer composition comprising S, Fe and one or more earth alkaline elements, including Ca and/or Mg, being suitable for administration onto a sulfur deficient soil

wherein a material, comprising Fe and sulfate ions, in form of a solid salt, filter cake, paste, slurry, or solution, is blended with at least one component being chosen from or comprising oxides, hydroxides or carbonates of the earth alkaline elements including at least one of Ca and Mg, preferably  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , dolomite  
5  $(\text{Ca,Mg})\text{CO}_3$ ,  $\text{MgO}$ , burnt dolomite  $(\text{Ca,Mg})\text{O}$ ,  $\text{CaO}$ , semi-hydrated dolomite  $\text{Ca}(\text{OH})_2\text{MgO}$ , or  $\text{Ca}(\text{OH})_2$  or mixtures thereof in molar ratio of  $(\text{Ca}+\text{Mg})/\text{Fe} = 2$  to 200, preferably 2.5 to 25, more preferably 10 to 25, and the blend is converted into an administration form.

10 Blending and converting into an administration form may be carried out simultaneously or subsequently, leading to a reaction mixture in a granulated, pelletized or powderous form depending on the ratio of the used components. Thus, the inventive process can be carried out in an apparatus which can also serve for compaction, granulation and/or pelletizing the reaction product

15 Blending and/or converting may be carried out in the presence of any of water, dilute sulfuric acid, preferably diluted,  $\text{CaSO}_4$ , elemental sulfur or other S containing compounds, other compounds useful for a fertilizer, such as micronutrients, preferably a boron compound, binder or granulation aids, or  
20 mixtures thereof, also assisting in obtaining the required form of the product.

In the inventive process, the material comprising Fe and sulfate ions may preferably be  $\text{FeSO}_4$  which may contain crystal water, such as  $\text{Fe}(\text{II})\text{SO}_4$  heptahydrate, preferably obtained from the titanium dioxide production process.

25 The at least one component comprising oxides, hydroxides or carbonates of earth alkaline elements which is generally used for neutralizing any acid such as any adhering sulfuric acid and also for increasing the pH-value may preferably be limestone, limestone, which is a natural material without critical contents of harmful  
30 substances with respect to agricultural applications. To provide suitable reactivity against  $\text{FeSO}_4$  in blending process as well as suitable reactivity and effect in soil, the limestone may consist of fine particles 95 % < 0,09 mm, and comprise >95 %  $\text{CaCO}_3$ .

The component comprising oxides, hydroxides or carbonates of earth alkaline elements can also be a slag from steel manufacturing or a reaction product from such a slag. The slag has a high basicity and is more reactive than  $\text{CaCO}_3$ .

5

For application on more acidic soils or if faster effects are required, the component comprising oxides, hydroxides or carbonates of earth alkaline elements can be burnt lime or burnt dolomite or hydrated lime, providing a higher neutralization potential and higher reactivity than  $\text{CaCO}_3$  and slag.

10

The neutralizing value of said at least one component being chosen from or comprising oxides, hydroxides or carbonates of the earth alkaline elements according to DIN EN 12945:2014-07 standard may be 1 to 55% (as CaO), preferably 20 to 55%, most preferably 33 to 48%.

15

In addition, at least one of starch, magnesium sulfates, citric acid, clay, mortar binder, cellulose glue, glucosidic binder such as starch, molasses, lignosulfonate, water, hydrated lime, water glass, bentonite, cellulose fibres, stearates, urea or combinations of these materials may be used as binder or granulation aid in a weight ratio of 0.1 to 10 weight-%, preferably 0.3 to 5 weight-%, most preferably 0.8 to 3 weight-%, related to the total mass of the composition comprising Fe and sulfate ions and the at least one component being chosen from or comprising oxides, hydroxides or carbonates of the earth alkaline elements Ca and Mg.

20

25 In an embodiment, the inventive process is carried out by blending:

- a material comprising Fe and sulfate ions,
  - a material comprising carbonates of the earth alkaline elements Ca and/or Mg, preferably  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , or dolomite, and
  - a material comprising oxides or hydroxides of earth alkaline elements,
- 30 preferably  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Mg(OH)}_2$ , or  $\text{Ca(OH)}_2$ ,

in the form of powder without any addition of water, with the reaction of these materials while being mixed and granulated in the same apparatus, thus leading to a granulated composition.

The present invention is also directed to a fertilizer composition comprising S, Fe and at least one earth alkaline element including at least one of Ca and/or Mg, wherein the molar ratio of (Ca+Mg)/Fe is in the range of 2 to 200, preferably 2.5 to 25, most preferably 10 to 25.

In the inventive fertilizer composition, the molar ratio of Fe to S in the inventive fertilizer composition may be 0.3 to 6, preferably 0.5 to 2, most preferably 0.8 to 1.2.

The main reaction products of the inventive process or in the inventive composition are calcium sulfate, iron hydroxide and unreacted earth alkaline compounds. The iron hydroxide obtained has two important functions: The first function is an effective and efficient binder for granulates; and the second function is partial retention of sulfate and trace element ions by adsorption. Therefore, a sulfur fertilizer comprising iron hydroxide (or reaction products of iron sulfate with alkaline compounds) has improved properties compared to a material without iron hydroxide as the sulfate is not washed out of the soil so easily. Besides of calcium sulfate being a reaction product during mixing, calcium sulfate may also be added additionally.

As stated, iron sulfate has been converted mainly or completely into earth alkaline sulfates in the composition. As crystal structures generally are determined by x-ray diffraction (XRD) and quantitative relation of XRD peaks with actual relation of crystal structures can be somewhat ambiguous, the ratio of XRD signals are compared rather than ratio of crystal structures for analyzing and defining the inventive fertilizer composition. Therefore, the ratio of  $(P*Q) / (I*J) > 8$ , preferably more than 5, most preferred more than 2, with P being the integral area of the x-ray diffraction peaks between  $2\theta = 20.0$  and  $21.5^\circ$ , Q the integral area of the XRD peaks between  $2\theta = 29.0$  and  $30.5^\circ$ , I the integral area of the XRD peaks between  $2\theta = 16.0$ , and  $20.0^\circ$  and J the integral area of the XRD peaks between  $2\theta = 23.4$  and  $28.0$  (measured using Cu-K $\alpha$ -radiation diffraction peaks).

Alternatively, the inventive fertilizer composition may have the ratio  $A/B > 1$ , preferably  $>5$ , most preferably  $>10$ , with A being the integral area of the x-ray diffraction peaks between  $2\theta = 20.2$  and  $21.5^\circ$  and B being the integral area of the x-ray diffraction peaks between  $2\theta = 25.0$  and  $28.0$ .

5

The invention also concerns a process for fertilizing S and one or more earth alkaline elements, preferably Ca and/or Mg wherein the above inventive fertilizer composition is applied, preferably in form of granulates, onto a sulfur deficient soil used for agriculture, preferably for fertilizing sulfur to plants supplying amino acids, proteins and/or oil, in particular cultures of alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, wheat, barley, maize, sunflowers, soybean, navy beans, sorghum, oats, triticale, cruciferous plants like brassicas, radish, rocket and allium crops like onion, leek and garlic.

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Advantage of this process is that fertilizing S and fertilizing Ca (and optionally Mg), and raising the soil pH is achieved at the same time with one single step. Therefore, costs and efforts for separate fertilizing steps can be avoided.

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Another advantage is that part of Ca (and optionally Mg) is available in soluble form (as  $\text{CaSO}_4$ ), whereas Ca (and optionally Mg) from conventional limestone or dolomite fertilizers is not soluble but has to get leached by contact with an acidic environment. A fertilizer composition offering both Ca (and optionally Mg) solubility and at the same time considerable alkaline character has a clear advantage over conventional fertilizer types. Even more, the content of soluble sulfur (as sulfate), valuable trace elements like Mn and Zn (and optionally B) and the low content of unwanted elements (e.g. As, Hg, Cd, Pb) and toxic organic compounds results in a highly valuable fertilizer type.

30

Preferably, said application on fields used for agriculture is made for base fertilization between summer and winter time, i.e. between August and December for areas north of the equator or between February and June for areas south of the equator, respectively, before the growth phase of the plants start.

Generally; the ratio of the (acidic) Fe(II)sulfate and the (alkaline) Ca and/or Mg compound may vary depending on soil pH:

5 For slightly acidic soils, a molar ratio (Ca+Mg)/S of >2 may be appropriate, whereas for more acidic soils a molar ratio (Ca+Mg)/S of >>2 may be appropriate. With typical data of 300 – 600 kg Ca / (ha \* a) for refreshing fertilizing with Ca and 30 kg S / (ha \* a) => molar ratio Ca/S = 7.5 – 15.

10 By applying the inventive fertilizer composition, the pH of the soil may be raised to above 5.8, preferably above >6.0, most preferably >6.2.

Generally, sulfur in the inventive fertilizer is available in the form of sulfate, but for calculation purpose sulfur virtually is expressed as S.

15 The present invention also provides the use of a solution comprising iron sulfate or the use of crystalline iron sulfate with more than 3 molecules of crystal water, preferably iron(II)sulfate heptahydrate, more preferably copperas as obtained as by-product from titanium dioxide manufacturing, for preparing a sulfur fertilizing composition and/or for moistening and/or granulating of powderous fertilizer materials.  
20

Advantages of the inventive products and processes are:

- Supply of bio-available soluble sulfur in large quantities and for low cost.
- The inventive compounds or the products of the inventive process exhibit  
25 optimum solubility of sulfur: Not too high and not too low.  
=> long-term supply of sulfur and calcium / magnesium improves soil structure and porosity.
- High alkalinity => useful also for neutralization of acidic soils. This leads to improved bio-availability of other applied fertilizing substances.
- 30 - Preferred is a granular free flowing and dust free form of the fertilizer.
- Iron hydroxide exhibits excellent stabilizing properties for the granules obtained. Also iron hydroxide due to its high capability for absorption of trace

elements is able to avoid the micronutrients present in the inventive fertilizer (Mn, Zn) to be washed out.

5 If the iron sulfate is taken from the by-product of the titanium dioxide process, the inventive fertilizer additionally comprises valuable plant nutrients and micronutrients, e.g. Mg, Mn, Zn. At the same time the product is free of Hg, Cd, As, Pb, Cr. The inventive composition can be used for all cultures, preferably those with high sulfur demand, e.g. alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, lucerne, wheat, barley, maize, sunflowers, soybean, navy  
10 beans, sorghum, oats and triticale; furthermore cruciferous plants like Brassicas, radish, rocket and allium crops like onion, leek and garlic, especially suitable for canola and rapeseed and most preferably during winter time.

The pH of the fertilizer can be 5.5 to 13, for most applications preferably 6.0 to 11,  
15 most preferably 6.5 to 8.5. When comprising calcium oxide or calcium dihydroxide for stronger and faster neutralizing effects, the pH of the fertilizer is preferably 8.5 to 13. As a consequence, no acidification of soil can be observed; jointly fertilizing with both S and Ca; iron sulfate is completely or nearly completely reacted and good stability of granulates is given.

20

The present invention also concerns:

- An inventive composition, wherein it contains Zn with mass ratio of Zn/Fe 0.0001 to 0.003, preferably 0.0002 to 0.0015, and/or Mn with the mass ratio of Mn/Fe 0.00001 to 0.01, preferably 0.00001 to 0.001; these elements are  
25 valuable micronutrients and therefore no separate application of Zn and Mn is necessary.
- Said inventive composition, wherein the mass ratio of Cr/Fe is 0.0000001 – 0.0001, preferably 0.0000001 – 0.00005, most preferably 0.1 - 0.00002; this concentration of Cr is sufficiently low to avoid detrimental effects.
- 30 - Said inventive composition, wherein mass ratio of Ti/Fe is 0.001 – 0.03, preferably 0.002 – 0.02, most preferably 0.003 – 0.015;
- Said inventive composition, wherein the pH according to ISO standard is 5.5 to 13, for most application preferably 6.0 to 11, most preferably 6.5 to 8.5, but

preferably 8.5 to 13 for compositions comprising calcium oxide or calcium dihydroxide. Hereby the pH is determined according to DIN EN ISO 787 part 3, whereby the pH measurement is made no earlier than 5 days after preparation of the sample and whereby the sample is ground prior to pH measurement.

5

- Said inventive composition, wherein the neutralizing value according to DIN EN 12945:2014-07 standard is 1 to 55% (as CaO), preferably 20 to 55%, most preferably 33 to 48%.

10

- Said inventive composition, wherein the fertilizer is granulated with volume based average granule size is 1 – 8 mm, preferably 2 – 6, most preferably 2 – 4 mm;

- Said inventive composition, wherein it is granulated in a pan granulator, or a granulation drum, or an intensive mixer.

15

- Said inventive composition, wherein it is granulated in a pan granulator, or a granulation drum, or an intensive mixer, without the addition of water to aid granulation.

- Said inventive composition, wherein it is granulated in a combination of an intensive mixer and a granulator such as a pan granulator or a granulation drum.

20

- Said inventive composition, wherein the fertilizer composition is obtainable by blending

○ Ca and/or Mg compound, preferably  $\text{CaCO}_3$  or dolomite  $(\text{Ca},\text{Mg})\text{CO}_3$

○ iron sulfate, preferably  $\text{Fe(II)SO}_4$  heptahydrate,

○ optionally  $\text{CaSO}_4$ ;

25

○ optionally CaO,  $(\text{Ca},\text{Mg})\text{O}$  or  $\text{Ca(OH)}_2$

○ optionally an iron sulfate monohydrate,

○ optionally an iron sulfate monohydrate obtained from  $\text{TiO}_2$

manufacturing, which has been reacted beforehand with lime or

limestone or slaked lime or burnt lime to yield a reaction product with a

30

typical pH of about 4;

○ Said inventive composition, wherein the fertilizer comprises iron sulfate and/or products obtained from neutralization of iron sulfate and at least

one calcium and/or magnesium compound and/or the reaction products of iron sulfate and calcium and/or magnesium compounds;

- 5           ○ Use of the composition as a sulfur fertilizer for alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, wheat, barley, maize, sunflowers, soybean, navy beans, sorghum, oats and triticale; furthermore cruciferous plants like Brassicas, radish, rocket and allium crops like onion, leek and garlic.
- 10          ○ Use of the composition between summer and winter time, i.e. between August and December for areas north of the equator or between February and June for areas south of the equator, respectively;
- Use of the composition as a calcium-sulfur fertilizer in such way that the pH of the soil is raised to >5.8, preferably >6.0, most preferably >6.2;

Further modifications of the invention can include:

- 15          - Adding other elements suitable for fertilizing purposes, e.g. trace element nutrients like boron, copper, molybdenum
- Additional elemental sulfur may be used; the presence of alkaline compounds can avoid acidification of soil.
- 20          - Preferably the calcium and/or magnesium compound has a pH >8, e.g. slag from steel manufacturing, burnt or hydrated lime / dolomite
- Low content of Sr or As.
- Passivation of the granule surface during granulation with limestone.
- Passivation of the granule surface during granulation with an iron sulfate monohydrate which has been reacted beforehand with limestone, or lime, or
- 25          slaked lime or burnt lime
- Thermal treatment / drying.
- Compacting with roller mill or pelletizer.

The present invention is further illustrated by the following Examples.

30

Example 1a - Preparation of compacted Ca-S-fertilizer with 2.4% S and neutralization value of 45% CaO equivalents and with low crushing strength

Two batches, each consisting of 2 kg copperas from the titanium dioxide production by the sulfate process, and 8 kg of powdered limestone were brought together and mixed in a ploughshare mixer for about 2 minutes. The molar ratio (Ca+Mg)/Fe was 12. These mixtures were fed at room temperature over a hopper with a screw conveyor onto a pair of rollers of a roller compactor and compressed into scabs. The contact pressure during densification was about 9.5 N/mm<sup>2</sup>. The scabs attained a density of about 2070 kg / m<sup>3</sup>, measured in paraffin oil, according to the Archimedes principle. The scabs were crushed, and of the resulting pellets a sieve fraction between 2 to 5 mm was collected. The granules had a residual moisture content determined by drying at 105 °C of 8.2 wt.%.  
5  
10

From this fraction, 10 fresh granules were arbitrarily taken out and crushed by applying a pressing force. The average crushing strength was 1.6 kg. The test was repeated in exactly the same way with fresh batches of copperas and limestone flour. The crushing strength of the fresh granules was 1.3 kg. After drying 10 granules at 105 °C overnight, the crushing strength was found to be 1.5 kg.  
15

Example 1b - Preparation of compacted Ca-S-fertilizer with 2.4% S and neutralization value of 45% CaO equivalents and with low crushing strength

Two batches, each consisting of 2 kg copperas from the titanium dioxide production by the sulfate process, and 8 kg of powdered limestone, which had been mixed by hand and aged for 1 week by occasional mixing by hand and with a molar ratio (Ca+Mg)/Fe of 12 were fed at room temperature over a hopper with a screw conveyor onto a pair of rollers of a roller compactor and compressed into scabs. The contact pressure during densification was about 8.0 N/mm<sup>2</sup>. The scabs attained a density of about 2320 kg / m<sup>3</sup>, measured in paraffin oil, according to the Archimedes principle. The scabs were crushed, and of the resulting pellets a sieve fraction between 2 to 5 mm was collected. The granules had a residual moisture content determined by drying at 105 ° C of 8.5 wt.%.  
20  
25

From this fraction, 10 fresh granules were arbitrarily taken out and crushed by applying a pressing force. The average crushing strength was 2.2 kg. Ageing of the mixture prior to compacting results in moderate improved crushing strength.  
30

Example 1c - Preparation of compacted Ca-S-fertilizer with 6% S and neutralization value of 22% CaO equivalents and with low crushing strength

Two batches, each consisting of 5 kg copperas from the titanium dioxide production by the sulfate process, and 5 kg of powdered limestone were brought together and mixed in a ploughshare mixer for about 2 minutes. The molar ratio (Ca+Mg)/Fe was 3. These mixtures were fed at room temperature over a hopper with a screw conveyor onto a pair of rollers of a roller compactor and compressed into scabs. The specific force during densification was about 9.0 N/mm<sup>2</sup>. The scabs attained a density of about 1840 kg / m<sup>3</sup>, measured in paraffin oil, according to the Archimedes principle. The scabs were crushed, and of the resulting pellets a sieve fraction between 2 to 5 mm was collected. The granules had a residual moisture content determined by drying at 105 ° C of 21.6 wt.%.

From this fraction, 10 fresh granules were arbitrarily taken out and crushed by applying a pressing force. The average crushing strength was 0.3 kg. Granules with a high residual moisture exhibit low crushing strength.

Example 1d - Preparation of compacted Ca-S-fertilizer with 6% S and neutralization value of 22% CaO equivalents and with high crushing strength

Two batches, each consisting of 5 kg copperas from the titanium dioxide production by the sulfate process, and 5 kg of powdered limestone, which had been mixed by hand and aged for 1 week by occasional mixing by hand and with a molar ratio (Ca+Mg)/Fe of 3 were fed at room temperature over a hopper with a screw conveyor onto a pair of rollers of a roller compactor and compressed into scabs. The contact pressure during densification was about 8.0 N/mm<sup>2</sup>. The scabs attained a density of about 2220 kg / m<sup>3</sup>, measured in paraffin oil, according to the Archimedes principle. The scabs were crushed, and of the resulting pellets a sieve fraction between 2 to 5 mm was collected. The granules had a residual moisture content determined by drying at 105 ° C of 7.9 wt.%.

From this fraction, 10 fresh granules were arbitrarily taken out and crushed by applying a pressing force. The average crushing strength was 3.5 kg. After drying

10 granules at 105 °C overnight, the crushing strength was found to be 8.9 kg. Ageing of the mixture prior to compacting results in improved crushing strength.

Example 2a - Preparation of granulated Ca-S-fertilizer with 5% S and neutralization value of 28% CaO equivalents and with high crushing strength

5 In a rotating and inclined (30°) mixing tank with a capacity of 150 liters and with eccentrically arranged, high-speed mixing tool and fixed wall scraper, 50 kg limestone powder, 50 kg copperas from the titanium dioxide production by the sulphate process and 6 kg of water were thoroughly mixed for 2 minutes in the co-  
10 current mode. The rotational speed of the mixing tool was 16.5 m/s, and the container was rotating at 1 m / s. This mixing process resulted in micro-granules that were granulated on a rotating and inclined pan granulator (diameter 1 m) with fixed deflector and rotating scraper. During granulation, about about 20 kg of limestone was added for drying purposes. The final composition had a molar ratio  
15 (Ca+Mg)/Fe of 4. The resulting granules were round. Of the granules about 80% by volume were between 2-6 mm.

From the volume fraction from 3.15 to 5 mm, 10 granules were arbitrarily taken out, dried overnight at 40 °C and crushed by applying a pressing force. The  
20 average crushing strength was 7.4 kg. Granulation with subsequent slow drying results in good crushing strength.

Example 2b - Preparation of granulated Ca-S-fertilizer with 5% S and neutralization value of 28% CaO equivalents and with high crushing strength

25 In a rotating and inclined (30°) mixing tank with a capacity of 150 liters and with eccentrically arranged, high-speed mixing tool and fixed wall scraper, 50 kg limestone powder, 50 kg copperas from the titanium dioxide production by the sulphate process, 1 kg of lignosulfonate and 4.5 kg of water were thoroughly mixed for 1.5 minutes in the co-current mode. The rotational speed of the mixing  
30 tool was 16.5 m/s, and the container was rotating at 1 m / s. This mixing process resulted in micro-granules that were granulated on a rotating and inclined pan granulator (diameter 1 m) with fixed deflector and rotating scraper. During granulation, about about 17.5 kg of lime was added for drying purposes. The final

composition had a molar ratio (Ca+Mg)/Fe of 4. The resulting granules were round. Of the granules about 90% by volume were between 2-6 mm.

From the volume fraction from 3.15 to 5 mm, 10 granules were arbitrarily taken out, dried overnight at 40 °C and crushed by applying a pressing force. The

5 average crushing strength was 3.0 kg.

Use of lignosulfonate resulted in lower water demand for granulation.

#### Example 2c

10 With the same setup as in example 2b 50 kg limestone powder, 50 kg copperas from the titanium dioxide production by the sulphate process and 5 kg of water were thoroughly mixed.

It was not possible to granulate this mixture on the pan granulator of example 2b as the water content was too low for generation of a granulation effect.

#### 15 Example 2d - Preparation of granulated Ca-S-fertilizer with 2% S and neutralization value of 46% CaO equivalents

In a rotating and inclined (30°) mixing tank with a capacity of 150 liters and with eccentrically arranged, high-speed mixing tool and fixed wall scraper, 80 kg limestone powder, 20 kg copperas from the titanium dioxide production by the sulphate process and 8 kg of water were thoroughly mixed for 2 minutes in the co-  
20 current mode. The rotational speed of the mixing tool was 16.5 m/s, and the container was rotating at 1 m / s. This mixing process resulted in micro-granules that were granulated on a rotating and inclined pan granulator (diameter 1 m) with fixed deflector and rotating scraper. During granulation, about about 20 kg of lime  
25 was added for drying purposes. The final composition had a molar ratio (Ca+Mg)/Fe of 15. The resulting granules were round. Of the granules about 80% by volume were between 2-6 mm.

30 From the volume fraction from 3.15 to 5 mm, 10 granules were arbitrarily taken out, dried overnight at 40 °C and crushed by applying a pressing force. The average crushing strength was 5.3 kg. Granulation with subsequent slow drying results in good crushing strength.

Example 2e - Preparation of granulated Ca-S-fertilizer with 6% S and neutralization value of 22% CaO equivalents

5 In a rotating and inclined (30°) mixing tank with a capacity of 150 liters and with eccentrically arranged, high-speed mixing tool and fixed wall scraper, 45 kg limestone powder, 5 kg burnt lime and 50 kg copperas from the titanium dioxide production by the sulphate process were thoroughly mixed for 30 minutes in the co-current flow mode. The molar ratio (Ca+Mg)/Fe was 3. The rotational speed of the mixing tool was 4 m/s, and the container was rotating at 1 m / s. During the  
10 mixing process the chemical reaction of the components resulted in a temperature increase to about 50°C.

This mixing process resulted in a black granular product with good handling properties. The resulting granules were round.

15 Example 3 - Determination of the alkaline content of a fertilizer

The alkaline content of the inventive fertilizer is determined by an acid-base titration. For this analytical method, about 1 g of a representative sample of the product is reacted in a beaker with 25 ml of a hydrochloric acid solution of a concentration of 1 mol per liter. The reaction of the calcium carbonate and  
20 hydrochloric acid produces carbon dioxide. The sample is left overnight in order for the reaction to complete and the bulk of the carbon dioxide to be emitted from the beaker. The next day, the beaker is briefly heated to just below the boiling point of water to emit any remaining carbon dioxide. Subsequently, the excess hydrochloric acid is back-titrated with a solution of sodium hydroxide of a  
25 concentration of 1 mol per liter. The extent of the titration is monitored by measuring the pH of the liquid, for example potentiometrically, and determining the consumption of sodium hydroxide solution at the equivalence point. The amount of alkaline substance is then expressed as equivalent percentage of CaCO<sub>3</sub>.

30 1.501 g of a fertilizer sample is reacted with 25 ml of 1 M hydrochloric acid with a titer of 0.9921 in a beaker. The reaction mixture is left overnight, after which the excess hydrochloric acid is titrated with 12.8726 ml of 1 M NaOH with a titer of 1.0031 until a pH of 7.454. This sample contained 39.6 wt.-% CaCO<sub>3</sub>.

Calculated is as follows:  $100\% \cdot \{[(25 \text{ ml HCl} \cdot 0.9921) - (12.8726 \text{ ml NaOH} \cdot 1.0031)] \cdot 0.001 \text{ L/ml} \cdot 100.087 \text{ g/mol CaCO}_3 \cdot 0.5 \text{ mol H}^+/\text{mol CaCO}_3\} / [1.501 \text{ g}]$   
 = 39.6 wt.-% CaCO<sub>3</sub>.

39.6 wt.-% of CaCO<sub>3</sub> corresponds to 22.2 wt.-% of CaO.

5

#### Example 4 - Elution tests of soil samples impregnated with sulfur fertilizer

In two soil incubation experiments the effect of limestone/FeSO<sub>4</sub> mixtures on the pH of two soils was analyzed. Application of limestone and of limestone/ FeSO<sub>4</sub> preparations result in an increase of pH in both soils one week after fertilization, see table 1 with pH data.

10

Table 1 - Effect of a fertilization of limestone and limestone/FeSO<sub>4</sub> mixtures on the pH of two soils

Soil	Control experiment	Limestone	Limestone/FeSO <sub>4</sub> 2 : 1	Limestone/ FeSO <sub>4</sub> 4 : 1
		4.0 g / kg soil	4.0 g / kg soil	4.0 g / kg soil
Aqualf, 30% clay	5,2	6.2	6.2	6.4
Alfisol, 20% clay	6.4	6.8	7.0	7.1

15 The soil pH was measured in a suspension of 1 part soil with 2.5 parts of a solution of 0.01 M CaCl<sub>2</sub>. The effect of the limestone / FeSO<sub>4</sub> preparations on pH is stronger than the effect of pure limestone!

#### Example 5 - Plant nutrition tests using sulfur fertilizer (pot experiments)

20 The effects of limestone/FeSO<sub>4</sub> mixtures on the growth of plants was investigated with summer rape and alfalfa under natural conditions in pot experiments in small Mitscherlich pots with 6 kg soil per pot. The experimental soil was a subsoil (0.4 – 0.8 m depth) from a luvisol derived from loess with a total S concentration of 0.027%. Summer rape (*Brassica napus* L, cv. Belinda) and alfalfa (*Medicago sativa* L, ) were cultivated in a treatment without lime and sulfur fertilization  
 25 (control), in a treatment with lime and without sulfur application and in treatments

with various limestone/FeSO<sub>4</sub> mixture applications with 50 mg S kg<sup>-1</sup> soil (= 0.3 g S / pot). Each treatment contained four replications for rape and alfalfa each. The soil in the pots was treated with nitrogen (1 g N / pot as NH<sub>4</sub>NO<sub>3</sub>), phosphorus and potassium (0.6 g P and 1.6 g K / pot as K<sub>2</sub>HPO<sub>4</sub> & KCl), magnesium (0.3 g Mg / pot as Mg(NO<sub>3</sub>)<sub>2</sub>), boron (3 mg B / pot as H<sub>3</sub>BO<sub>3</sub>), copper (30 mg Cu / pot as CuCl<sub>2</sub>), manganese (120 mg Mn / pot as MnCl<sub>2</sub>), molybdenum (0.6 mg Mo / pot as NH<sub>4</sub> molybdate) and zinc (60 mg Zn / pot as ZnCl<sub>2</sub>). After mixing the fertilizers with the soil and an incubation period of one week at 60% of the water holding capacity, rape and alfalfa were sown. The seeds of alfalfa were inoculated with *Rhizobium melilotii*. After germination rape plants were thinned on three plants / pot and alfalfa on 20 plants / pot. Then rape plants were fertilized with 0.5 g / pot in liquid form as NH<sub>4</sub>NO<sub>3</sub>. In contrast to summer rape, alfalfa was not further applied with mineral nitrogen in order to analyze effect of a S fertilization in form of the new products on the N<sub>2</sub> fixation.

Three months after sowing, summer rape plants were harvested and alfalfa was cut three times during the vegetation period. After the 1<sup>st</sup> and 2<sup>nd</sup> harvest alfalfa was fertilized with 0.5 g K / pot in liquid form as K<sub>2</sub>HPO<sub>4</sub>. In the following tables, the effects of sulfur fertilization in form of gypsum and various limestone/FeSO<sub>4</sub> mixtures on the yields of summer rape are presented.

Application of sulfur in form of limestone/FeSO<sub>4</sub> mixtures resulted in an increase of the growth of summer rape. In the treatments without S fertilization rape plants showed the typical S deficiency symptoms at the older leaves. Such symptoms were not visible at the leaves in the treatments with sulfur fertilization with lime/FeSO<sub>4</sub> fertilization. The sulfur deficiency was so strong that summer rape did not produce any seeds in the control without sulfur treatment, as it can be seen from Table 2 and Figure 1.

Table 2 - Effect of a sulfur fertilization (0.3 g S / pot) in form of various limestone/FeSO<sub>4</sub> mixtures on the seed and straw yield of summer rape

Treatment	Seed yield (dry matter) g / pot	Straw yield (dry mater) g / pot
Control experiment	0	10.0
Limestone (Control experiment)	0	10.5
Limestone & FeSO <sub>4</sub> , 1:1	8.5	25.5
Limestone & FeSO <sub>4</sub> , 4:1	8.0	26.0
Limestone & FeSO <sub>4</sub> , 10:1	7.8	25.4
Basic slag from steel production & FeSO <sub>4</sub> , 2:1	8.6	25.0

The here presented results of the effect of lime/FeSO<sub>4</sub> mixtures show that the  
 5 inventive products are suitable as mineral sulfur and lime fertilizers for agricultural plants.

In a further experiment we have tested the effects of S fertilization in form of the  
 various limestone/FeSO<sub>4</sub> mixtures on the yield of alfalfa. In contrast to summer  
 rape S fertilization did not result to an initial significant yield increase. The soil had  
 10 enough sulfur for a first growth of alfalfa. However, an increasing part of CaCO<sub>3</sub> resulted to a decrease of the shoot biomass at the first harvest, s. Table 3.

This is due to the sensitivity of alfalfa to “free lime” in the soil solution which may  
 have result to a OH<sup>-</sup> ion toxicity. At the 2<sup>nd</sup> and 3<sup>rd</sup> harvest, however, there was  
 found a clear positive effect for the limestone/FeSO<sub>4</sub> mixtures. The highest  
 15 cumulative shoots biomass was produced in the treatment with basic slag lime /FeSO<sub>4</sub> mixture.

Table 3: Effect of a sulfur fertilization (0.3 g S / pot) in form of various limestone/FeSO<sub>4</sub> mixtures on the soil pH before sowing of alfalfa and on the shoot yields of alfalfa

Treatment	Soil pH in a soi/0.01 M CaCl <sub>2</sub> suspension of 1:10	1 <sup>st</sup> Harvest g dry matter pot <sup>-1</sup>	2 <sup>nd</sup> Harvest g dry matter pot <sup>-1</sup>	3 <sup>rd</sup> Harvest g dry matter pot <sup>-1</sup>	Σ of Harvests g dry matter pot <sup>-1</sup>
Control	6.5	16.6	13.5	2.0	32.1
Lime	6.8	16.9	14.5	2.0	33.4
Lime & FeSO <sub>4</sub> , 1:1	6.8	18.2	18.6	7.8	44.6
Lime & FeSO <sub>4</sub> , 4:1	7.1	13.0	18.3	8.1	39.4
Lime & FeSO <sub>4</sub> , 10:1	7.4	11.6	19.0	8.5	39.1
Basic slag lime from steel production & FeSO <sub>4</sub> , 2:1	7.0	17.5	20.9	9.7	48.1

5

Conclusion: The here presented results of the effect of limestone/FeSO<sub>4</sub> mixtures show that the products are suitable as mineral sulfur and limestone fertilizers for agricultural plants. Limestone/FeSO<sub>4</sub> mixtures should not applied to legumes in a ratio greater than 1:1.

10

Claims:

1. Process for manufacturing a fertilizer composition comprising S, Fe and one or more earth alkaline elements, including Ca and/or Mg, being suitable for administration onto a sulfur deficient soil wherein a material, comprising Fe and sulfate ions, in form of a solid salt, filter cake, paste, slurry, or solution, is blended with at least one component being chosen from or comprising oxides, hydroxides or carbonates of the earth alkaline elements including at least one of Ca and Mg, preferably  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , dolomite  $(\text{Ca,Mg})\text{CO}_3$ ,  $\text{MgO}$ , burnt dolomite  $(\text{Ca,Mg})\text{O}$ ,  $\text{CaO}$ , semi-hydrated dolomite  $\text{Ca}(\text{OH})_2\text{MgO}$ , or  $\text{Ca}(\text{OH})_2$  or mixtures thereof in molar ratio of  $(\text{Ca}+\text{Mg})/\text{Fe} = 2$  to 200, preferably 2.5 to 25, more preferably 10 to 25, and the blend is converted into an administration form.
2. Process for manufacturing a fertilizer composition according to claim 1 wherein blending and converting is carried out simultaneously.
3. Process for manufacturing a fertilizer composition according to any of claims 1 or 2 wherein blending and/or converting is carried out in the presence of any of water, dilute sulfuric acid, preferably diluted,  $\text{CaSO}_4$ , elemental sulfur or other S containing compounds, other compounds useful for a fertilizer, such as micronutrients, preferably a boron compound, binder or granulation aids, or mixtures thereof.
4. Process for manufacturing a fertilizer composition according to any of claims 1 to 3, wherein the material comprising Fe and sulfate ions is  $\text{FeSO}_4$  which may contain crystal water.
5. Process for manufacturing a fertilizer composition according to claim 4, wherein  $\text{FeSO}_4$  is  $\text{Fe}(\text{II})\text{SO}_4$  heptahydrate, preferably obtained from the titanium dioxide production process.

- 5
6. Process for manufacturing a fertilizer composition according to any of claims 1 to 5, wherein the at least one component comprising oxides, hydroxides or carbonates of earth alkaline elements is limestone, consisting of fine particles 95 % < 0,09 mm and comprising >95 % CaCO<sub>3</sub>.
- 10
7. Process for manufacturing a fertilizer composition according to any of claims 1 to 5, wherein the at least one component comprising oxides, hydroxides or carbonates of earth alkaline elements is burnt lime, burnt dolomite or hydrated lime.
- 15
8. Process for manufacturing a fertilizer composition according to any of claims 1 to 5, wherein the at least one component comprising oxides, hydroxides or carbonates of earth alkaline elements is a slag from steel manufacturing or a reaction product from such a slag.
- 20
9. Process for manufacturing a fertilizer composition according to any of claims 1 to 8, wherein at least one of starch, magnesium sulfates, citric acid, clay, mortar binder, cellulose glue, glucosidic binder such as starch, molasses, lignosulfonate, water, hydrated lime, water glass, bentonite, cellulose fibres, stearates, urea or combinations of these materials is used as binder or granulation aid in a weight ratio of 0.1 to 10 weight-%, preferably 0.3 to 5 weight-%, most preferably 0.8 to 3 weight-%, related to the total mass of the composition comprising Fe and sulfate ions and the at least one component being chosen from or comprising oxides, hydroxides or carbonates of the
- 25
- earth alkaline elements Ca and Mg.
- 30
10. Process for manufacturing a fertilizer composition according to any of claims 1 to 9, wherein the process is carried out in an apparatus which can also serve for compaction, granulation and/or pelletizing the reaction product.
11. Process for manufacturing a fertilizer composition according to claim 10, wherein the granulation is carried out by blending:
- a. a material comprising Fe and sulfate ions,

- b. a material comprising carbonates of the earth alkaline elements Ca and/or Mg, preferably  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ , or dolomite, and
- c. a material comprising oxides or hydroxides of earth alkaline elements, preferably  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Mg}(\text{OH})_2$ , or  $\text{Ca}(\text{OH})_2$ ,
- 5 in the form of powder without any addition of water, with the reaction of these materials while being mixed and granulated in the same apparatus.
12. Process according to any of claims 1 to 11, wherein the neutralizing value of the at least one component being chosen from or comprising oxides,
- 10 hydroxides or carbonates of the earth alkaline elements according to DIN EN 12945:2014-07 standard is 1 to 55% (as  $\text{CaO}$ ), preferably 20 to 55%, most preferably 33 to 48%.
13. Fertilizer composition comprising S, Fe and at least one earth alkaline
- 15 element including at least one of Ca and/or Mg, wherein the molar ratio of  $(\text{Ca}+\text{Mg})/\text{Fe}$  is in the range of 2 to 200, preferably 2.5 to 25, most preferably 10 to 25.
14. Fertilizer composition according to claim 13, wherein the molar ratio of Fe to
- 20 S is 0.3 to 6, preferably 0.5 to 2, most preferably 0.8 to 1.2.
15. Fertilizer composition according to any of claims 13 and 14, wherein the ratio of the peak areas P, Q, I and J in the XRD spectrum  $(P*Q) / (I*J)$  is more than 8, preferably more than 5, more preferably more than 2, with P being the
- 25 integral area of the x-ray diffraction peaks between  $2\theta = 20.0$  and  $21.5^\circ$ , with Q being the integral area of the XRD peaks between  $2\theta = 29.0$  and  $30.5^\circ$ , with I being the integral area of the XRD peaks between  $2\theta = 16.0$ , and  $20.0^\circ$  and with J being the integral area of the XRD peaks between  $2\theta = 23.4$  and  $28.0$ .
- 30
16. Fertilizer composition according to any of claims 13 to 15, wherein the ratio of the peak areas A/B is more than 1, preferably more than 5, more preferably more than 10, with A being the integral area of the x-ray diffraction peaks

between  $2\theta = 20.2$  and  $21.5^\circ$  and with B being the integral area of the x-ray diffraction peaks between  $2\theta = 25.0$  and  $28.0$ .

- 5 17. Fertilizer composition according to any of claims 13 to 16, wherein it contains Zn with mass ratio of Zn/Fe from 0.0001 to 0.003, preferably from 0.0002 to 0.0015, and/or Mn with the mass ratio of Mn/Fe from 0.00001 to 0.01, preferably from 0.00001 to 0.001.
- 10 18. Fertilizer composition according to any of claims 13 to 17, wherein the fertilizer is in a granulated form with volume based average granule size in the range from 1 to 8 mm, preferably 2 to 7, most preferably 3 to 6 mm.
- 15 19. Fertilizer composition, in particular according to any of claims 13 to 18, which is obtainable according to the process of any of claims 1 to 12.
- 20 20. Process for fertilizing S and one or more earth alkaline elements, preferably Ca and/or Mg wherein a fertilizer composition according to claim 19 is applied, preferably in form of granulates, onto a sulfur deficient soil used for agriculture, preferably for fertilizing sulfur to plants supplying amino acids, proteins and/or oil, in particular cultures of alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, wheat, barley, maize, sunflowers, soybean, navy beans, sorghum, oats, triticale, cruciferous plants like brassicas, radish, rocket and allium crops like onion, leek and garlic.
- 25 21. Process according to claim 20, wherein the application onto a sulfur deficient soil is made for base fertilization between summer and winter time.
- 30 22. Process according to claim 20 or 21, wherein the fertilizer composition according to claim 19 is applied onto the sulfur deficient soil in an amount that the pH of the soil is raised to above 5.8, preferably above  $>6.0$ , most preferably  $>6.2$ .

23. Use of a composition according to claim 19 as a sulfur fertilizer for fertilizing sulfur to plants supplying amino acids, proteins and/or oil, in particular to alfalfa, canola (rapeseed), cotton, clovers, phalaris, barrel medic, wheat, barley, maize, sunflowers, soybean, navy beans, sorghum, oats and triticale, cruciferous plants like brassicas, radish, rocket and allium crops like onion, leek and garlic.
- 5
24. Use of iron sulfate, preferably iron(II)sulfate heptahydrate, more preferably copperas as obtained as by-product from titanium dioxide manufacturing, for preparing a sulfur fertilizing composition.
- 10
25. Use of a solution comprising iron sulfate or use of crystalline iron sulfate with more than 3 molecules of crystal water, preferably iron(II)sulfate heptahydrate, more preferably copperas as obtained as by-product from titanium dioxide manufacturing, as aid for moistening and/or granulating powderous fertilizer materials.
- 15

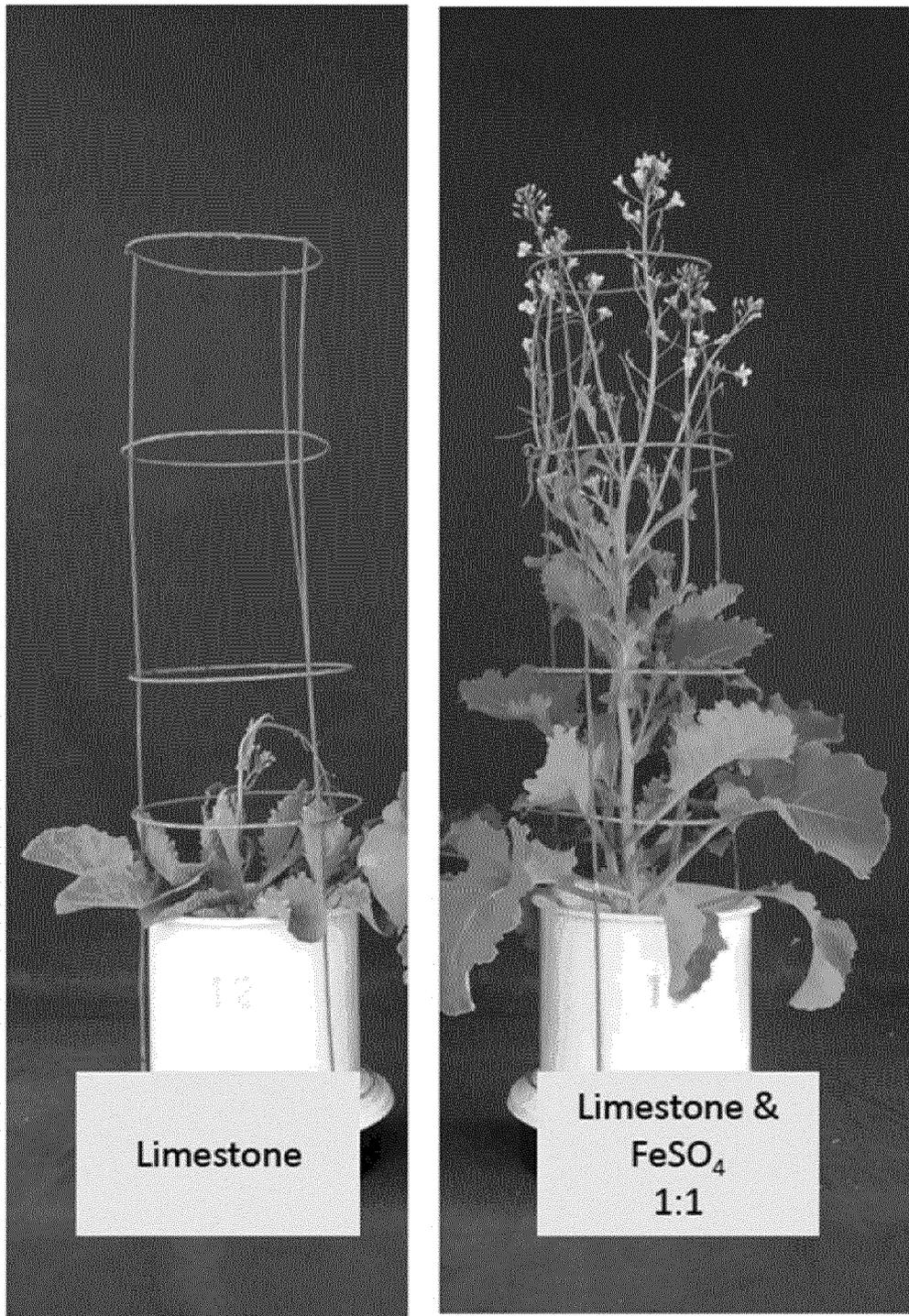


Figure 1/1

INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/060769

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C05D3/00 C05D5/00 C05D9/02 C05F7/00  
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)  
C05D C05F C05B C01F  
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)  
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C. DOCUMENTS CONSIDERED TO BE RELEVANT		
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Further documents are listed in the continuation of Box C.  See patent family annex.

\* Special categories of cited documents :

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Date of the actual completion of the international search  27 August 2015	Date of mailing of the international search report  07/09/2015
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Cardin, Aurélie
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International application No  
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