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(54) Title: SULPHUR FERTILIZER AND GRANULATED SULPHUR FERTILIZER MANUFACTURING METHOD

(57) Abstract: The invention covers sulphur fertilizer, in form of globular granules or pellets constituting solidified mixture of liquid sulphur, bentonite and lignosulfonates, and alternatively fertilizing additives. In its solidified mixture, the fertilizer contains 60-95% of sulphur, 4-20% of sodium or calcium bentonite, and 1-8% of calcium or sodium lignosulfonate. According to the invention, the method applied to produce granulated sulphur fertilizer is characterised by the following: the mixture of liquid sulphur with bentonite and alternatively with lignosulfonate or fertilizing additives is splashed in the granulator at the temperature of 120-150° C to form micro-drops, onto a curtain made by falling granules. Then, micro-drops are solidified layer by layer on surfaces of falling granules at the temperature of 90-115° C in a stream of air flowing through the curtain. At the same time, additional coolant is sprayed to cool the air. Granules and worn out coolant with air and dust are removed from the process in separate streams, while granules leaving the process are kept at the temperature of 40-90° C, and subgrain returned to the process favourably cools down to the temperature under 30° C.

## **Sulphur fertilizer and granulated sulphur fertilizer manufacturing method**

The invention covers sulphur fertilizer in form of globular granules or pellets, and the method used to manufacture granulated sulphur fertilizer.

Sulphur-bentonite fertilizer is a known substance in form of globular granules and pellets, containing elementary sulphur and bentonite.

Known fertilizer placed in humid soil gets reduced in size. In contact with soil moisture, bentonite contained in the fertilizer swells and blows out granules into molecules, which facilitates ground down sulphur contact with soil environment. In soil, sulphur molecules are subject to microbiological oxidation and obtain sulphatic nutritious form, which is available for plants.

A commonly used sulphur-bentonite fertilizer is the one in form of hemispherical pellets, derived due to formation of drops from mixture of liquid sulphur in a dropping apparatus called Rotoformer. This apparatus is demonstrated, among other things, in "Sandvik Process Systems" catalogues. Drops formed in Rotoformer are solidified into pellets on an "endless" cooling line.

Whereas, the American Patent Specification No. US 4,394,150 describes globular granules of sulphur-bentonite fertilizer containing 88–89% of sulphur and 11–12% of bentonite. According to the above-mentioned American invention, the granules are formed by mixing ground down bentonite with liquid sulphur and dropping liquid mixture passed through holes in the bottom of tank containing the mixture, while drops are solidified into granules in liquid manure salt solutions. The material inside ready granule has moisture content reaching up to 0.1%, while after drying moisture content near the granule outer surface reaches up to 1.5%.

On the other hand, Polish Specification of the invention, reported for patenting under ref. no. P. 319706, describes sulphur-bentonite fertilizer in form of globular granules containing 85–93% by weight of elementary sulphur and 7–15% by weight of ground down dry bentonite.

According to the above-mentioned invention, fabrication method for the sulphur-bentonite fertilizer granules involves preparation of bentonite suspension in liquid sulphur. At the same time, bentonite is dried up by heat contained in liquid sulphur, then the suspension is let through sprinkling screens of the granulation column, while drops of sulphur-bentonite suspension developed on the screen are solidified into granules in a stream of cool air delivered from the bottom of the granulation column.

This fertilizer possesses micropores, which facilitates bentonite contact with moisture everywhere inside the granule.

Moreover, British Invention Specification No. GB 2292140 describes sulphur-bentonite fertilizer in form of globular granules containing micronised elementary network sized from 5 to 130  $\mu\text{m}$ .

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The above-mentioned fertilizer manufacturing process involves the following: micronised sulphur is mixed with bentonite powder and with water solution of lignosulfonate. Then, the mixture is granulated in a disk-type granulator/pelletizer, or compacted. After this, the granules are dried. This fertilizer easily disperses in soil, turning into sulphur micro-particles sized as above.

Granules made of micronised sulphur disperse in humid soil into much smaller sulphur particles than fertilizer granules formed by solidifying the mixture of liquid sulphur and bentonite.

Known fertilizers containing both micronised sulphur and solidified mixture of liquid sulphur and bentonite, provide the base for the production of fertilizers containing main and residual additional fertilizing additives or microelements, apart from sulphur and bentonite.

The paper from M. Beeson "Another approach to S forming. Degradable sulphur", published by "SULPHUR" (September-October 1995), discusses sulphur-bentonite fertilizer in form of globular granules, containing 10% of bentonite and 90% of sulphur, obtained from the mixture of liquid sulphur and bentonite in a rotary drum-type granulator with fluidized bed, according to the FDG process (Kaltenbach-Thuring S.A, France, Fluid Drum Granulation – FDG process).

The paper published by Denis Lauchard and Marie-Astrid Kordek (Kaltenbach-Thuring S.A.) "Granulation KT'S Progress using fluidized drum granulation (FDG) Technology" presents specification of a process involving the production of sulphur-bentonite granules in a granulator (FDG) provided with fluidized bed, nozzles, vanes and chute.

Granulation system consists of the above-mentioned granulator with fluidized bed supplied from the bottom with air, and sulphur-bentonite mixer heated up with steam, a pump for sulphur-bentonite mixture, system exhausting air from the granulator, and filter separating dust from contaminated air.

Known granulation method in the FDG granulator with vanes and chute involves the following operations: fluidized bed is supplied the bottom with cool air via screen, granulation subgrain is brought into the bed, and the mixture of liquid sulphur and bentonite is sprayed onto the subgrain. Then, the mixture is solidified on the granules in cool air. Thus obtained granulated product is sieved out of the granulator, and its undersized part is returned to the granulator. Hot air received from the granulator is subject to dedusting and cooling out of the granulator, and then it is returned to it. Sulphur-bentonite granules obtained through the above-mentioned method possess required mechanical strength and low moisture content of approximately 0.15%.

There is a hazard of ignition and sulphur dust explosion in the granulator during granulation of liquid sulphur-bentonite mixture in air.

The purpose of the invention is to develop a composition of sulphur fertilizer, in form of globular granules or pellets, which would contain solidified mixture of liquid sulphur and bentonite, and disperse in contact with soil moisture

into sulphur molecules of much smaller size than that is in case of known fertilizers of this type.

Moreover, the purpose of the invention is to develop environment-friendly and inexpensive method of sulphur fertilizer production in form of globular granules characterised by low moisture content.

According to the invention, sulphur fertilizer, either in form of globular granules or pellets that constitute solidified mixture of liquid sulphur and bentonite, and favourably additional components and fertilizing microelements, is characterised by its content: 60–95% of sulphur, 4–20% of bentonite and 1–8% of lignosulfonate.

According to the invention, the fertilizer contains calcium or sodium lignosulfonate and sodium or calcium bentonite.

Favourably, bentonite and lignosulfonate have the form of powders suspended in solidified mixture with grain sizes up to 120  $\mu\text{m}$ .

In the method of granulated sulphur fertilizer production, liquid sulphur is mixed with bentonite and favourably with additional components and fertilizing microelements. Then the mixture is subject to granulation in a rotary drum-type granulator with nozzles and vanes. This is effected by spraying liquid mixture through the nozzles onto the granules cyclically poured through by vanes in the granulator, and by solidifying the mixture layer by layer on the granules in air, while subgrain is returned to the granulator. According to the invention, the above-mentioned method is characterised by splashing liquid mixture at the temperature of 120–150<sup>0</sup> C to form micro-drops, onto a curtain made by falling granules. Then, the micro-drops are solidified layer by layer on granule surfaces at the temperature of 90–115<sup>0</sup> C in a stream of air flowing through the curtain. At the same time, additional coolant is sprayed, which cools the air.

Granules and worn out coolant with air and dust are removed from the process in separate streams, while granules leaving the process are kept at the temperature of 40–90<sup>0</sup> C, and subgrain returned to the process favourably cools down to the temperature under 30<sup>0</sup> C.

Favourably, liquid mixture splashes into micro-drops under the pressure of 0.5–2 MPa, while, in particular, sodium or calcium lignosulfonate is added to the liquid mixture. Then, the mixture with lignosulfonate is splashed onto a curtain of falling granules at the temperature under 130<sup>0</sup> C.

According to the invention, in one version of the method the air is cooled down with an additional coolant in form of water mist. In particular, water mist is delivered directly into the air stream.

In another version of the method the air is cooled down with additional gaseous coolant, especially nitrogen or carbon dioxide, while gaseous coolant is delivered into the air stream.

According to the invention, since it contains solidified liquid sulphur, bentonites and lignosulfonates, the fertilizer disperses in humid soil into smaller sulphur molecules that it is in the case of known fertilizers, in which only bentonite is the dispersant of solidified liquid sulphur.

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Lignosulfonates support bentonite in the process of dispersing sulphur contained in the fertilizer. According to the invention, in individual versions of fertilizers containing bentonites and calcium or sodium lignosulfonates, the fertilizers may disperse into sulphur molecules of various size and at different rates, depending on intended use of a given fertilizer.

In the method described in the invention, additional air cooling with water mist during formation of granules allowed for considerable reduction in volume of generated sulphur dusts. This allowed to eliminate fire spreading or dust explosion hazards during the granulation process.

Total evaporation of water micro-drops during air cooling allows to obtain product with low moisture content. The fertilizer remains dry also in the case, when air is cooled with gas. Dry bentonite contained in the fertilizer and obtained using the method specified in the invention effectively bursts the fertilizer into sulphur micro-molecules, as it is able to swell when the fertilizer contacts moisture contained in soil.

Moreover, the method applied to produce globular sulphur fertilizer granules according to the invention is cheaper than known method of sulphur-bentonite fertilizer granulation in the granulator with fluidized bed.

Sulphur fertilizer in form of globular granules and pellets and the method applied to produce granulated sulphur fertilizer are specified in the following examples of the invention implementation.

Example 1:

Sulphur fertilizer was prepared in form of globular granules, 2–4 mm in diameter; pH = 8.7; w = 0.1% (moisture content), containing solidified mixture of liquid sulphur, bentonite and lignosulfonate, at the following composition by weight:

sulphur - 88.0%;  
sodium bentonite - 5.0%;  
calcium bentonite - 5.0%;  
calcium lignosulfonate - 2.0%.

The granules have high mechanical strength. The volume of dust generated during mechanical distribution of the fertilizer is small. The fertilizer in form of globular granules works better than pellets in the production of mixes with other granulated fertilizers.

Fertilizer granules were placed in water, and after 8 days it was found that 60% of sulphur contained in the fertilizer had micro-particles smaller than 150  $\mu\text{m}$ , and 95% under 250  $\mu\text{m}$ .

Elementary sulphur sized as above easily goes through microbiological oxidation in soil to obtain sulphatic form, which is available for plants.

The fertilizer is intended first to feed sulphur-philic plants, and also to control the pH in soil.

Sodium and calcium bentonite, 50 kg of each, and 20 kg of calcium lignosulfonate, in form of dry powders with particles smaller than 75  $\mu\text{m}$ , are proportioned uniformly to 880 kg of liquid sulphur and the above-mentioned

components are evenly mixed at the temperature of 125–130<sup>0</sup> C in a steam-heated mixer.

Then, the fertilizer nuclei of crystallization are poured into tilted, rotary drum-type granulator with vanes, nozzles and chute. These nuclei constitute granulation subgrain, at the beginning of the process in form of sulphur powder.

The mixture of liquid sulphur, bentonite and lignosulfonate is splashed through nozzles in rotating granulator at the temperature ranging from 125 to 130<sup>0</sup> C at nozzle outlet. The mixture is sprayed by nozzles at the pressure of 0.8 MPa onto the curtain made by granulation subgrain. The subgrain cyclically pours through the vanes in the granulator. The mixture is solidified on granulation subgrain at the temperature of 105–110<sup>0</sup> C in the stream of air flowing along the granulator through the curtain of falling subgrain.

In the granulator, additional coolant is sprayed by nozzles into the air stream, while, according to the invention implementation example, the coolant is constituted by water sprayed into micro-drops of water mist, which evaporates and cools the air.

Granules leaving the process at the granulator outlet are kept at the temperature of 50–60<sup>0</sup> C, and subgrain returned to the granulator is cooled out of it down to the temperature under 30<sup>0</sup> C. Granules and air with steam and sulphur-bentonite dusts are removed from granulator in separate streams, via the outlet for granulated product and air outlet from granulator, respectively.

Undersized granulated product (smaller than 2 mm), as a subgrain, is returned to the granulator, whereas granules with diameters above 4 mm, as a supergrain, is sent to the mixer for remelting and mixing with other fertilizer components.

Example 2:

Sulphur fertilizer was prepared with additives, in form of pellets 2–4 mm in diameter; pH = 8.4; w = 0.15% (moisture content), containing solidified mixture of liquid sulphur, bentonite, lignosulfonate, magnesium oxide, manganese oxide and copper oxide, at the following composition by weight:

sulphur - 80.0%;  
magnesium oxide - 5.0%;  
manganese oxide - 1.5%;  
copper oxide - 1.5%;  
sodium bentonite - 10.0%;  
calcium lignosulfonate - 2.0%.

Fertilizer pellets have been fabricated by solidifying drops of liquid sulphur mixture with bentonite powders and the above-mentioned fertilizing additives sized under 75 µm, to form pellets on a cooling line.

Pellets have high mechanical strength, and they are suitable for mechanical fertilizer distribution in soil. Pellet edges crumble to negligible extent. Fertilizer pellets sized from 2 to 4 mm were placed in water and after 8 days it was found that 70% of molecules contained in dispersed fertilizer, including elementary sulphur, were smaller than 100 µm, and 95% were under 200 µm.

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Elementary sulphur sized as above easily goes through microbiological oxidation to sulphatic form, which is available for plants. Moreover, the fertilizer contains microelements in form of micro-particles of magnesium oxide, manganese oxide and copper oxide, which are nutritious for plants.

Example 3:

130 kg of dry sodium bentonite with particles smaller than 100  $\mu\text{m}$  is proportioned at uniform rate to 870 kg of liquid sulphur, and simultaneously mixed with liquid sulphur at the temperature of 140<sup>o</sup> C in a steam-heated mixer.

Then the fertilizer nuclei of crystallization are poured into tilted, rotary drum-type granulator with vanes, nozzles and chute. These nuclei constitute granulation subgrain, at the beginning of the process in form of sulphur-bentonite powder.

Liquid sulphur-bentonite mixture is splashed through nozzles in rotating granulator at the pressure of 0,5 MPa and temperature reaching 135<sup>o</sup> C at nozzle outlet onto the curtain made by granulation subgrain. This results from cyclic pouring of the subgrain by vanes in the granulator. The mixture is solidified on granulation subgrain at the temperature of approximately 105<sup>o</sup> C.

At the same time, air stream is delivered to the granulator and air flow direction stabilises along the granulator, across falling subgrain.

Nitrogen is delivered through nozzles into the air stream flowing through the granulator. Hot air and granules being formed are cooled simultaneously with air and decompressed nitrogen, while granules at granulator outlet are kept at the temperature of 60–65<sup>o</sup> C.

Granules and gaseous cooling agents with sulphur-bentonite dust are removed from the granulator in separate streams, via the outlet for granulated product and air outlet from granulator, respectively.

Undersized granules smaller than 2 mm are returned to the granulator, and oversized granules, larger than 4 mm in diameter, are crumbled and then sent to the mixer for remelting with other fertilizer components.

The method specified in this invention implementation example allowed to obtain sulphur-bentonite in form of globular granules sized from 2 to 4 mm, containing 87% of sulphur and 13% of bentonite with moisture content of 0.1%.

Formed granules were placed in water. After 8 days it was found that 52% of elementary sulphur contained in the fertilizer were micro-particles smaller than 150  $\mu\text{m}$ , and 85% were under 250  $\mu\text{m}$ .

Example 4:

Sulphur fertilizer was prepared in form of globular granules 2–4 mm in diameter; pH = 8.2; w = 0.1% (moisture content), with additives, containing solidified mixture of liquid sulphur, bentonite, lignosulfonate and gypsum, at the following percentage:

elementary sulphur - 75.0%;

gypsum - 15.0%;

sodium bentonite - 8.0%;

calcium lignosulfonate – 2.0%.

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Fertilizer granules were placed in water, and after 8 days it was found that 50% of molecules contained in the fertilizer were micro-particles smaller than 150 $\mu\text{m}$ , and 80% were under 250 $\mu\text{m}$ .

Elementary sulphur sized as above easily goes through microbiological oxidation in soil to obtain sulphatic form, which is available for plants. Already at the beginning the fertilizer contains sulphur from gypsum in sulphatic form. The fertilizer is intended for feeding sulphur-philic plants.

80 kg of sodium bentonite and 20 kg of calcium lignosulfonate and 150 kg of gypsum in form of dry powders with grains smaller than 80  $\mu\text{m}$  are proportioned at uniform rate to 750 kg of molten, liquid sulphur. The components specified above are uniformly mixed at the temperature of approximately 125<sup>0</sup> C in a steam-heated mixer.

Then, the mixture is subject to granulation according to the method specified in example 1 of the invention implementation.

Example 5:

Sulphur fertilizer was prepared with additives, in form of globular granules 2–4 mm in diameter; pH = 8.2; w = 0.1% (moisture content), containing solidified mixture of liquid sulphur, bentonite, lignosulfonate phosphorite and magnesium oxide, at the following percentage:

elementary sulphur - 70.0%;

soft phosphorite - 15.0%;

magnesium oxide - 5.0%;

sodium bentonite - 8.0%;

calcium lignosulfonate - 2.0%.

Fertilizer granules sized from 2 to 4 mm. were placed in water and after 8 days it was found that 55% of molecules contained in the fertilizer were micro-particles smaller than 150  $\mu\text{m}$ , and 85% under 250  $\mu\text{m}$ .

In one season, elementary sulphur sized as above easily goes through microbiological oxidation in soil to obtain sulphatic form, which is available for plants.

At the same time, phosphorite molecules are acidified in soil. The fertilizer is intended to supply plants with sulphur, phosphorus and magnesium at the same time.

80 kg of sodium bentonite and 20 kg of calcium lignosulfonate and 150 kg of soft phosphorite, all dry powders, with grains smaller than 75  $\mu\text{m}$ , are proportioned at uniform rate to 700 kg of liquid sulphur, and the above-mentioned components are subject to uniform mixing at the temperature of 130<sup>0</sup> C in a steam-heated mixer.

Then, the mixture is subject to granulation according to the method specified in example 1 of the invention implementation.

### Claims

1. Sulphur fertilizer in form of globular granules or pellets, constituting solidified mixture of liquid sulphur and bentonite, and favourably additional components and fertilizing microelements, characterised in that it contains: 60–95% of sulphur, 4–20% of bentonite, and 1–8% of lignosulfonate.
2. Fertilizer, according to claim 1, characterised in that it contains calcium ligno-sulfonate.
3. Fertilizer, according to claim 1, characterised in that it contains sodium ligno-sulfonate.
4. Fertilizer, according to claim 1, characterised in that it contains sodium bentonite.
5. Fertilizer, according to claim 1, characterised in that it contains calcium bentonite.
6. Fertilizer, according to claim 1, characterised in that it contains bentonite and lignosulfonate in the form of powders with grains sized up to 120  $\mu\text{m}$ .
7. Method applied to produce granulated sulphur fertilizer, in which liquid sulphur is mixed with bentonite and favourably with additional fertilizing components and microelements, then the mixture is granulated in a rotary drum-type granulator with nozzles and vanes by spraying the liquid mixture through the nozzles onto the granules cyclically poured through by vanes in the granulator and solidifying the mixture layer by layer on the granules in air, while subgrain is returned to the granulator, characterised by splashing the liquid mixture at the temperature of 120–150<sup>0</sup> C to form micro-drops, onto a curtain made by falling granules and then the micro-drops are solidified layer by layer on granule surfaces at the temperature of 90–115<sup>0</sup> C in a stream of air flowing through the curtain, and at the same time, an additional coolant is sprayed to cool the air, and the granules and worn out coolant with air and dust are removed from the process in separate streams, while granules leaving the process are kept at the temperature of 40–90<sup>0</sup> C, and subgrain returned to the process favourably cools down to the temperature under 30<sup>0</sup> C.
8. Method, according to claim 7, characterised in that the liquid mixture is splashed into micro-drops under the pressure of 0.5–2 Mpa.

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9. Method according to claim 7, characterised in that sodium or calcium lignosulfonate is added to the liquid mixture and then the mixture containing lignosulfonate is splashed onto a curtain of falling granules at the temperature under 130° C.
10. Method according to claim 7, characterised in that the air is cooled with an additional coolant in the form of water mist.
11. Method according to claim 10, characterised in that the air is cooled with complete water mist evaporation.
12. Method according to claim 10, characterised in that the water mist is sprayed into the air stream.
13. Method according to claim 7, characterised in that the air coolant is cooled with an additional gaseous coolant, especially nitrogen or carbon dioxide.
14. Method according to claim 13, characterised in that the gaseous coolant is delivered into the air stream.