(54) Title: ADDITIVE FOR PREVENTING DEPOSITS AND CORROSION OF HEATING FURNACES OR STEAM GENERATORS, AND METHOD FOR ITS OBTAINING

(57) Abstract: An additive is described as preventing deposits and corrosion of heating furnaces or steam generators, which is characterized by the fact that it is a water solution, containing 25±40 g/l K⁺ ions, 60±80 g/l NO₃⁻ ions, a maximum amount of 50 mg/l chromium, ethylic alcohol or mono ethylene glycol in a maximum proportion of 35 % wt., 5±11 g/l NH₄⁺ ions, and having a pH value 8 and a congealing temperature in the range of -5±20 °C. The method for obtaining this additive comprises dissolution of components, filtration of solutions, homogenization and addition of the mixture, followed by adjusting its pH to a value equal or greater than 8. The present additive is useful for preventing corrosion phenomena and deposits resulted in furnaces and steam generators, which use any gaseous, liquid or solid fuels.
ADDITIVE FOR PREVENTING DEPOSITS AND CORROSION OF HEATING FURNACES OR STEAM GENERATORS, AND METHOD FOR ITS OBTAINING

The present invention describes an additive for preventing deposits and corrosion of heating furnaces or steam generators, and a method for its obtaining, this additive being useful for the treatment of the combustion gases by injection in the combustion chamber or in the fuel just before its entrance to the burner.

For heating generation in technological, domestic or energetic purposes, the gaseous liquid or solid fuels are burned resulting in various compounds responsible of the low and high temperature corrosions, of the formation of deposits and environmental pollution.

One of the commonly used methods for preventing corrosion, deposit formation and environmental pollution phenomena is the use of additives. There are a large variety of liquid and solid additives [1-5] in industrial practice.

Prior art patents related to the present invention include the following:

RO Pat. No. 114507B describes a composition for the combustion air treatment at furnace equipments, containing sodium nitrate, potassium nitrate, ammonium nitrate and/or cerium nitrate, in concentration of 0,25...150g/l, with or without magnesium nitrate, in concentration of 100...800g/l and/or potassium dichromate, in concentration of 0,4...104g/l, in function of the flow and the characteristics of the fuel, as well as in function of the flow and the temperature of the treated air fraction.

RO Pat. No. 114507B mentions the improving of the combustion air with the suspensions of burning improver and deposit control, using 0,025-0,25ppm Cr⁶⁺, 0,15-1,5ppm NO₃⁻ and 0,75-7,5ppm Ce⁴⁺ in the fuel oil.

These additives have the following disadvantages:

- they influence negatively on the burners by alteration of the atomizer passage of fuels
- they are obtained through laborious processes and with equipments of high energy consumption (colloidal mills, centrifugal settlers, methods of obtaining in situ colloidal dispersions);
- they need complex equipments of dosage at stack gases or fuels treatment (blenders, dispensing devices);

The technical problem solved by the invention is the increasing additive stability at transport and storage, at low temperatures (till -21°C).

The additive, in conformity with this patent, eliminates the disadvantages, by solving the technical problem mentioned above and being made of watery solution and containing 25-40 g/l K⁺ ions, derived from KNO₃, 60-80 g/l NO₃⁻ ions derived from KNO₃ and NH₄NO₃, 5-11 g/l NH₄⁺ ions, derived from (NH₄)₂Cr₂O₇, NH₄OH and NH₄NO₃, 30-50 mg/l Cr⁶⁺, derived from (NH₄)₂Cr₂O₇,
5-35% wt. ethylic alcohol or mono ethylene glycol, and having a pH value of 8 and a congealing temperature in the range of -5 to -20°C.

The method for obtaining the additive, in conformity with the patent, eliminates the disadvantages mentioned and characterized by preparing a solution of potassium nitrate, by blending 4-10 parts KNO3 with 30-100 parts demineralized water, and a solution of NH4NO3, by blending 1-4 parts ammonium nitrate with 5-25 parts demineralized water, by filtering these two solutions and by mixing in a proportion of 5-30 parts of filtered solution of ammonium nitrate to 35-110 parts of filtered solution of potassium nitrate, by adding to this mixture 0.6-1.5 parts solution of 1% wt. ammonium dichromate in water, by homogenizing using mechanical stirring, by adding 5-35 parts ethylic alcohol or mono ethylene glycol, by adding a 25% ammonia solution to adjust pH to a value equal or greater than 8, the parts being expressed in wt.

The use of this invention presents the following advantages:
- it provides the stability of the product on a large temperature range (+50 to -21°C);
- it reduces the complexity of additive synthesis process through simple dissolving operations, through filtration and homogenization;
- it reduces the energetic consumption in the process of additive fabrication;
- it facilitates combustion processes due to the Cr^6+ ions derived from (NH4)2Cr2O7, in the concentration already mentioned, ions which provide advanced ionization of the gases;
- it eliminates the disadvantage of alteration of the burners, extending their life time through direct injection of additive in the combustion room;
- it reduces the quantity of deposits on the heat exchanger surfaces, facilitating their cleaning operations;
- it reduces the air pollution by reducing considerably the content of NOx, SO2 and SO3 in the stack gases, due to the decreasing temperature in the combustion room and to the presence of K+ ion in the concentration already mentioned;
- it increases the furnace efficiency as a result of the increasing degree of heat recovery from the stack gases;
- it increases the durability of equipments as a result of corrosion phenomena preventing on the stack gases flow.

As follows, there are presented four examples for obtaining the additive, in conformity with the invention.
Example 1.

4.1 parts wt. of potassium nitrate and 48 parts wt. of demineralized water are introduced into an 800-cm³ cylindrical glass vessel, at room temperature, and the mixture is homogenized using a magnetic stirrer up to the total dissolution of the nitrate. In a similar vessel, 5 parts wt. of demineralized water and 1.7 parts wt. of ammonium nitrate are homogenized using a magnetic stirrer until the ammonium nitrate is completely dissolved. These two solutions obtained as described previously are filtered separately and mixed in a proportion of 52 parts of potassium nitrate solution to 7 parts wt. of ammonium nitrate solution, followed by mechanical homogenization for 30 minutes. To the new obtained solution is added mono ethylene glycol or ethylic alcohol and an 1% wt. ammonium dichromate solution in water in a proportion of 0.6 parts wt. relative to the mixture of the two solutions. The resulting mixture is adjusted for a pH 10.8, using a 25% wt. solution of ammonia in distilled water.

By this procedure, it is obtained an additive for preventing deposits and corrosion of heating furnaces or steam generators. characterized by the fact that it is a water solution containing 26.8 g/l K⁺ ions, 63.7 g/l NO₃⁻ ions, 6 g/l NH₄⁺ ions, 30 mg/l chromium, 5% mono ethylene glycol or ethylic alcohol, having a pH value 10.8 and a congealing temperature of -6°C.

Example 2.

Into a cylindrical vessel like the one described in Example 1, 9 parts of potassium nitrate and 100 parts of demineralized water are added and stirred with a magnetic stirrer up to the total dissolution of the nitrate. Into another similar vessel, 4 parts of ammonium nitrate and 12 parts of demineralized water are added, followed by stirring until the nitrate is completely dissolved. These two solutions are filtered and mixed in a proportion of 110 parts potassium nitrate solution to 16 parts of ammonium nitrate and to this mixture is added 10% wt. mono ethylene glycol or ethylic alcohol and a 1% wt. solution of ammonium dichromate is added in a proportion of 1 part wt., followed by homogenization for 15 minutes. The new product obtained is corrected for a pH value equal or greater than 8, using an ammonia solution of 25% wt. in distilled water.

Thus, it is obtained an additive for preventing deposits and corrosion of heating furnaces or steam generators, characterized by the fact that it is a water solution having a pH value 10.8, containing 35.1 g/l K⁺ ions, 65 g/l NO₃⁻ ions, 6 g/l NH₄⁺ ions, 40 mg/l chromium, 10% mono ethylene glycol or ethylic alcohol and having a congealing temperature of -6°C.

Example 3.

Into a cylindrical vessel like the one described in Example 1, 7 parts of potassium nitrate and 30 parts of demineralized water are added and stirred, at room temperature, up to the total dissolution of the nitrate. Into another similar vessel, 3 parts of ammonium nitrate and 25 parts of demineralized water are added, followed by stirring until the salt is completely dissolved. These two solutions are filtered and mixed in a proportion of 37 parts potassium nitrate solution to 28
parts of ammonium nitrate. The newly obtained solution is mixed with ethylic alcohol in a proportion of 85% wt. to 35 %wt., respectively, and then to this mixture a 1% wt. solution of ammonium dichromate is added in a proportion of 1.5 parts wt. The mixture obtained is corrected for a pH value equal or greater than 8, using an ammonia solution of 25 % wt. in distilled water.

Thus, it is obtained an additive for preventing deposits and corrosion of heating furnaces or steam generators, containing a watery solution of 29 g/l K⁺ ions, 65 g/l NO₃⁻ ions, 6.5 g/l NH₄⁺ ions, 50 mg/l chromium, 35% wt. mono ethylene glycol or ethylic alcohol and having a pH value 8 and a congealing temperature of -21°C.

Example 4.

Into a cylindrical vessel like that described in Example 1, 9 parts of potassium nitrate and 40 parts of demineralized water are added and stirred with a mechanical device up to the total dissolution of the nitrate. Into another similar vessel, 4 parts of ammonium nitrate and 18 parts of demineralized water are added, followed by stirring until the salt is completely dissolved. The solutions thus obtained are filtered separately and mixed in a proportion of 49 parts potassium nitrate solution to 22 parts of ammonium nitrate. The solution obtained is then mixed with mono ethylene glycol for a final proportion of 29% wt. mono ethylene glycol. To this mixture, a 1% wt. solution of ammonium dichromate is added in a proportion of 1.5 parts wt., and then the pH is corrected for a value equal or greater than 8, using an ammonia solution of 25 % wt. in distilled water.

Thus, it is obtained an additive for preventing deposits and corrosion of heating furnaces or steam generators, characterized by the fact that it is a water solution, containing 36 g/l K⁺ ions, 77 g/l NO₃⁻ ions, 10 g/l NH₄⁺ ions, 50 mg/l chromium, 29% mono ethylene glycol and having a pH value 8 and a congealing temperature of -21°C.
APPLICATIONS

It is introduced in an autoclave a quantity of 413 kg demineralized water which is heated under permanent stirring at a temperature of 50-60°C after which it is added 72.5 potassium nitrate. The autoclave content is maintained under stirring for 1 h at a temperature of 50-60°C.

It is introduced in another autoclave 100 kg demineralized water, which is heated at 30-40 °C, and then it is introduced 30kg ammonium nitrate.

The blending is maintained at 30-40 °C for 1 h, under permanent stirring, then the solution obtained is filtrated. A clear ammonium nitrate solution is obtained, which is blended with the potassium nitrate solution. The blending of the two solutions is homogenized for 30 min at 30-40 °C. The solution obtained is alkalized by treatment with ammonium watery solution. For this purpose, in the autoclave with nitrates solution it is introduced 6.7 kg ammonia solution of 25% wt.

Then, in the autoclave it is added 428 Kg mono ethylene glycol and the blending is maintained under permanent stirring, for 30 min, at 30-40°C.

To control in time the pH value, to the product it is added 6.8 Kg alcoholic solution of phenolphthelein. Then, to the solution from the autoclave it is added 10 Kg solution of ammonium dichromate 1% in water. The product is kept under stirring for 30 min at 20-35°C.

Thus, it is obtained a clear red product, with pH = 8.5, d₂₀ = 1.056 and congealing temperature = -21°C, which is used at stack gases treatment in the heating furnaces and steam generators.

In the refinery furnace, which burns liquid fuel with 0.62% wt sulfur it results a concentration of SO₂+SO₃ of 365-400 mg/Nm³ and a corrosion rate of stack gases flow 0.1 mm per year.

By treating stack gases with the product obtained as described above in doses of 1l/8h, injected during 2-3 min in the combustion room, it is obtained a reduction of SO₂ and SO₃ concentration in the stack gases to 240-280 mg / Nm³, and the corrosion rate to 0.03-0.035 mm per year. Applying the treatment, deposits from the air pre-heater are eliminated by reducing the stack gases temperature at chimney from 270°C to 210°C and resulting a temperature increase of the preheated air from 180 °C to 250 °C.

Stack gases treatment at a steam boiler, which consumes liquid fuel with a sulfur content of 0.7% wt., by continuously injecting the obtained product in the combustion room at a treatment rate of 0.6 % wt. relative to the burned fuel, reduces the SO₂ and SO₃ content in stack gases from 420 mg/Nm³ to 200 mg/Nm³, extending the working time of the boiler between two cleanings with 100 % and reducing the fuel consumption with 8% wt. The corrosion rate on the stack gases flow was reduced from 0.12 mm per year to 0.035 mm per year.
CLAIMS

What is claimed is:

1. An additive for preventing deposits and corrosion of heating furnaces or steam
   generators, characterized by the fact that it is a watery solution, containing 25-40 g/l K⁺ ions,
   derived from KNO₃, 60-80 g/l NO₃⁻ ions derived from KNO₃ and NH₄NO₃, 5-11 g/l NH₄⁺ ions,
   derived from (NH₄)₂Cr₂O₇, NH₄OH and NH₄NO₃, 30-50 mg/l Cr₆⁺, derived from (NH₄)₂Cr₂O₇, 5-35% wt.
   ethylic alcohol or mono ethylene glycol, and having a pH value of 8 and a congealing
   temperature in the range of -5 to -20°C.

2. The method for obtaining the additive of claim 1 is characterized by preparing a solution
   of potassium nitrate, by blending 4-10 parts KNO₃ with 30-100 parts demineralized water, and a
   solution of NH₄NO₃, by blending 1-4 parts ammonium nitrate with 5-25 parts demineralized water,
   by filtering these two solutions and by mixing in a proportion of 5-30 parts of filtered solution of
   ammonium nitrate to 35-110 parts of filtered solution of potassium nitrate, by adding to this mixture
   0.6-1.5 parts solution of 1% wt. ammonium dichromate in water, by homogenizing using
   mechanical stirring, by adding 5-35 parts ethylic alcohol or mono ethylene glycol, by adding a
   25% ammonia solution to adjust pH to a value equal or greater than 8, the parts being expressed
   in wt.